

Linear Block Copolymer Synthesis

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Cite This: *Chem. Rev.* 2022, 122, 14471–14553



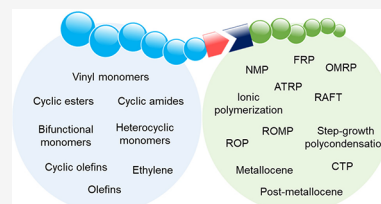
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ABSTRACT: Block copolymers form the basis of the most ubiquitous materials such as thermoplastic elastomers, bridge interphases in polymer blends, and are fundamental for the development of high-performance materials. The driving force to further advance these materials is the accessibility of block copolymers, which have a wide variety in composition, functional group content, and precision of their structure. To advance and broaden the application of block copolymers will depend on the nature of combined segmented blocks, guided through the combination of polymerization techniques to reach a high versatility in block copolymer architecture and function. This review provides the most comprehensive overview of techniques to prepare linear block copolymers and is intended to serve as a guideline on how polymerization techniques can work together to result in desired block combinations. As the review will give an account of the relevant procedures and access areas, the sections will include orthogonal approaches or sequentially combined polymerization techniques, which increases the synthetic options for these materials.



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Received: March 22, 2022

Published: August 12, 2022



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1. INTRODUCTION

Block copolymers play a dominant role in polymer science as their segmented structure is the source of a unique self-assembly behavior that cannot be achieved by random copolymers and has governed the development of research fields in which block copolymer compositions and their properties have been exploited.^{1–6} Their macro- and microscopic behavior is unique and cannot be afforded by any other polymer architecture.^{7,8} For example, nanostructure formation such as vesicles, micelles, and disks can be guided by block copolymer composition and functional group incorporation.^{9,10} For the generation of porous membranes, coatings, and devices,^{11–14} techniques have been developed to dictate the porous diameter and hierarchical structure of the membranes^{15,16} to work as water purification systems,^{17,18} in biomedical applications,¹⁹ or are developed for energy storage applications^{20,21} in the form of battery membranes²² and dielectric capacitors and supercapacitors.^{23,24} The influence of the block copolymer architecture and resulting nanoscopic structures can influence the outcome of biomedical applications.^{25,26} Moreover, the addition of block copolymer-derived nanoscopic structures to hydrogels and lubrication fluids can have significant effects on their resulting mechanical and shear-stress behavior.^{27,28} The directed self-assembly of block

copolymers has developed into a versatile method to produce device-relevant structures in sub-10 nm length scales in thin films and has circumvented the feature size limits of conventional photolithography.^{29,30} Bottom-up nanopatterning techniques have surpassed optical lithography gaining importance for high-volume manufacturing in the semiconductor industry.^{31–34} The behavior of block copolymers in high-resolution guiding patterns will increase patterning efficiency and limit defects density.³⁵ The leading commodity plastics are increasing their volume each year by over 10%, however, many of them do not fulfill the expectations we require of high-performance materials. The enforcement of plastic materials, which can also stem from waste streams, with other polymers, specifically block copolymers, working as interface “stitches”, can either form blends to combine properties or upgrade plastics.^{36–39} One promising pathway is the generation of embedded nanostructures to achieve a toughening by facilitating complex heterogeneities to dissipate a large amount of impact energy through the self-assembly of block copolymers.⁴⁰ In enabling copolymer dispersions or nanostructured bicontinuous plastics and inducing microphase separation to act as compatibilizers, block copolymers will play a critical role to open up commodity polymers to a broader application.

Because in most of the aforementioned applications the block copolymers are of linear origin and are arguably the most investigated class of block copolymers, we have focused in this review article on linear block copolymers, which are identified as structures in which the second polymeric block is formed through a connecting unit of the block. We are excluding block copolymers with brush-type architectures and multiarmed structures. The emphasis is directed toward the ability of current polymerization techniques to facilitate the most diverse linear block copolymers, which can then lead to structures with specifically tailored properties to resolve current challenges, deepen and open many more areas in polymer science. Synthetic strategies are at the center of this review.

Representative synthetic strategies for diblock copolymers can be divided into block copolymers from chain growth polymerization and polycondensation (Figure 1), which are each divided into their main approaches for block copolymer formation. In the sequential monomer addition approach, monomers with the similar reactivity and the same mechanism are used to produce linear block copolymers. Alternatively, chain extensions from dual initiators with distinctive functionalities can also give access to diblock copolymers. Depending on the reaction conditions such as monomer choices, solvent, temperature, or time, the chain extension can be conducted concurrently or sequentially. It is noteworthy that two functional groups should be completely selective toward the monomer types to obtain “clean” block copolymers. The third strategy employs the transformation of polymerization techniques from one mechanism to another mechanism, commonly via chain end-modification. This method is usually applied to create “hybrid” materials wherein the two monomers of each building block are not polymerizable using the same initiator or mechanism. The last method in chain-growth polymerization to prepare block copolymers is the coupling of two complementary end-functionalized homopolymers that were previously generated by different mechanisms. “Click” reactions including azide–alkyne cycloaddition and thiol–ene are the chemistry of choice as the high efficiency helps to minimize the contamination of the unwanted homopolymers.

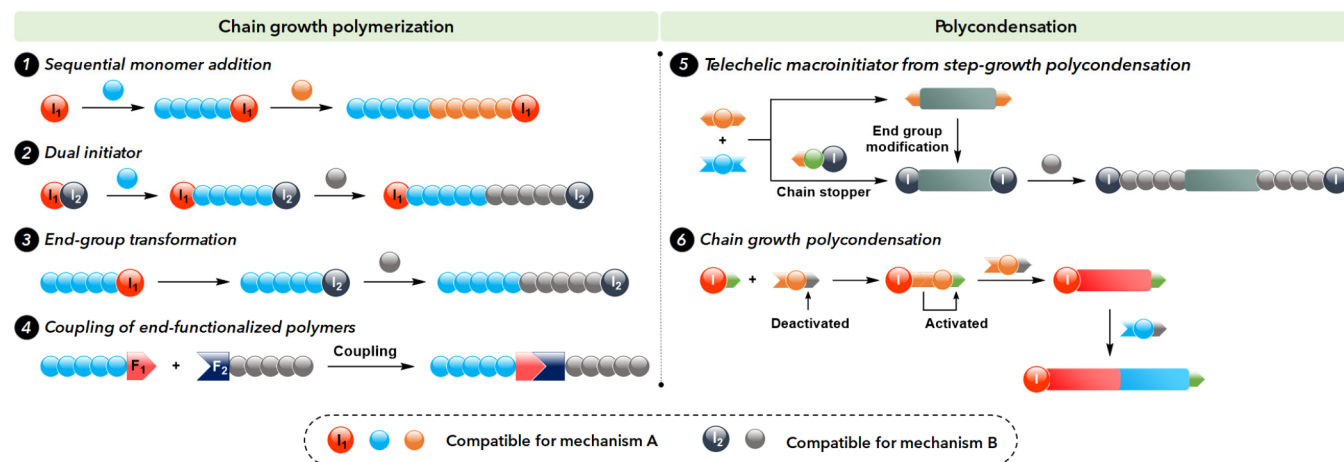


Figure 1. Common synthetic strategies for block copolymers.

With block copolymers that include segments obtained by polycondensation, traditional step-growth polymerization can be employed to produce telechelic macroinitiators through end group modification or in situ chain capping. This results in the formation of ABA type block architecture after subsequent chain extension. Chain growth polycondensation offer a better alternative in the preparation of well-defined block copolymers thanks to its living nature. Via this method, block copolymers including both nonconjugated and conjugated block can be obtained.

Among the aforementioned methods, sequential monomer addition and end-group transformation are by far the most widely used thanks to the broad range of materials they can offer. By using these strategies, a combination of the monomer and the polymerization technique that is utilized to generate the first block will dictate the options for the transformation and initiation of the consecutive block. To give the reader the best guideline in the overbearing field of block copolymers, we structured the review into five main sections and in which each of the approaches are implemented. The first section, the Introduction, is followed by the second part, describing block copolymer formation in which the first block originated from vinyl monomers which were polymerized either through ATRP, RAFT, NMP, and OMRP polymerization as well as cationic and anionic polymerization. For each CRP polymer and ionic polymerization, we first discuss blocks which are generated through the same mechanism and document how the chemical structure of the first block can dictate the sequential method for block copolymer formation. We then review for each method the conditions for block copolymer formation with other vinyl monomers, transformation from one to another mechanism, followed by combined approaches. The third section discusses block copolymer synthesis in which the first block is started from ring-opened polymers to continue with polymerizations such as controlled radical polymerizations. The fourth chapter discusses block copolymers from polycondensation, including the long-established step-growth polycondensation and the newly developed chain-growth polycondensation. The methods of preparing linear block copolymers containing important materials such as conjugated polymers were also presented in this section. The last part discusses polyolefin-based block copolymers. Here, the first block is either generated through metallocene polymerization or by ring-opened metathesis polymerization. Postmetallocene polymerization reactions

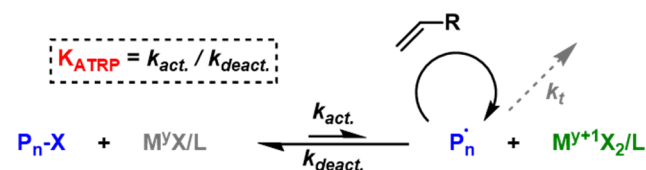
used for the first block will finalize this last section. The Conclusion/Outlook gives an evaluation of the current and future direction in block copolymer synthesis and the future trends.

2. BLOCK COPOLYMERS FROM VINYL POLYMERS

2.1. Block Copolymers from Atom Transfer Radical Polymerization

Atom transfer radical polymerization (ATRP) is a reversible deactivation radical polymerization (RDRP) technique that was independently discovered by both Matyjaszewski⁴¹ and Sawamoto⁴² in 1995. RDRP techniques achieve control over molecular weight by establishing a dynamic equilibrium between active propagating radicals and dormant species, thereby lowering the radical concentration and minimizing termination reactions. In ATRP, this equilibrium is mediated by a transition metal species which can abstract a halide from an alkyl halide in a single electron transfer to give a carbon-centered radical. The transition metal species is simultaneously oxidized to a higher oxidation state. This higher oxidation state complex can then transfer the halide back to the propagating radical, yielding a dormant polymer chain and the starting complex. A simplified representation of this mechanism is shown in Scheme 1. The equilibrium between active and dormant species is known

Scheme 1. Simplified Mechanism of ATRP^{41,42}



as KATRP. Establishing a faster rate of deactivation than activation (minimizing K_{ATRP}) ensures that the radical concentration is very low, suppressing termination.

ATRP with a generic transition metal (M) and polymeric alkyl halide species, P_n-X . Possible termination by radical–radical coupling/disproportionation is denoted by the rate coefficient k_t . The ratio between rate coefficients of activation (k_{act}) and deactivation (k_{deact}) gives the ATRP equilibrium constant K_{ATRP} .

While initially limited to aprotic solvents and certain monomers, the scope of ATRP has been expanded to include well-controlled polymerizations of monomer families including

(meth)acrylates, (meth)acrylamides, and styrene in both homogeneous and heterogeneous systems.^{43,44} Of the transition metals employed, the most ubiquitous is undoubtedly copper; although many studies have utilized metals such as iron, nickel, and ruthenium to a great effect. Detailed mechanistic studies into catalyst activity have also identified systems in which highly controlled polymerizations can be conducted without deoxygenation,⁴⁵ or in water, and even complex biological media.⁴⁶ The highly versatile nature of ATRP has cemented its reputation as one of the most useful techniques in the modern polymer chemist's toolkit. Perhaps the most valued aspect of RDRP and controlled/living polymerizations, in general, is the ability to synthesize block copolymers. Such materials are highly valued due to their unique properties afforded by their segmented architecture. This section of the review will detail the extraordinary efforts to optimize and enhance conditions for block copolymer synthesis by ATRP and explore the potential of ATRP to be combined with other polymerization techniques for the synthesis of "exotic" block copolymers that would be otherwise impossible to synthesize.

2.1.1. ATRP Block Copolymerization. Two main criteria must be met for an ATRP to be capable of well-defined block copolymer synthesis: limited termination and fast initiation to ensure concurrent growth of chains.^{47,48} This section will explore the chemistry governing these choices and establish guidelines to achieve ATRP with the necessary conditions for block copolymer synthesis.

Efficient block copolymer synthesis in ATRP relies heavily on the concept of "end group fidelity" defined as the percentage of polymer chains that have not undergone termination or side reactions, thus retaining the halogen at the chain end.⁴⁹ If end group fidelity is 100%, then all chains can reinitiate when an aliquot of the second monomer is added and potentially form block copolymers. Less than 100% fidelity will result in a fraction of homopolymer from the termination/side reactions during the synthesis of the first block. Judicious choice of reaction conditions, reagents such as ligand, solvent, and initiator, and employing secondary reactions can all combine to fulfill these criteria and give a polymerization system capable of synthesizing multiblock copolymers with high molecular weights and excellent control over molecular weight distribution.⁴⁴

In the simplest terms, block copolymers with ATRP can be synthesized by adding a second aliquot of monomer after the first aliquot has reached very high conversion, allowing for a "one-pot" approach to block copolymer synthesis. However, this approach is rarely employed, and it is much more common that the first block is synthesized and purified by precipitation or dialysis, followed by adding fresh catalyst and monomer to reinitiate and form the block copolymer. The reason for this added synthetic complexity lies in the equilibrium established in "traditional" ATRP. Radical termination, which is minimized but not totally precluded in ATRP, will result in a buildup of M^{n+1} deactivating species, the persistent radical effect, leaving 2 equiv of M^{n+1} for each termination as radicals are destroyed in pairs.⁵⁰ This will subsequently alter the position of the ATRP equilibrium and slow or even stop the reaction completely. In terms of end-group fidelity, this can mean that a homopolymer can be formed with >95% end group fidelity, but the excess of deactivator will stop the reaction from proceeding above a certain percentage conversion, necessitating the purification procedure between blocks to remove the excess deactivator and unreacted monomer.⁵¹

This problem in ATRP has been solved by employing a secondary process to transform any excess M^{n+1} back to M^n , known as activator (re)generation. This allows reactions to achieve very high conversions which are essentially quantitative in some cases while maintaining high end-group fidelity. Hence, block copolymers can often be synthesized by the much more straightforward one-pot approach with sequential monomer additions. Activator regeneration has been achieved by numerous methods, including the addition of conventional free radical initiators, known as initiators for continual activator regeneration (ICAR), the addition of reducing agents for activation regeneration (ARGET), an electrochemical stimulus, or even photoreduction. Figure 2 shows how activator

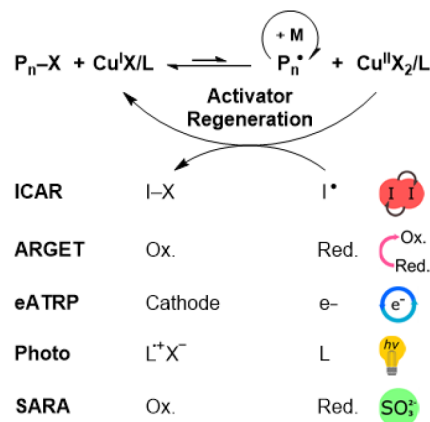


Figure 2. Regeneration of activating Cu^I species by external regulation using ICAR ATRP, ARGET ATRP, eATRP, photoATRP, and SARA ATRP.

(re)generation is applied to copper-mediated ATRP, with examples of commonly employed approaches. Aside from facilitating one-pot block copolymer synthesis, activator regeneration also has the benefits of allowing for reactions to be started from more air-stable Cu^{II} species and for substoichiometric amounts of catalyst which are as low as ppb levels for some systems.

Activator (re)generation methods greatly enhance the synthetic versatility and applicability of ATRP, but their implementation requires a careful selection of catalysts and conditions. Low catalyst loadings, typically in the ppm range, require the use of highly active catalyst systems so that k_{act} is sufficiently high enough to sustain a reasonable rate of polymerization.⁴³ Fundamental mechanistic studies have revealed many catalyst parameters which affect K_{ATRP} , including ligand denticity, the halide employed, and the electron-donating ability of the donor nitrogen atom.⁵² The effect of the donating ability of the ligand was demonstrated in a study of substituted 2,2'-bipyridine ligands, revealing that strongly electron-donating groups stabilize copper(II) deactivator species, raising K_{ATRP} .⁵³ Importantly, the redox potential of a ligand $E_{1/2}$ shows a linear correlation with $\ln(K_{ATRP})$, meaning that a new catalyst's reactivity can be estimated by measuring only the redox potential.⁵⁴ Rational design of ligands led to the development of tris(pyridylmethyl)amine (TPMA) derivatives with highly electron-donating groups to tune the donor ability of the pyridyl nitrogen. NMe_2 groups *para* to the pyridyl nitrogens gives the TPMA^{NMe2} ligand, which has been measured to have a K_{ATRP} as high as 1.⁵⁵ This incredibly high value indicates that control over molecular weight distributions and high end group fidelity can

be achieved in polymerizations with catalyst loadings in the low ppm range.

Another important factor in controlling ATRP is the choice of the initiator; initiation must be significantly faster than propagation to ensure that all chains have an equal chance of propagating.⁵⁶ Fast initiation is achieved by selecting an initiator with higher radical stability than the propagating chain end so that radical formation on the initiator will preferentially occur over radical formation on the chain end. This does not necessarily affect the chain end fidelity of the polymerization but does act to lower the dispersity to give better control over the polymerization.

In ATRP, and RDRP more generally, the order of monomer addition is of great importance for efficient block synthesis.⁵⁷ The reason for this is closely related to the rationale behind the choice of initiators. Chain extending from a synthesized first block can be thought of as analogous to carrying out an ATRP from a macroinitiator. Because of this, the stability of the radical at the chain end must be considered for control to be maintained. If the stability of the radicals formed on the macroinitiator is more stable than that formed with the new propagating monomer, then initiation from the macroinitiator will be favored and low dispersity will be maintained. **Figure 3**

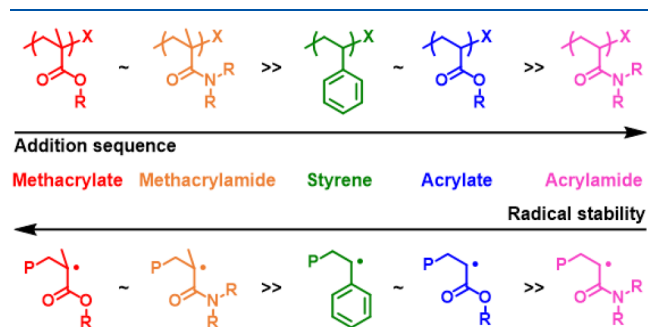


Figure 3. Preferred sequence of monomer addition for low dispersity block copolymers via ATRP and relative stability of the initiating/propagating radical for different macroinitiators. Adapted from ref 56. Copyright 2011 American Chemical Society.

shows this with commonly employed monomers in ATRP: methacrylates and methacrylamides give a tertiary propagating radical so should be polymerized first, followed by styrenic monomers and the secondary radical is stabilized by resonance, then acrylates, followed by acrylamides.

If it is desirable to synthesize a block copolymer that reverses the ideal order, then a halogen exchange reaction can be

employed to maintain low dispersity.⁵⁷ In a typical halogen exchange process, a macroinitiator (e.g., polystyrene) with a bromine chain end will be chain extended with a monomer (e.g., a methacrylate) and a copper chloride catalyst system. K_{ATRP} is typically 1–2 orders of magnitude lower for the chloride system compared to the analogous bromide, therefore activation of the polystyrene-Br macroinitiator will be faster than reactivation from polystyrene-*b*-polymethacrylate-Cl. Halogen exchange can only be employed in “traditional” ATRP reactions which use large amounts of catalyst, as low ppm systems lack large amounts of the new halogen to be exchanged. For low ppm systems (e.g., ICAR and ARGET) addition of 10 mol % of styrene to chain extensions of polystyrene with methyl methacrylate has been demonstrated to significantly improve the quality of block copolymers.⁵⁸

The state-of-the-art in block copolymer synthesis with ATRP is the efficient preparation of multiblock copolymers; block copolymers comprising three or more block copolymers which are obtained by repeated reinitiation of the macroinitiator. Synthesis of such polymers with narrow molecular weight distribution (low dispersity) pushes ATRP systems to their limits, demonstrating the incredibly high end group fidelity that is achievable with modern techniques. In 2011, Whittaker et al. reported a new approach for the facile synthesis of multiblock acrylate copolymers via sequential monomer addition and a Cu(0) mediated polymerization reaction.⁵⁹ By propagating each block to near full conversion, chain extension could be achieved by simply adding a new aliquot of monomer. Hexablock copolymers were prepared with low dispersity, although the molecular weights were low and gel permeation chromatography (GPC) traces indicated some termination. This approach was later expanded upon by Haddleton and Whittaker for high molecular weight multiblocks on a multigram scale.⁶⁰ A one-pot aqueous system utilizing Cu(0) generated from a disproportionation reaction⁶¹ was also able to be optimized for multiblock synthesis of alkylacrylamide monomers, with hexablocks being reported with dispersity at low as 1.11.⁶² The most powerful and versatile technique for multiblock copolymer synthesis by ATRP is the photopolymerization system first reported by Haddleton in 2014.⁶³ Utilizing Cu(II)Br₂ and tris[2-(dimethylamino)ethyl]amine (Me₆Tren), UV light is absorbed by free ligand which drives the reduction of Cu(II) species to Cu(I), establishing an ATRP equilibrium. Polymerizations are generally very fast and proceed to high conversions (>99%) with high end group fidelity. One-pot block copolymer and multiblock copolymers of a variety of monomers with

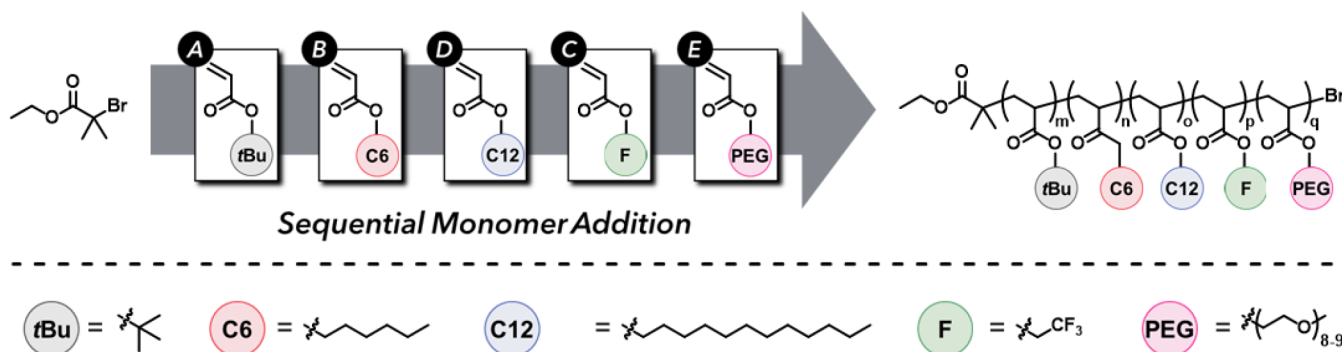


Figure 4. One-pot multiblock copolymer synthesis with hydrophobic, hydrophilic, and semifluorinated monomers via sequential monomer additions with a photoATRP catalytic system. ATRP First: combined approaches for block copolymer synthesis.

hydrophobic,⁶⁴ hydrophilic,⁶⁵ and fluorinated⁶⁶ moieties have been achieved with unprecedented control (Figure 4).

The ability to perform chain extensions in one pot without purifying the first block and reinitiating it with a fresh catalyst is a popular technique for block copolymer synthesis in ATRP. However, this approach may seem impossible if we consider the implications of high-end group fidelity at high conversions.

The dead chain fraction, DCF, defined as the fraction of chains that are unable to reinitiate is proportional to the degree of polymerization (DP) and the rate constant of termination (k_t) and is inversely proportional to the rate constant of propagation.⁴⁹ Matyjaszewski used this to explain that ideal conditions for end group fidelity, including low DP, low conversion, and high monomer concentration. However, this seems at odds with the large body of literature describing efficient chain extensions at high monomer conversions, as described in the paragraph above. Recently Asua and Ballard explained that this apparent discrepancy can be explained by the fast deactivation of the propagating radical. Their results show that when termination reactions are adjusted to consider the rate of radical diffusion then a large reduction in termination can be expected for fast deactivating systems.⁶⁷

In summary, ATRP is a powerful tool for block copolymer synthesis, however, it is important to judiciously select the catalyst system, initiator, and monomer sequence for optimal end group fidelity. Using a highly active catalyst with a high KATRP allows for activator regeneration methods to be employed and the overall catalyst loading reduced to low parts per million while retaining high end group fidelity.

Initiator choice determines the dispersity of the resultant polymer, with initiation needing to be much faster than propagation. Monomer sequence is dictated by the radical stability of the propagating radical. Finally, new evidence is emerging that rapid deactivation can show beneficial deviations from traditional radical kinetics, suppressing termination to near zero, giving high end group fidelity at high monomer conversions and allowing for one-pot block copolymerizations with no need to purify macroinitiators.

2.1.2. ATRP First: Combined Approaches for Block Copolymer Synthesis. Although ATRP is capable of synthesizing block copolymers of common vinyl monomers such as (meth)acrylates, (meth)acrylamides, and styrene with a very high degree of control, there are nevertheless vinyl monomer families which are yet to be optimized with ATRP. An example of such a monomer is vinyl acetate, which is polymerized on an industrial scale to produce polyvinyl acetate (PVAc) and poly(vinyl alcohol) (PVA). This monomer is known as a less activated monomer (LAM) because the double bond is adjacent to a saturated heteroatom, in contrast to its structural isomer, methyl acrylate, a more activated monomer, (MAM) with the double bond adjacent to a carbonyl group. The lower activity of VAc means that a very high K_{ATRP} catalyst is required to polymerize the monomer at a reasonable rate with good control. Although powerful new ATRP catalysts are approaching the values of K_{ATRP} required, reliable protocols for controlled ATRP of VAc are not yet available. If a block copolymer containing a VAc block is required from an ATRP macroinitiator, it is therefore advisable to employ a secondary polymerization technique to achieve high degrees of control.

Another scenario in which combining ATRP with other polymerization techniques might be beneficial is when a block copolymer is required with specific physical properties that cannot be easily obtained with ATRP alone. If a degradable

polymer is required, for example, then ATRP is severely limited as radical polymerizations cannot easily produce polymers with heteroatoms within the main chain. In this case, it is beneficial to employ a ring-opening polymerization from an ATRP macroinitiator to give block copolymers with a vinyl A block and a ring-opened B block. Block copolymers containing polyolefin segments also require a combined approach with ATRP because the low radical stability of halide-capped olefin chain ends essentially precludes a controlled polymerization by ATRP. Radical polymerization in general is not suited to the polymerization of α -olefins, which tend to undergo chain transfer instead of propagation.

The opportunity of combining other polymerization techniques with ATRP allows for the synthesis of polymers that would otherwise be impossible to obtain. Many publications have used combined approaches to synthesize block copolymers by ATRP, often using similar approaches to introduce new functionality necessary to combine different techniques. Figure 5 shows the typical structure of an ATRP polymer highlighting

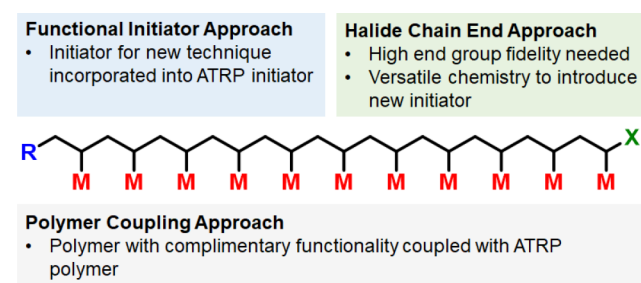


Figure 5. Common approaches to combining ATRP with other polymerization techniques include halide chain end, functional initiators, and polymer coupling.

the most common features that are exploited for introducing groups to initiate other polymerization techniques or to introduce a second block directly. The halide chain end approach leverages the high-end group fidelity obtained through carefully controlled ATRP and the versatile reactivity of alkyl halides. The functional initiator approach exploits the high tolerance of ATRP to many functional groups and incorporates a handle for further reactivity into the alkyl halide initiator itself, whereas polymer coupling separates the synthesis of two polymers, avoiding any potential competing side reactions, joining the two blocks postpolymerization.

2.1.2.1. Halide Chain End Approach. An inherent component of an ATRP reaction is the alkyl halide located at the ω end of the polymer chain. This alkyl halide is a highly versatile functional group for postpolymerization modification by standard organic procedures, e.g., S_N2 substitution. Such procedures have been extensively studied to vary the end group functionality for bioconjugation and to introduce groups capable of undergoing a complementary polymerization technique. This section will discuss the factors that govern the reactivity of the halide end group and give key examples of protocols that have introduced groups to initiate different polymerization techniques to form block copolymers.

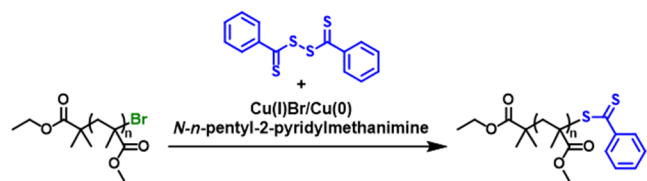
The most important factor in the efficacy of the halide chain end approach to combine polymerization techniques with ATRP is end group fidelity: a very high proportion of chains must contain the alkyl halide at the chain end if block copolymer synthesis is to be effective because otherwise significant amounts of ATRP homopolymer will remain. Strategies to maximize end-

group fidelity are extensively discussed in section 2.1.1. The reactivity of the alkyl halide is governed by two main factors: the nature of the halide and the nature of the last monomer unit in the chain.⁶⁸ Bromine is a better leaving group than chlorine because of its larger size, hence it can better stabilize a negative charge. Model reactions of the nucleophilic displacement of halide end groups with sodium azide showed that bromo derivatives react about 100 times faster than chloro analogues.⁶⁹ Just as K_{ATRP} changes with monomer, so too does reactivity in nucleophilic substitution reactions.

Hydrolysis on the alkyl halide chain end is a common side reaction in aqueous ATRP systems which results in a “dead” polymer chain with hydroxyl functionality. The rate of hydrolysis of the chain end has been demonstrated to be independent of copper concentration, indicating that metal-catalyzed hydrolysis is not significant. Despite being a deleterious side reaction, hydrolysis of the chain end is also a potential tool for installing hydroxyl functionality which could then be used to initiate ring-opening polymerization. This approach was taken by Haddleton and co-workers, where they first identified that the aqueous Cu(0) mediated polymerizations were much faster than the rate of hydrolysis. They demonstrated that allowing a polymerization to achieve very high conversion then leaving the reaction at room temperature for 24 h resulted in a near quantitative transformation of the P–Br chain end to P–OH.⁶⁹ In a similar report, preforming the polymerization in organic media an $\text{S}_{\text{N}}2$ substitution of the chain end with mercaptoethanol installed primary alcohol at the chain end with near quantitative conversions. This was subsequently utilized to form block copolymers through ring-opening polymerization of ϵ -caprolactone.⁷⁰

Aside from substitution reactions, radical reactions at the halide chain end also offer a versatile means of installing new mediators and initiators. A seminal example of this is the conversion of an ATRP macroinitiator into a macro chain transfer agent such as dithiobenzoates for RAFT polymerization, reported by Bon and co-workers in 2004.⁷¹ An ATRP macroinitiator is subjected to typical reactivation conditions, which would, in the presence of monomer, result in reinitiation and propagation. However, Bon and co-workers instead employ a 5-fold excess of bis(thiobenzoyl) disulfide. The copper catalyst cleaves the polymer halide bond to yield a polymeric radical, which then attacks the disulfide bond, forming the RAFT end-functionalized polymer. Any residual RAFT radicals will terminate by combination either with another RAFT radical and regenerating to disulfide or with a polymeric radical and yielding another equivalent of the desired product. This process is shown in Scheme 2 for poly(methyl methacrylate)-Br, but the authors also demonstrate its versatility by converting a tertiary amine functional ATRP polymer, poly(*N,N*-dimethylaminoethyl methacrylate) to the corresponding RAFT analogue.

Scheme 2. Conversion of ATRP Macroinitiators to MacroRAFT Agent by Activation with Cu Complexes and Subsequent Attack on Bis(thiobenzoyl) Disulfide⁷¹

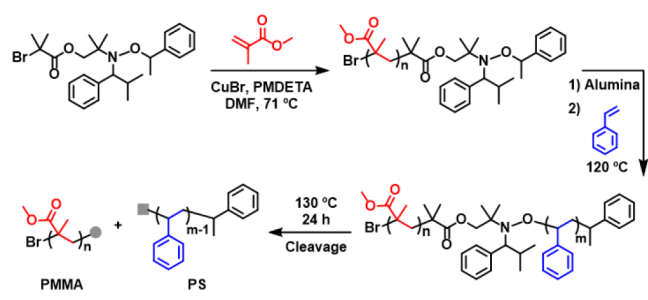


Capping of alkyl halides, either small molecules or ATRP macroinitiators with nitroxides, is a highly efficient transformation that is achieved through a similar means with ATRP activation to Bon's RAFT conversion discussed above. Nicholas and co-workers have used copper ATRP catalysts to convert small molecule alkyl halides, including many common ATRP initiators into nitroxide mediated polymerization initiators in a process that can be carried out to high yields at ambient temperatures, although they did not report any similar reactions from polymeric alkyl halides.⁷² Monteiro and co-workers have used nitroxide radical coupling on ATRP macroinitiators, installing a variety of functionalized TEMPO derivatives.⁷³ Wei and Luo have utilized nitroxide radical coupling from a poly(styrene) macroinitiator prepared by ATRP to install TEMPO at the chain end and use the resulting macroinitiator to polymerize a second block of 4-vinylpyridine, a monomer that is not well tolerated in ATRP due to complexation with the catalyst.⁷⁴

2.1.2.2. Initiator Approach. Initiation in ATRP occurs from an alkyl halide undergoing an atom transfer with a catalyst to give a propagating radical. As discussed in the Introduction, the substituents of the alkyl halide determine the reactivity and hence the degree of control observed in the reaction. Functional groups on this alkyl halide initiator which are further away from the C–X bond have a much smaller effect on reactivity than those directly adjacent which significantly affect radical stability. The incorporation of functional groups into the initiator is a powerful method of functionalizing polymers at the α chain end. Because many modern ATRP reactions can be conducted at mild temperatures and without external sources of initiating radicals, unlike conventional RAFT polymerizations, most polymer chains will have the selected functionality at the α chain end. It contrasts with the halide chain end approach discussed in the previous section, which requires careful selection of reaction conditions to maximize the end group fidelity.

In 2007, Ruehl reported an asymmetric initiator bearing both an α -bromoester (ATRP initiator) and an *N*-alkoxyamine NMP initiator.⁷⁵ This difunctional initiator was first used to initiate an ATRP of methyl methacrylate, followed by purification by passing over an alumina column to remove copper salts. Because of the lower temperature employed in the ATRP (71 °C) scission of the NMP agent did not occur, thus demonstrating orthogonality between the two techniques. Heating the purified PMMA macroinitiator with styrene at 120 °C resulted in a controlled NMP of styrene. Kinetic comparisons between the PMMA macroinitiator and an analogous small molecule *N*-alkoxyamine showed that the rate of polymerization was unaffected by the molecular weight of the *N*-alkoxyamine employed. This approach to block copolymer synthesis is potentially useful because NMP cannot adequately control methacrylate polymerizations to the same extent as styrene, and ATRP has been documented to have problems reinitiating from styrene macroinitiators (see section 2.1.1). The junction between the two blocks can also be cleaved through prolonged heating, cleaving the nitroxide cap, giving a stimuli-responsive polymer capable of degradation into its substituent homopolymers (Scheme 3).

Aside from ATRP, one of the most popular controlled radical polymerization techniques is reversible addition termination chain transfer (RAFT) polymerization. One particular advantage of RAFT over ATRP is the ability to control polymerizations of less activated monomers (LAMs) such as vinyl acetate and *N*-

Scheme 3. Synthesis of PMMA-*b*-PS and Thermal Cleavage to Nitroxide Linkage⁷⁵

vinylpyrrolidone (NVP). One of the first examples of an initiator capable of both ATRP initiation and RAFT chain transfer was reported by Matyjaszewski and co-workers in 2008.⁷⁶ RAFT polymerization in the absence of ATRP catalysts yielded controlled polymerizations, however, reactions in which ATRP catalysts were present demonstrated “reshuffling”, whereby propagating radicals from the ATRP initiating sites would undergo chain transfer with the trithiocarbonate moieties of the RAFT CTAs. Depending on the ligand employed, it was also seen that ATRP could occur through both the halide chain ends and the trithiocarbonate. This pseudohalide behavior of certain RAFT agents is discussed further in [section 2.1.2.4](#).

In 2009, Matyjaszewski and co-workers investigated haloxanthate iniferters for successive RAFT polymerization of *N*-vinylpyrrolidone and ATRP of styrene, methyl acrylate, and methyl methacrylate.⁷⁷ Iniferters with bromoesters were found to give a quantitative dimerization of NVP, chloroester containing iniferters were instead utilized. PNVP-*b*-PS, PNVP-*b*-PMMA, and PNVP-*b*-PMA block copolymers were prepared by both RAFT-first and ATRP-first approaches, however, the orthogonality was somewhat lacking in some examples due to significant “reshuffling” reactions. A RAFT-first protocol gave well-controlled poly(NVP), but subsequent chain extension with MA exhibited poor control due to a reshuffling reaction between the xanthate (CTA) moiety and propagating acrylate radicals. The ATRP-first approach yielded a controlled polymerization of MMA only, with styrene and MA exhibiting the same side reaction. The paper concludes that chloroxanthate iniferters provide access to well-defined block copolymers of NVP with poly(styrene) and poly(MMA) but not poly(MA). The versatility and applicability of combining ATRP and RAFT have been demonstrated by Pun and co-workers, who utilized a dual ATRP/RAFT inifer to prepare a well-defined cationic block copolymer containing a hydrophilic oligoethylene glycol and a tetraethylenepentamine-grafted polycation. This block effectively condenses plasmid DNA into salt-stable particles for drug delivery applications.⁷⁸

2.1.2.3. Coupling Polymers. Altering an ATRP react to enable conversion to another polymerization either through the halide chain end or through a functional initiator allows for many diverse block copolymers to be synthesized that would be impossible through one technique alone. However, if a polymer/polymerization technique or solvent is required that is highly incompatible with ATRP, it is advisable to adopt a convergent approach whereby two polymers are synthesized by two different techniques separately and then coupled together. A good example is a polymerization involving highly acidic species which are not well tolerated by ATRP.

The term “click chemistry” was defined by Sharpless, Kolb, and Finn as a set of reactions that is orthogonal, gives high yields,

and requires little purification.⁷⁹ Many reactions have been identified as click reactions, but the most widely studied is the copper-catalyzed azide–alkyne Huisgen cycloaddition (CuAAC), which has been widely applied to polymer coupling applications.⁸⁰ Alkyl halides (the chain-end of ATRP polymers) can be simply and efficiently converted to azides, and both alkynes and azides are stable under typical ATRP conditions.⁸¹

Webster and co-workers utilized CuAAC to couple poly(*t*-butyl acrylate) prepared by ATRP with poly(*n*-butyl acrylate) prepared by RAFT polymerization.⁸² A propargyl functionalized RAFT agent was used to introduce an alkyne functionality, and the necessary azide group was introduced at the ATRP chain-end by reacting the ATRP polymer with NaN₃ at room temperature in DMF. The two polymers were coupled in THF at room temperature with a reaction time of 50 h. This process was expanded to other polymers prepared by ATRP and RAFT to give a library of 24 different block copolymers. Although click chemistry is a powerful tool for coupling small molecules, large polymers show a lower reactivity, with clear evidence of uncoupled homopolymer present GPC traces.

2.1.2.4. Catalyst Approach. The catalyst used in ATRP can also be directly involved in switching the mechanism to a different polymerization technique. This section will discuss some current chemistries which have been developed to perform this, as well as explore some proposed routes to enable greater synergy between ATRP and other polymerization techniques.

By far the most common initiators in ATRP are alkyl halides, as described in detail in [section 2.1.2.1](#). However, it is also possible to use “pseudo” halogen groups like dithiocarbamates and dithioesters to generate radicals in the presence of a typical ATRP catalytic system. Mechanistically, such polymerization systems have been found to operate as a combination of RAFT and ATRP mechanisms.⁸³ Utilizing a pseudo halogen that is also an efficient chain transfer agent for RAFT polymerizations gives a mechanism whereby radicals are generated by atom transfer and reversible chain transfer occurs to control the molecular weight distribution.⁸⁴ Such systems show increased end group fidelity compared to traditional RAFT polymerizations, which generate radicals with a conventional thermal initiator. However, to the best of our knowledge, there are no reports of this pseudo halogen behavior of CTAs being exploited to form block copolymers containing monomer classes which do not polymerize well via ATRP. It could be envisioned that this method could be a way to control the polymerization of monomers which cannot be polymerized via ATRP (e.g., LAMs such as vinyl acetate or *N*-vinylpyrrolidone.)

One of the first metals utilized in ATRP was ruthenium, as reported by Sawamoto and co-workers in 1995.⁴² Ruthenium is also widely used in metathesis catalysts, as pioneered by Grubbs.^{85,86} In 2000, Bielawski and co-workers reported an alkylidene ruthenium catalyst with a tethered alkyl halide ATRP initiator.⁸⁷ Concurrent polymerization of MMA and cyclooctadiene (COD) resulted in block copolymers, with the ruthenium acting simultaneously as a metathesis catalyst and an ATRP catalyst.

Organometallic mediated radical polymerization (OMRP) commonly employs transition metals such as iron and cobalt, both of which are also metals used in ATRP. In 2014, Shaver and co-workers reported tetradentate amine-bis(phenolate)iron(III) halide complexes as efficient catalysts for controlled radical polymerization. Mechanistic studies implicated a multimechanism system with elements of both ATRP and OMRP. To the best of our knowledge, a single catalyst has not been reported that can

be switched between OMRP and ATRP mechanisms. Such a catalyst would be valuable as a potential route to block copolymers of LAMs (via OMRP) and MAMs (via ATRP).

2.1.3. Outlook. ATRP is a powerful and robust technique for block copolymer synthesis, with state-of-the-art ATRP allowing polymerization of a wide range of monomer classes capable of forming well-defined diblock and even multiblock copolymers. The high functional group tolerance of ATRP also means that it can often be combined with other techniques to form block copolymers which would be impossible to synthesize through a single technique. The most common approaches to achieve a combination of ATRP with other polymerization techniques are halide end-group modification, functional initiators, and direct coupling of polymers. Each of these techniques has specific advantages and disadvantages with respect to orthogonality, dispersity, and control and synthetic complexity. We identify multiple areas where cooperative catalysis and switchable systems could potentially be developed to further the scope and ease of combining other polymerization techniques with ATRP.

2.2. Reversible Addition–Fragmentation Chain-Transfer Radical Polymerization RAFT

One of the most extensively used reversible deactivation radical polymerization (RDRP) techniques, RAFT, reversible addition–fragmentation chain-transfer radical polymerization, was first discovered at CSIRO Australia in 1998.⁸⁸ Like other RDRP techniques, the RAFT polymerization involves the mechanism of suppressing termination to the point of it being negligible by reversible and temporary deactivation of the propagating radicals. However, the difference in RAFT polymerization relies on a degenerative chain transfer process facilitated by a thiocarbonylthio chain transfer agent (CTA)/RAFT agent to achieve control over molecular weight. RAFT agents are compounds with a structure (ZC(=S)SR), such as dithioesters, trithiocarbonates, xanthates, dithiocarbonates, dithiocarbamates, and xanthates (Figure 6A).

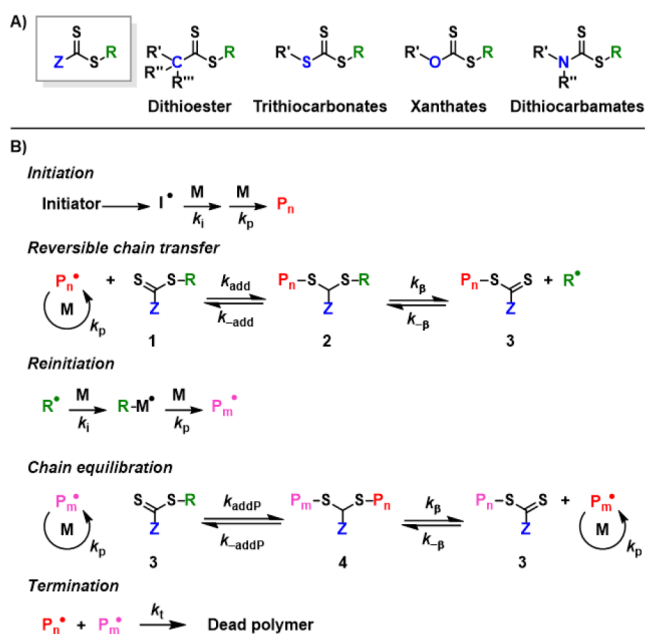


Figure 6. (A) Typical RAFT reagent structures. (B) Mechanism of RAFT polymerization. Adapted from ref 88. Copyright 1998 American Chemical Society.

The groups Z and R control the reactivity of RAFT agents. During RAFT polymerization (Figure 6 B), the propagating radical chain $P_n^\bullet$ adds to the RAFT agent (1) and is trapped by the RAFT agent to create an intermediate radical species (2), which then fragments to release $R^\bullet$ radical and a new polymeric thiocarbonylthio species (3) in the reversible chain transfer step, often called the pre-equilibrium step. For this step to proceed, the reactivity of the $R^\bullet$ and $P_n^\bullet$ radicals should be similar, and the Z group should facilitate the exchange. In the next step, $R^\bullet$ radical reinitiates the polymerization, producing $P_m^\bullet$, which then proceeds to the chain equilibration step, also known as the main equilibrium step. Propagating radical chain $P_m^\bullet$ adds to (3), creating another intermediate radical species (4), which then fragments to produce (3) and the $P_n^\bullet$ radical chain. Through this rapid equilibrium between the propagating radicals $P_n^\bullet$ and $P_m^\bullet$, and the dormant species (3), all chains get an equal probability to grow, thus a narrow polydispersity is achieved ($k_{addP} \gg k_p$ and $k_f \gg k_{-f}$). RAFT polymerization also provides high end-group fidelity for the vast majority of polymer chains.⁸⁹

RAFT polymerization is the most versatile RDRP technique due to its high tolerance of functional groups and providing great control over the polymerization of broad monomer families, including, acrylates, (meth)acrylates, acrylamides, styrene, vinyl esters, vinyl amides, and ethylene.^{90–93} In addition, RAFT polymerization is compatible with both homogeneous and heterogeneous systems including aqueous media^{94–96} and various organic solvents⁹² with the exceptions of nucleophilic solvents that could degrade the RAFT agent. An important factor in the success of RAFT polymerization is the selection of a RAFT agent with the appropriate R and Z group for the desired monomer. The monomers can be divided into two broad classes depending on their ability to react in a free radical process, the MAMs and the LAMs. The MAMs are monomers where the double bond is conjugated to an aromatic ring, a carbonyl group, or a nitrile, and the LAMs are monomers where the double bond is adjacent to a saturated carbon, an oxygen, nitrogen lone pair, or the heteroatom of a heteroaromatic ring. In terms of the RAFT agent functionality, the Z group affects the rate of addition of propagating radicals $P_n^\bullet$ and $P_m^\bullet$ to the thiocarbonylthio species (1) and (3) and the rate of fragmentation of (2) and (4), meanwhile, the R group must be a good homolytic leaving group compared to the $P_n^\bullet$, to ensure a rapid fragmentation of (2) in favor of (3) and $R^\bullet$, which must be able to reinitiate polymerization effectively (Figure 6B).⁸⁹ Both R and Z groups together dictate which type of monomer can be polymerized from the RAFT agent as shown in Figure 7.⁸⁹

Since its discovery, there have been many exciting advances in RAFT polymerization. The utilization of thio-containing compounds as iniferters in light-mediated polymerization was first reported by Otsu.⁹⁷ RAFT agents can also undergo direct photolysis and act as an iniferter to initiate polymerization without any exogenous radical source through the fragmentation of the C–S bond (Figure 8).

Direct photolysis of RAFT agents can be achieved with not only UV light^{99,100} but different wavelengths of visible light.^{98,101–105} Visible light initiation was achieved by exciting the RAFT agent species through a secondary absorption band, $n \rightarrow \pi^*$ spin forbidden electronic transition at a visible region (Figure 8).⁹⁸ Although this region shows weak molar absorption, RAFT agents investigated were able to produce well-defined polymers with high end-group fidelity at high

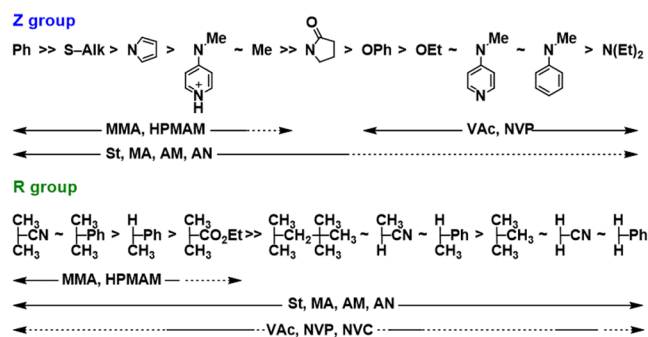


Figure 7. Guidelines for selection of Z and R groups of RAFT agents. A dashed line indicates partial control. Z: Addition rates decrease and fragmentation rates increase from left to right. R: Transfer coefficients and fragmentation rates decrease from left to right. Adapted from ref 89. Copyright 2012 American Chemical Society.

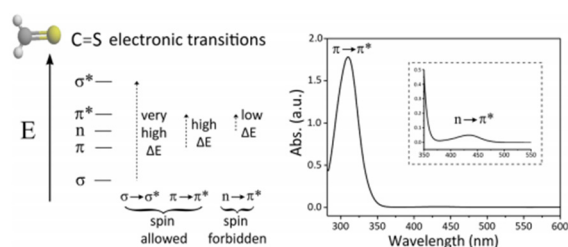


Figure 8. Simplified electronic energy level diagram for thiocarbonyl compounds and representative UV-vis absorption spectra. The inset shows the spin-forbidden $n \rightarrow \pi^*$ absorption band. Adapted from ref 98. Copyright 2015 American Chemical Society.

monomer conversions. Furthermore, it was shown that with increasing light intensity, the polymerization could proceed in the visible light region, additive-free and open to air.¹⁰⁶

Another advance in RAFT polymerization is the photo-induced electron/energy-transfer (PET) RAFT. In this process, a photoredox catalyst gets excited by visible light and transfers an electron or energy to the RAFT agent producing a radical anion, followed by the RAFT process. While the direct photolysis of RAFT agents produces a sulfur-centered radical followed by the RAFT process, the PET-RAFT process has been shown to be more controlled due to the increased stability of the radical anion (Figure 9). The versatility of PET-RAFT was

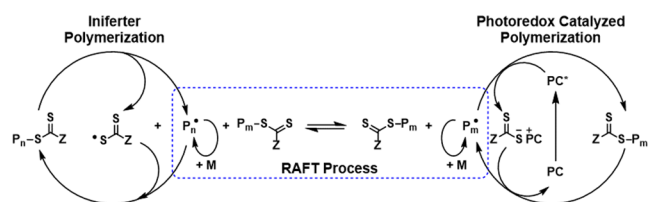


Figure 9. Mechanism comparison of iniferter and PET-RAFT polymerization. Adapted from ref 101. Copyright 2015 American Chemical Society.

demonstrated through the use of many different catalysts, such as an iridium complex (*fac*-[Ir(ppy)₃],¹⁰⁷ ruthenium complex (Ru(bpy)₃Cl₂),¹⁰⁸ chlorophyll A,^{109,110} metalloporphyrins,^{111,112} metal-free organo-dyes,^{113,114} 10-phenylphenothiozine (PTH),^{102,103,115,116} and organic amines.^{117,118}

Detailed investigations into catalytic activity have also revealed that the polymerization could take place without

degassing due to the photoreducing nature of the catalysts allowing for a single electron reduction of oxygen in solution and it all to be consumed before polymerization.^{107,111,119}

2.3. RAFT Block Copolymerization

RDRP is an excellent tool to synthesize an assortment of polymers with a variety of functionalities and complex architectures. Given its monomer versatility, high control over molecular weight and dispersity, and the ability to produce polymers with high end group fidelity, RAFT polymerization is an ideal candidate for the synthesis of block copolymers. Additionally, there are many different RAFT polymerization systems to choose from, in terms of RAFT agent, solvent, initiator, catalyst, and stimulus. In this section, the chemistry necessary to conduct a successful RAFT polymerization of a block copolymer is discussed.

The most common method to prepare block copolymers using the RAFT polymerization is through a sequential polymerization of two or more monomers with a purification step before the addition of the next monomer. The polymer synthesized from the first step acts as a macro-RAFT agent for the next polymerization. The choice of RAFT agent (R/Z groups) should reflect the desired monomers (MAMs, LAMs) to be polymerized so as not to lose control over the polymerization of participating monomers. Although it is impossible to completely suppress the formation of some defects, such as initiator derived block copolymers and homopolymers, in which the polymer does not contain the R group, and dead chains due to the mechanism of RAFT polymerization, with the correct selection of reaction conditions, these can be minimized to result in well-defined block copolymers.¹²⁰ Additionally, the order of monomer addition and the effect of initiator concentration on end-group fidelity needs to be considered. As mentioned above, the first block acts as a macro-RAFT agent for a block copolymer synthesis, thus the first polymer chain is the macro-R group, which would fragment during polymerization. The macro-R group should have the same requirements as the R group, such as that it should be a good homolytic leaving group relative to the propagating radical of the second monomer and that it must be able to initiate the polymerization of the second monomer efficiently. For those reasons, the order of addition of monomer is crucial. The better leaving group ability is determined by the steric stability of the radical, thus monomers that produce stable tertiary propagating radicals should be polymerized before monomers that produce secondary propagating radicals, which should be polymerized before monomers produce more active secondary propagating radicals.¹²¹ Not having a proper order of addition would produce unwanted side products, complicate the purification step, and broaden molecular weight dispersity. Guidelines for selecting the order of addition of monomers are shown in Figure 10.

Equally important as the order of monomer addition is the end-group fidelity for the synthesis of block copolymers. From a mechanistic perspective, high end-group fidelity is obtained by having the highest possible yield of homopolymers from the first polymerization and minimal termination. The effect of initiator concentration on those results, and thus on the end-group fidelity, can be significant. If the initiator concentration is too high relative to the concentration of the RAFT agent, it may lead to an increase in termination reactions and dead chains. Meanwhile, having a low initiator concentration in the polymerization reduces these defects, although the initiator

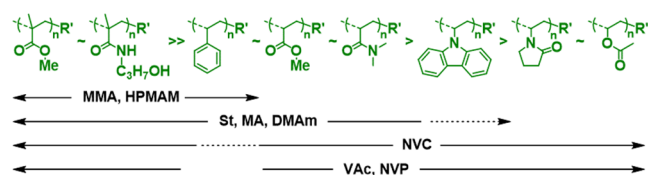


Figure 10. Guidelines for selection of macro-R group for the preparation of block copolymers. Dashed lines indicate partial control over polymerization. Adapted with permission from ref 121. Copyright 2014 Royal Chemical Society.

concentration needs to be sufficiently high to provide satisfactory rates of polymerization. However, it should be noted that this concern can be circumvented by utilizing direct photolysis of RAFT agents, as it does not require an initiator for the polymerization.

Although the common method for synthesizing block copolymers with RAFT polymerization is sequential polymerization of each monomer involving purification steps, the RAFT technique also allows for one-pot synthesis of block copolymers, even multiblock copolymers.^{122,123} Perrier et al.¹²⁵ demonstrated the synthesis of icosablock copolymer (20 blocks) consisting of multifunctional monomers. To achieve a successful one-pot, sequential addition polymerization monomers must be fully converted before the addition of the next monomer. In this way, the need for a purification step is eliminated, thus the process can take place in one pot. One shortcoming with synthesizing block copolymers through RAFT polymerization is that, for the chain extension to work, the monomers should belong in the same category (MAMs and LAMs), i.e., similar reactivity. The difference in reactivity of desired monomers for the block copolymer can be compensated utilizing the following methods.

One way to synthesize block copolymers consisting of LAMs and MAMs is to utilize a universal/switchable RAFT agent.¹²⁴ Researchers at CSIRO have reported a class of stimuli-responsive RAFT agents that can be switched to have good control over polymerization of both MAMs and LAMs. Their approach was to reversibly modify the electronic properties of the nitrogen in *N*-(4-pyridinyl)-*N*-methylthiocarbamate, which is an effective RAFT agent with VAc and other LAMs and is also an effective RAFT agent with MAMs in its protonated form in the presence of a strong acid (Figure 11). In the synthesis of block copolymers, the block of MAMs was synthesized first, followed by the synthesis of the block of LAMs due to the propagating species, with terminal LAMs being poor radical leaving groups relative to that of MAMs. Universal/switchable RAFT agents have been utilized for the synthesis of block copolymers with a variety of LAMs and MAMs.^{125,126}

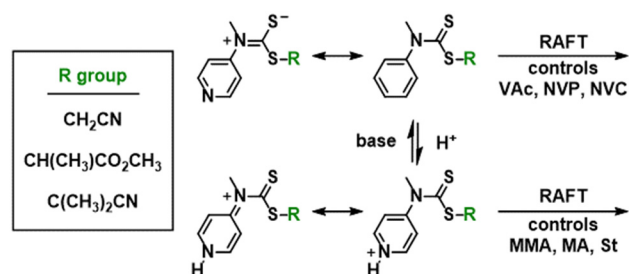


Figure 11. Switchable RAFT agents. Adapted from ref 124. Copyright 2009 American Chemical Society.

Although the process allows access to block copolymers of LAMs and MAMs, some concerns such as efficiently adding LAM to a propagating radical of the MAM chain remain a challenge.

Another approach to synthesizing block copolymers with monomers with distinct reactivities through RAFT polymerization is to synthesize two homopolymers with functionalities that would allow for postpolymerization coupling. Several techniques, namely click chemistries, such as alkyne–azide, thiol–ene, thiol–yne, and hetero Diels–Alder, have been utilized for postpolymerization coupling due to the high yield it provides.¹²⁷ That is not to say, the method is free of limitations as coupling between macromolecules with high molecular weight is thermodynamically unfavorable, thus it requires significant optimization.¹²⁸

The advancement in RAFT polymerization, such as the utilization of universal or switch RAFT agents or postpolymerization coupling has made it possible to synthesize block copolymers of LAMs and MAMs. Although both methods compensate to a certain degree for the failure to produce block copolymers of MAMs and LAMs through traditional RAFT polymerization, there are alternative ways to synthesize these block copolymers efficiently. In addition, other monomers that are not in the category of LAMs and MAMs would require different techniques to be polymerized.

2.4. RAFT First: Combined Approaches for Block Copolymer Synthesis

While RAFT polymerization is versatile and provides control over polymerization of a wide range of monomer families including some LAMs, limitations still exist for the synthesis of block copolymers. When synthesizing block copolymers, utilization of a single polymerization technique is not always enough due to dissimilar reactivities of monomers. To access block copolymer structures that cannot be produced through a single technique, multiple polymerization techniques are combined to make it possible. There are four main approaches in which the RAFT polymerization technique is combined with other techniques. The first and most common approach is through functional RAFT agents, in which the RAFT agent is functionalized to facilitate another polymerization technique in addition to RAFT polymerization. The second approach is through functional macro-RAFT agents, in which the chain end of the RAFT agent is modified after the RAFT polymerization to access the secondary polymerization technique. The third approach is through the coupling of polymer chains, in which homopolymers are synthesized separately with different techniques and linked together via postpolymerization coupling reactions. The fourth and last approach is to utilize the mechanistic transformation of RAFT agents. In this method, the same RAFT agent facilitates the RAFT polymerization, and the secondary polymerization with the addition of an external reagent or stimuli that alter the mechanism the RAFT agent would normally follow. In the following sections, each of these methods is discussed in further detail.

2.4.1. Functional RAFT Agents. Functional RAFT agents, often called “dual initiators”, are commonly exploited to access complex polymeric architectures, specifically block copolymers from monomers with dissimilar reactivities. In this approach, RAFT and the complementary polymerization techniques take place simultaneously or sequentially without any chemical or mechanistic transformations in between techniques. The initial presence of dual functionality provides the advantage of

Table 1. Examples of Dual Initiators to Combine RAFT Polymerization and ROP^{129,130,132–141}

Entry	Secondary Technique	Dual initiator	RAFT Monomers	Secondary monomers	<i>D</i> range	Ref.
1			St	CL	1.50–2.10	130
2			St	CL	1.21–1.57	129
3			St, MMA, BMA, t-BMA, SMA, NIPAm, BA, MA	LA, VL, CL, TMC	1.06–1.16	132
4			MMA, BMA, t-BMA	CL, VL	1.10–1.14	133
5			VP, VK	LA	1.18–1.23	134
6			DMA, OEGMA	LA	1.30–1.37	135
7	ROP		MA	CL	1.08–1.15	136
8			DMA, NIPAm	LA	1.07	137
9			VC	CL	1.29–1.33	138
10			NAS, NIPAm	CL	1.62	139
11			MMA, St, BnMA	CO ₂ , PO, HO, CHO	1.09–1.14	140
12			MMA, MA, BA, tBA, BMA, tBMA, NIPAm	MeOx, EtOx	1.12–1.31	139
13			DMA	iPrOx	1.14–1.39	141

circumventing the need for any postpolymerization coupling or end-group modification. The dual initiator approach to combining RAFT polymerization with other techniques is especially attractive due to the high tolerance of RAFT agents toward functional groups. RAFT agents can be modified with a variety of functionalities to facilitate different techniques, such as, $-\text{OH}$, $-\text{COOH}$, $-\text{OTs}$ for ROP, $-\text{Cl}$, $-\text{Br}$ for ATRP, and alkoxyamines for NMP (Table 1).

However, a careful selection of RAFT agents and functional groups to install are still required. There are key points to consider when choosing RAFT agents and the functional groups for the other polymerization technique. The first point is inevitably the compatibility and orthogonality of the two techniques. The techniques should take place without affecting the functional groups of the other or at least with negligible effect. Another point is the compatibility of the RAFT agent and the monomer to be polymerized by the RAFT polymerization as the selection of R and Z groups can dramatically alter the control the RAFT agent. Additionally, whether the functional group is installed on the R or Z group could give rise to different byproducts and affect the properties of the resulting polymer (Figure 12).¹²⁹ During an external radical initiated RAFT polymerization a side reaction could take place and produce initiator-driven homopolymers without the R group.¹²⁶ In that case, if the functional group is on the R group, no initiation of the secondary polymerization will take place from those initiators-driven homopolymers. On the other hand, if the functional group is on the Z group, the resulting blocks will be covalently

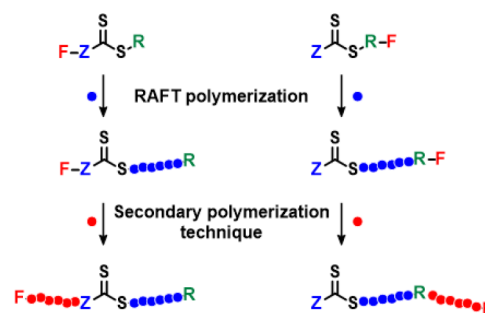


Figure 12. Types of block copolymers synthesized based on the position of secondary functionality (F).

bonded through the thiocarbonylthio group, in which case, the block copolymer can be cleaved by processes that would cleave the thiocarbonylthio group.¹²⁹ Both cases offer a possibility to further chain extend the block copolymer with another block at different positions depending on where the functionality resides.

2.4.1.1. Dual Initiators for the Combination of RAFT-ROP Techniques. Among reported works on RAFT dual initiators to combine RAFT and other polymerization techniques, a combination of RAFT polymerization and ROP are most common, as the resulting polymers contain biodegradable and biocompatible polyesters. ROP-RAFT combination is typically carried out, with ROP being first followed by RAFT as the ROP is more sensitive to impurities. The dual initiators carry various functional groups such as $-\text{OH}$, $-\text{COOH}$, and $-\text{OTs}$ to

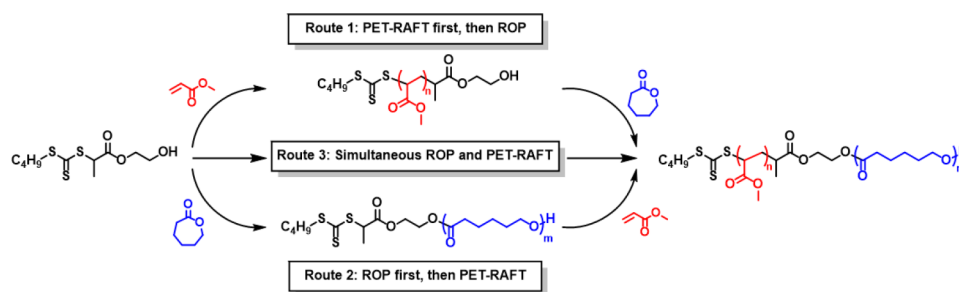


Figure 13. One-pot synthesis of PCL-*b*-PMA block copolymer by combining DPP catalyzed ROP of CL and PET-RAFT polymerization of MA. Adapted from ref 136. Copyright 2016 American Chemical Society.

initiate the ROP. Discussed below are reported works, in which the RAFT polymerization was carried out first or two polymerizations were carried out simultaneously or sequentially in one pot, which enables block copolymer synthesis with no purification steps.

In the work of Howdle et al., the first example of metal-free and simultaneous ROP and RAFT polymerization was demonstrated (Table 1, entry 1).¹³⁰ Trithiocarbonate (TTC) with a hydroxy terminal on Z substituent was used to synthesize PS-*b*-PCL (polystyrene-*b*-polycaprolactone) block copolymer and the TTC used is a similar species to a RAFT agent previously reported to have low cytotoxicity.¹³¹ The reactions proceeded in supercritical CO₂ and a high-pressure vessel and the RAFT polymerization was initiated by AIBN, and the ring-opening polymerization was catalyzed by lipase B-based enzyme, Novozym-435, complementing the biocompatibility of the system. Different ratios of monomer feed, RAFT agent, and initiator were tested, and the block copolymers' composition and crystallinity were analyzed.

Utilizing the same RAFT agent, Giacomelli et al.¹²⁹ (Table 1, entry 2) have also reported the simultaneous or one-pot sequential addition synthesis of PS-*b*-PCL, testing two different catalysts DPP (diphenyl phosphine) and Sn(Oct)₂ (stannous octoate) for the ring-opening polymerization and VAZO-88 for the initiation of RAFT polymerization. While DPP catalyzed simultaneous RAFT and ROP process yielded polymers with monomodal distribution, experimental data suggested that the presence of Sn(Oct)₂ in the simultaneous process disrupts the RAFT polymerization due to an interaction between the catalyst and the TTC species, resulting in some polymer chains with no TTC fragment and multimodal distributions. Compatibility of -OH functionalized TTC,¹³² dithiobenzoate,¹³³ and dithiocarbamate.¹³⁴ RAFT agents with various vinyl monomers and cyclic monomers in a one-pot polymerization were shown by Youk et al. in several publications. In the case of TTC (Table 1, entry 3),¹³² well-defined block copolymers composed of one block of vinyl monomer (styrene, acrylates, methacrylates, and acrylamides) and the second block of δ -valerolactone (VL), ϵ -caprolactone (CL), trimethylene carbonate (TMC), or L-lactide (LA) were synthesized using either DPP or DMAP as a ring-opening polymerization catalyst and AIBN initiator for the RAFT polymerization. The catalysts did not interfere with RAFT polymerization and the simultaneous process showed high control over polymerization. In another case, DPP-catalyzed ROP and V-70 initiated RAFT polymerizations were employed in the simultaneous synthesis of block copolymers of methacrylic monomers and lactones (CL and VL), initiated from hydroxy functionalized dithiobenzoate RAFT agent and showed excellent control at 30 °C (Table 1, entry 4).¹³³

Additionally, hydroxy functionalized dithiocarbamates were utilized in the one-step synthesis of amphiphilic, biocompatible block copolymers, poly(*N*-vinylpyrrolidone)-*b*-poly(L-lactide) (PVP-*b*-PLLA) and poly(*N*-vinylcarbazole)-*b*-poly(L-lactide) (PVK-*b*-PLLA) (Table 1, entry 5).¹³⁴ Dithiocarbamate RAFT agents were chosen due to its compatibility with the monomer VP and AIBN was used as an initiator for the RAFT process. As for the ROP process, DMAP was utilized as a catalyst as it was compatible with ROP of LA, additionally, the RAFT agent was stable to DMAP aminolysis. This one-step process yielded well-defined block copolymers that could carry properties such as photoconductivity for the PVK-*b*-PLLA and self-assembly into micelles for the PVP-*b*-PLLA. A simultaneous RAFT-ROP process catalyzed by DMAP and AIBN was also utilized in the synthesis of block copolymers PLA-*b*-PDMA or PLA-*b*-POEGMA from hydroxy functional dithiobenzoate (Table 1, entry 6).¹³⁵

In 2016, Boyer et al. (Table 1, entry 7) have demonstrated the orthogonality of DPP-catalyzed ROP of CL and iridium-catalyzed PET-RAFT polymerization of MA from a hydroxy functionalized TTC RAFT agent by synthesizing PCL-*b*-PMA block copolymer in a one-pot process either sequentially or simultaneously (Figure 13).¹³⁶ In contrast to most reported works on dual initiators for the combination of RAFT and ROP techniques, this case shows a facile method at room temperature and utilizes low-intensity blue light, which facilitates temporal control of the PET-RAFT polymerization as well. The sequential routes were able to produce well-defined block copolymers regardless of polymerization orders. In addition, simultaneous ROP and RAFT polymerization was successfully conducted without any interference with each other.

The combination of the RAFT-ROP process can produce polymers with interesting potential applications. Okano et al. have designed surface-functionalized thermoresponsive micelles with biodegradable cores from P(NIPAm-*co*-DMA)-*b*-PLA block copolymer¹³⁷ as a drug carrier. The block copolymer was synthesized from a hydroxy functionalized dithiobenzoate RAFT agent (Table 1, entry 8) through sequential RAFT copolymerization of NIPAm and DMA initiated by thermal initiator VA-086, followed by Sn(Oct)₂ catalyzed ROP of LA. Obtained diblock copolymers underwent aminolysis to yield thiol terminated polymer, which was then capped with maleimide in one pot. In a follow-up publication,¹⁵² it was further demonstrated that intracellular uptake of the micelles could be thermally regulated due to the thermoresponsive phase transition of PNIPAm throughout its lower critical solution temperature (LCST). Another demonstrated application of block copolymers synthesized through RAFT-ROP process was PVC-*b*-PCL block copolymer as nonmigratory plasticizers

and compatibilizers prepared by sequential RAFT polymerization initiated by thermal initiator ABVN, followed by DPP catalyzed ROP.¹³⁸ A hydroxy functionalized xanthate RAFT agent was employed as xanthates are known to provide good control over the polymerization of VC (Table 1, entry 9) and produced well-defined block copolymers. As it is a sequential process, a purification step in between the polymerization steps was necessary. Although a simultaneous route was tested, it was proven to be difficult to control the monomer ratio in the polymer through the monomer feed ratio due to the large difference in rate of polymerization of VC and CL.

The ROP can also be initiated from a carboxylic acid functionality, $-\text{COOH}$, which some RAFT agents inherently possess^{153,154} (Table 1, entries 10 and 11). The carboxylic acid functionality of a TTC RAFT agent facilitated a ring-opening copolymerization (ROCOP) of CO_2 and epoxide monomers catalyzed by 5,10,15,20-tetrakis(2-chlorophenyl)porphyrin aluminum(III) chloride, and simultaneously RAFT polymerization of styrene, methyl methacrylate, or benzyl methacrylate took place (Figure 14).¹⁵⁴ The porphyrin catalyst is typically

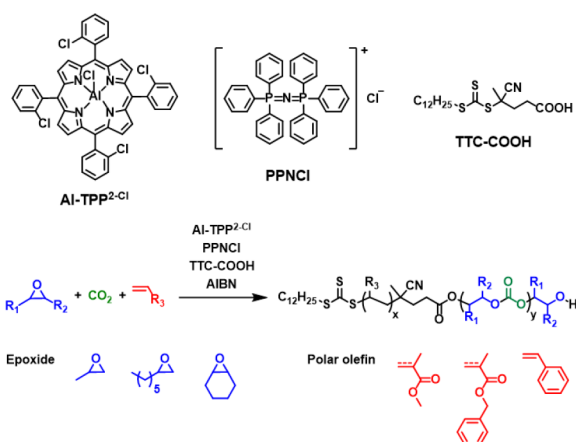


Figure 14. Synthesis of CO_2 -based block copolymer via one-step terpolymerization of CO_2 , epoxide, and vinyl monomer. Adapted with permission from ref 154. Copyright 2018 Wiley.

regarded to serve as an initiator for copolymerization of CO_2 and epoxides, thus some polymers were expected to be terminated with chloride and not contain TTC. However, all polymer chains produced by ROCOP contained TTC, and it was explained by a possible axial group exchange between the catalyst and the RAFT agent before initiation. The block copolymers produced from the simultaneous RAFT/ROCOP process had narrow polydispersity, and the polycarbonate block had a completely alternating structure. Some cyclic monomers, such as 2-oxazoline, require an electrophilic species such as tosylates, triflates, and halides as initiators for the cationic ROP.¹⁵⁵ Youk et al. (Table 1, entry 12) have employed a tosylate functionalized TTC RAFT agent for the one-step synthesis of well-defined amphiphilic block copolymers consisting of 2-oxazoline monomers and acrylates, methacrylates, or acrylamides.¹³⁹ The RAFT polymerization was initiated by AIBN and the ROP proceeded through the nucleophilic attack of the nitrogen atom of 2-oxazoline monomers on the RAFT agent, forming a cationic oxazolinium propagating species. The rate of polymerization of this process could be significantly enhanced from 18 h to minutes by utilizing microwave radiation (Table 1, entry 13).¹⁴¹

2.4.1.2. Dual Initiators for the Combination of RAFT-ATRP/NMP Techniques. Block copolymers of MAMs and LAMs can be efficiently synthesized through the combination of CRP techniques, RAFT, ATRP, or NMP. The most straightforward ways these techniques could be combined are through dual initiators containing functional groups capable of initiating both techniques. Commonly employed are halide functionalized RAFT agents or alkoxyamine functionalized RAFT agents to combine RAFT-ATRP or RAFT-NMP techniques, respectively. The discussion below includes reported literature in which two techniques were combined and the RAFT polymerization takes place first or both techniques take place simultaneously.

Dual initiators containing alkoxyamine and thiocarbonylthio moieties to carry out NMP and RAFT polymerizations could give rise to different structures depending on whether the alkoxyamine is in the R group or the Z group. Conditions of NMP are not orthogonal because of the thiocarbonylthio moiety reacting with propagating radicals of NMP, which leads to tandem NMP/RAFT polymerization. Conditions of RAFT polymerization, however, are orthogonal as NMP is initiated at a higher temperature. In a RAFT-first approach, polymerization of monomer A followed by tandem NMP/RAFT polymerization of B, AB block copolymer would be produced if the alkoxyamine is positioned on the Z group. On the other hand, having the alkoxyamine on the R group would give rise to BAB block copolymers.^{140,142}

The first NMP/RAFT dual initiator, dithiobenzoate containing alkoxyamine on the R group was synthesized by Guerrero-Santos et al. (Table 1, entry 1).¹⁴⁰ Amphiphilic block copolymers BAB were synthesized by the first polymerizing of EOMA or NIPAm through RAFT polymerization, followed by tandem NMP/RAFT polymerization of styrene. Additionally, CABC block copolymers were achieved by first synthesizing AB block copolymer (PAA-*b*-PBA or PtBA-*b*-PS) through RAFT polymerization followed by tandem NMP RAFT polymerization of C (St or ClS, respectively). The block copolymers were analyzed by SEC and SEM, and the SEM analysis displayed nanostructures formed through the self-assembly of amphiphilic block copolymers synthesized. In another work by Guerrero-Santos et al., the synthesis of penta- and heptablock copolymers were achieved utilizing a trifunctional symmetric dialkoxyamine-trithiocarbonate dual initiator (Figure 15, Table 2, entry 2).¹⁴² The advantage of using symmetric RAFT agents in the synthesis of block copolymers is that they provide easier access to block copolymers compared to nonsymmetric RAFT agents. When the homopolymer of A synthesized from such RAFT agents is chain extended with monomer B, it gives rise to ABA block copolymers. Additionally, tandem NMP/RAFT polymerization of C from homopolymer A produces pentablock copolymer CACAC, and polymerization of C from block copolymer ABA produces heptablock copolymer CABCAC.

Although NMP conditions applied to RAFT/NMP dual initiators are not chemically selective, it is possible to initiate only NMP when the RAFT moiety is physically inaccessible. Guerrero-Santos et al. demonstrated the synthesis of alkoxyamine functionalized latex nanoparticles via PISA.^{156,157} In this work, the dialkoxyamine-trithiocarbonate dual initiator was used to synthesize PAA, which was then chain extended with a hydrophobic monomer St through surfactant-free dispersion polymerization to produce PAA-*b*-PS-*b*-PAA with alkoxyamines on chain ends. Upon polymerization of St, stable latex nanoparticles with alkoxyamine on their surface were formed

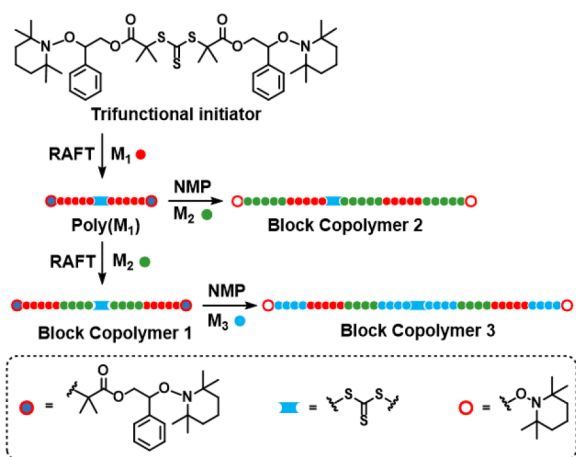


Figure 15. Synthesis of multiblock copolymers through RAFT polymerization and in tandem RAFT/NMP. Adapted with permission from ref 142. Copyright 2014 Royal Chemical Society.

via PISA. The latex nanoparticles with PS core were used to carry out surface-initiated NMP of SSNa. As the TTC moiety is inside the hydrophobic core of the nanoparticle, it is inaccessible to the water-soluble monomer SSNa, which is then only polymerized from the water-soluble PAA chains on the outside of the stabilized latex.¹⁵⁷

While the pairing of RAFT and ATRP techniques could be orthogonal, reaction conditions must be carefully chosen as ATRP could take place from the thiocarbonylthio moiety in the RAFT agent (ATRP_S) in some cases.¹⁴³ Detailed investigation of ATRP reaction conditions applied to a dual initiator, symmetric dibromo TTC was demonstrated by Matyjaszewski et al.¹⁴³ Concurrent and sequential ATRP and RAFT polymerization of block copolymers were also shown (Table 2, entry 3). *O*-Alkyl xanthate RAFT agents are known to have great control over the polymerization of some LAMs, such as vinyl acetate, *N*-vinylpyrrolidone, and *N*-vinylcarbazole. ATRP typically provides minimal control over the polymerization of these monomers, thus the combination of two techniques was utilized to access block copolymers of such LAMs and MAMs. A series of haloxanthate dual initiators were reported to facilitate the

Table 2. Examples of Dual Initiators to Combine RAFT Polymerization and ROP^{140,142–151,153}

Entry	Secondary technique	Dual Initiator	RAFT Monomers	Secondary monomers	Đ range	Ref.
1	NMP		EOMA, NIPAm, AA, BA, tBA,	St, ClSt	1.4–2.3	140
2			BA, NIPAm, PEGMEA	St	1.23–1.74	142
3			St	MMA	1.30–1.40	143
4	ATRP		VAc	St	1.36–1.46	144
5			NVP	MMA	<1.3	145
6			NVK	St	<1.5	146
7			VAc	St	1.18–1.24	147
8			VAc	St, MA, MMA	1.14–1.32	148
9			NVP	St	<1.4	146
10			NVK	MMA	<1.35	153
11			MA	MMA	-	149
12			tBA, St	St, tBA	1.13–1.33	150
13			OEGMEA	GMA	1.29	151

synthesis of such block copolymers. The block copolymers of VAc with St,^{144,147,148} MA, and MMA¹⁴⁸ were successfully synthesized from chloro- or bromoxanthates. Li et al.¹⁴⁴ have demonstrated the difference between reactivity and compatibility of chloro- and bromoxanthates in the polymerization of PVAc-*b*-PS. The two dual initiators were designed based on the compatibility of xanthates and different ATRP initiators. Chloroxanthate (Table 2, entry 4) was used for sequential RAFT polymerization of VAc first, followed by ATRP of St, as the ATRP initiator did not interfere with the RAFT polymerization. Although both blocks were polymerized with good control, broad dispersity was observed. On the other hand, the bromoxanthate was used for the ATRP first, followed by the RAFT technique, resulting inside reactions during both polymerizations due to the influence of the ATRP initiator. Matyjaszewski et al.¹⁴⁸ demonstrated the synthesis of PVAc-*b*-PS, PVAc-*b*-PMMA, and PVAc-*b*-PMA block copolymers from two bromoxanthates with either secondary or tertiary bromide. Bromoxanthate that produces tertiary radical during ATRP was shown to result in polymers with bimodal SEC traces from polymerizations of MMA and St, possibly due to polymerization taking place through the xanthate moiety to some extent. Thus, the sequential polymerization of the block copolymers was facilitated by the bromoxanthate with secondary bromide (Table 2, entry 8). RAFT polymerization of VAc took place first, followed by ATRP of the monomers, each involving different ligands based on their compatibility with the monomer. Although ATRP of all three monomers from the PVAc macro iniferter showed initiation efficiency between 71% and 88%, unreacted PVAc macro iniferter could be removed by precipitation. The initiation efficiency of ATRP of MMA was the lowest, 71%, which could be brought up to 84% through post RAFT polymerization “halogen exchange” to chlorine. Ultimately, well-defined block copolymers were obtained, with necessary purification steps. While PVAc block copolymers could be synthesized with good control with these dual initiators, hydrolysis of PVAc to the corresponding PVA blocks could not be achieved selectively due to the presence of esters in the initiators. This limitation was overcome by utilizing haloamide–xanthate iniferters¹⁴⁷ (Table 2, entry 7) Utilization of haloxanthates for the synthesis of well-defined block copolymers of PNVP,¹⁴⁵ PNVK¹⁴⁶ was also reported (Table 2, entries 5 and 9).

The choice of RAFT agent is evidently a big factor when it comes to the orthogonality of a system. However, if the initiator for the secondary polymerization technique is not necessarily selective toward the monomer to be polymerized, other factors of the system could be manipulated to access orthogonality. Boyer et al.¹⁴⁹ have demonstrated an orthogonal PET-RAFT/O-ATRP sequential polymerization of PMA-*b*-PMMA utilizing halide functionalized TTC and the same photocatalyst for both polymerization techniques (Table 2, entry 11). The sequential RAFT first approach is orthogonal to the ATRP because the RAFT polymerization of MA requires significantly less amount of catalyst than the ATRP. The second step, ATRP polymerization of MMA, is orthogonal to the RAFT process because the TTC moiety in the dual initiator is incompatible with the monomer MMA. The process showed good control over both polymerization, and the resulting polymer has a monomodal dispersity. The dual RAFT-ATRP initiators have also been utilized for the synthesis of cleavable block copolymers that have several applications. Gao et al.¹⁵⁰ have designed a dual initiator containing an acid-cleavable acetal junction, which can be

cleaved postpolymerization to fabricate nanoporous structures (Table 2, entry 12). Pun et al.¹⁵¹ have demonstrated a dual initiator containing disulfide linkage that could be reduced postpolymerization for the synthesis of neuron-targeted polymers that can shed a shielding block when necessary (Table 2, entry 13).

The dual initiators approach to synthesizing block copolymers utilizing RAFT polymerization and other techniques is arguably the most common due to the ability of RAFT agents to withstand many different reaction conditions and functional groups. Additionally, the fact that the RAFT agent can be designed in different ways to allow for the polymerization of monomers from different families truly highlights the versatility of this technique and opens many avenues for the synthesis of block copolymers.

2.4.1.3. Functional Macro-RAFT Agents. In block copolymer synthesis employing the RAFT polymerization technique, the RAFT end group can be modified after polymerizing the RAFT block to facilitate another technique. This method is most beneficial when the next polymerization technique requires reaction conditions or functional groups that are incompatible with the thiocarbonylthio moiety. A commonly employed secondary technique is ROP by altering the $-Z$ or $-R$ of the thiocarbonylthio moiety into $-OH$,^{158–161} $-NH_2$,^{162–166} $-SH$,¹⁶⁷ or, in a unique example, a OH bearing monomer is inserted while keeping the RAFT functionality intact¹⁶⁸ (Figure 16).

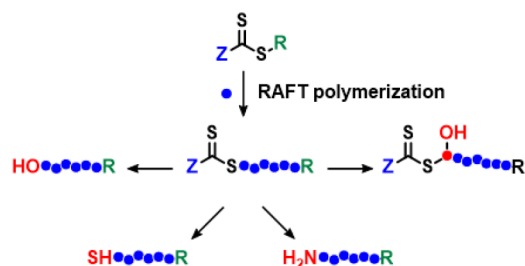


Figure 16. Modification of RAFT polymers into functional macro-RAFT agents to facilitate ROP.

Pan and co-workers have demonstrated the synthesis of miktoarm star copolymers by first synthesizing PS by RAFT polymerization and inserting a $-OH$ bearing monomer HECA, which cannot undergo radical polymerization. The $-OH$ functionality is then used to carry out cationic ROP of 1,3-dioxepane (DOP). Although the insertion yield of HECA was around 80%, polymer chains without HECA were removed through precipitation after the CROP to obtain PS-*b*-PDOP. The RAFT moiety here is still intact, thus it is used to carry out RAFT polymerization of MMA to obtain ABC miktoarm star copolymers.¹⁶⁸ Barner-Kowollik et al. have demonstrated a method to convert acrylate and methacrylate polymers with a dithioester end group into sulfur-free hydroxy-functional polymers.^{158,159} Utilizing this method, they synthesized PS through RAFT polymerization followed by the conversion of dithioester group into a hydroxy moiety, which was then used to initiate ROP of CL, giving access to sulfur-free PS-*b*-PCL.¹⁶¹ In another instance, the technique was used to synthesize 2-arm linear PCL-*b*-PS-*b*-PCL or 4-arm star PS-*b*-PCL block copolymers facilitated by two or four dithioesters connected through their R groups.¹⁶⁰ The most common way the end-group of RAFT polymers is removed is through aminolysis,

giving rise to polymers terminated with thiols, which are then often capped to avoid disulfide coupling. In the work demonstrated by Barner-Kowollik et al., a symmetric TTC RAFT agent was used to synthesize PS, followed by aminolysis of the TTC moiety to obtain two PS chains terminated with thiol.¹⁶⁷ The thiol group was then used to initiate ROP of LA to obtain PS-*b*-PLA block copolymers. As it is known that primary or secondary amines are used for the RAFT end-group removal process, ROP of *N*-carboxyanhydride monomers initiated by primary amines can be conducted after the RAFT polymerization is complete and the RAFT end group is modified.^{165,166} Zhang et al. have employed TTC functionalized with $-\text{NH}\text{Boc}$ to synthesize PNIPAm through RAFT polymerization, followed by RAFT end-group removal by capping the $-\text{R}$ group with AIBN.¹⁶² The terminal amine is then deprotected with TFA into an amine salt, which was deprotonated to give the primary amine group. The ROP of γ -benzyl-L-glutamate *N*-carboxyanhydride (BLG-NCA) took place from the PNIPAm macroinitiator with a terminal amine to yield double hydrophilic PBLG-*b*-PNIPAm block copolymer. Although the authors did attempt the ROP of BLG-NCA from a PNIPAm with terminal amine salt without removing the RAFT end-group, the dispersity of the block copolymers were higher than expected due to aminolysis of the RAFT end group. In another instance, a similar sequential process was used to synthesize PBLG-*b*-PNIPAm by employing a TTC functionalized with Fmoc protected amine.¹⁶³ McCormick et al.¹⁶⁵ demonstrated poly(2-hydroxypropyl)-methacrylamide (PHPMA) synthesized from TTC through RAFT polymerization could undergo simultaneous aminolysis and thiol-ene Michael addition with *N*-(3-aminopropyl)-methacrylamide to yield PHPMA with a terminal amine. The macroinitiator PHPMA- NH_2 is then used to initiate ROP of BLG-NCA to yield PHPMA-*b*-PBLG block copolymer. The benzyl group on the BLG was removed through hydrolysis to produce pH responsive PHPMA-*b*-P(L-Glu) block copolymer. Tennikova et al. employed poly(2-deoxy-2-methacryloylamido-*b*-glucose) (PMAG) synthesized from dithiobenzoate through RAFT polymerization to modify the end-group to an amine salt.¹⁶⁶ The PMAG-DTB was subjected to end group removal by reduction with NaBH_4 to yield terminal thiol, which was then coupled with cysteamine hydrochloride to produce the terminal amine salt. The hydrochloride was then removed through deprotonation in an alkali solution to yield terminal amine group to synthesize PMAG-*b*-PPhe deblock copolymer through ROP of L-phenylalanine (Phe).

The postpolymerization modification after the RAFT process is an ideal pathway when an initiator species for the secondary technique is incompatible with thiocarbonylthio moiety. The end-group modification of RAFT agents can be conducted efficiently in many ways. As shown above, the initiator of the secondary technique can be installed postpolymerization or prepolymerization in a protected state. However, the postpolymerization method may allow for fewer synthetic steps as the end group removal and the functionalization can take place simultaneously.

2.4.1.4. Coupling of Polymers. One of the approaches taken to produce block copolymers is certainly coupling of polymer chains post polymerization. Typically, well-known click chemistries are employed to ensure all chains are coupled as molecular weight of polymers affect the kinetics of the chain in solution.

Coupling of polymer chains can also be a good method when synthesizing complex nanostructures. Polymers synthesized

through the RAFT process allow for an efficient post modification to install functional groups to participate in the coupling reaction, or often the chain transfer end group can stay intact during reactions to install these functional groups, so the RAFT polymer no longer requires post-polymerization modification. Below, we discuss examples of polymers synthesized through RAFT polymerization participating in coupling reactions to produce block copolymers (Figure 17).

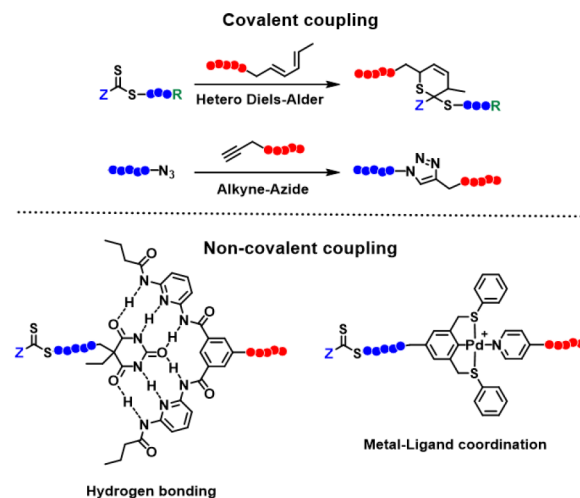


Figure 17. Covalent and noncovalent coupling used to prepare block copolymers.

Conjugation of homopolymers PS and PCL through hetero Diels–Alder (HDA) cycloadditions utilizing electron-deficient dithioesters was first shown by Barner-Kowollik et al.¹⁶⁹ In this work, PS ($\bar{M}_n = 1.11\text{--}1.14$) was synthesized from the electron-deficient dithioester and the PCL ($\bar{M}_n = 1.37$) was synthesized from hydroxyl bearing dienophile. Homopolymers were subjected to a coupling reaction via HDA $[4 + 2]$ cycloaddition in the presence of ZnCl_2 or TFA to obtain PS-*b*-PCL ($\bar{M}_n = 1.28\text{--}1.24$, respectively). The method is atom-efficient, as it does not require any modification to the end-group prior to the coupling reaction and provides quantitative conversion. Additionally, the coupling reaction utilizes a nontoxic catalyst and does not involve dry or inert procedures. The HDA click chemistry can also be used in the synthesis of complex nanostructures such as multiarm star block copolymers, as demonstrated by Barner-Kowollik et al.¹⁷⁰ A star shaped ATRP initiator with 12 terminal bromine was used to synthesize poly(isobornyl acrylate), followed by modification of bromine end groups to a diene ($\bar{M}_n = 1.11$). Separately, PS ($\bar{M}_n = 1.13$) was synthesized through RAFT polymerization from dithioester. The star polymer with diene terminals were then coupled with PS via ZnCl_2 catalyzed by HDA click chemistry to access multiarm star block copolymer ($\bar{M}_n = 1.10$) combining ATRP and RAFT polymerizations.

Another prevalent click chemistry is alkyne–azide, which was utilized to couple PVA synthesized through RAFT polymerization and PLLA synthesized through ROP.¹⁷¹ As xanthates are known to effectively polymerize VAc, azide bearing xanthate was synthesized and used to synthesize azide terminated PVAc, which was then converted into PVA. The RAFT end group was converted into a thiol in the process. The ROP of LLA was initiated with alkyne bearing alcohol to synthesize alkyne terminated PLLA with various molecular weights. The homopolymers PLLA and PVA were then coupled through

alkyne–azide click chemistry to produce PVA-*b*-PLLA, an amphiphilic block copolymer capable of self-assembly in aqueous media. In addition to well-known click chemistries, exploitation of noncovalent interactions to access supramolecular block copolymers have been reported.^{172–175}

In addition to well-known click chemistries, exploitation of noncovalent interactions to access supramolecular block copolymers have been reported.^{172–175} O'Reilly et al.¹⁷² demonstrated the utilization of noncovalent metal–ligand coordination to create hollow shell cross-linked nanostructures. TTC RAFT agent functionalized with SCS pincer ligand capable of complexing with a Pd(II) precursor was synthesized and used to polymerize MA and then chain extended with tBA to produce the PtBA-*b*-PMA block copolymer. The RAFT end group was removed with AIBN before complexation with Pd(II) precursor as the TTC moiety can coordinate with the palladium center. After end-group removal, the PtBA-*b*-PMA-SCS polymer was complexed to palladium, followed by deprotection of the *t*-butyl ester groups to yield amphiphilic block copolymers containing poly(acrylic acid) PAA-*b*-PMA-SCS-Pd. The palladium center was then used to couple PAA-*b*-PMA-SCS-Pd with pyridine functionalized PS coordination to produce the triblock copolymer PAA-*b*-PMA-SCS-Pd-PS. The amphiphilic metallo triblock copolymer was self-assembled into noncovalently connected micelles.

2.4.1.5. Switch/Mechanistic Transformation of RAFT Agents. The synthesis of block copolymers utilizing RAFT polymerization, and another polymerization technique is often accomplished by functionalizing the RAFT agent before or after the RAFT polymerization to facilitate the second polymerization method. However, there are instances where the RAFT agent does not need to be modified, as it allows for another polymerization technique to take place due to the addition of external reagents. In this section, these examples are discussed and referred to as mechanistic transformation of RAFT agents.

Nishikubo et al. have demonstrated the synthesis of block copolymers PS-*b*-PMT and PDMA-*b*-PPS using dithiobenzoate and dithiocarbamate RAFT agents.¹⁷⁶ In both cases, the RAFT block is synthesized first, and the 2-methyl thiirane (MT) block is synthesized second, initiated by the dithiocarbonyl moiety and catalyzed by tetraphenylphosphonium chloride (TPPCL). You et al. showed that by utilizing symmetric TTC RAFT agents, multiblock copolymers of cyclic thiiranes (MT and POMT (2-phenoxyethyl thiirane)) and acrylamides (NIPAm and DMA) with desired block lengths can be synthesized in one pot with a switch in polymerization mechanism.¹⁷⁷ The AROP takes place by heating of the reaction mixture catalyzed by TPPCL and the PET–RAFT process takes place catalyzed by Ir(ppy)₃ upon irradiation with blue light. Block copolymers could be synthesized either by PET–RAFT first or AROP first approaches followed by the other technique with an easy switch of the stimuli. In TTC RAFT agents, there are two thiocarbonyl groups present, providing two initiating sites for AROP. The advantage of a symmetric TTC is the easy access to multiblock copolymers such as undecablock copolymers and a ABCDCBA heptablock quadricopolymer in one pot with A and C being cyclic sulfide monomers and B and D being acrylamide monomers. The reaction mixture initially contained monomers A and B and in each process the monomers were converted fully before switching to another technique. Followed by the AROP of A and PET–RAFT of B, monomers C and D were added, and AROP and PET–RAFT were conducted respectively to yield the heptablock copolymer.

You et al. also showed that AIBN catalyzed RAFT polymerization of NIPMAm and TPPCL catalyzed AROP of MT can be carried out in one pot using TTC RAFT agent to synthesize block-like copolymers based on the discrepancy between the rate of polymerization of the two monomers.¹⁷⁸ The polymerization of MT is initiated at both sides of the TTC, and the polymerization of NIPMAm takes place on the –R side of the TTC. The long induction period of PMT polymerization allows for the homopolymerization of NIPMAm, which slowed down significantly as the PS started to polymerize, giving access to block-like copolymer.

Another example of a RAFT agent undergoing in situ mechanistic transformation is allowing living cationic polymerization of vinyl esters with the addition of Lewis acids.^{179,180} Demonstrated by Kamigaito et al.,¹⁷⁹ utilizing TTC RAFT agent, RAFT homopolymerization of MA, copolymerization of MA/IBVE or MMA/IBVE can undergo mechanistic transformation into a living cationic polymerization of IBVE in the presence of SnCl₄/EtOAc. The RAFT polymerization in this instance is initiated by an azo-initiator, and the presence of IBVE results in a copolymerization through a radical mechanism with a slower conversion of IBVE. Upon addition of Lewis acid in EtOAc, a fast consumption of only IBVE is observed, producing block copolymers. In the case of PMA-*b*-PIBVE, IBVE is added after homopolymerization of MA to change the majority of acrylate terminal unit into vinyl ether, followed by the addition of SnCl₄ in EtOAc inducing a living cationic polymerization of IBVE. Moreover, vinyl ether derived TTC, dithiocarbamate, dithiobenzoate, and xanthate RAFT agents were analyzed in the presence of radical initiator and a ZnCl₂ Lewis acid with MA and IBVE in order to induce interconvertible radical and cationic copolymerization.¹⁸⁰ Among the tested RAFT agents, dithiobenzoate showed no conversion of MA and TTC, and dithiocarbamate and xanthates showed similar rates of polymerization for both monomers. However, copolymerization with dithiocarbamate showed a broader GPC trace than TTC and with xanthates a bimodal trace was observed, indicating slower interconversion than with TTC. Thus, utilization of TTC provided efficient interconversion between cationic and radical mechanism to give access to multiblock structures.

The interconvertible cationic and radical polymerization system with TTC was also demonstrated by Fors et al. using two different photocatalysts that can be manipulated with different wavelengths.¹⁸¹ The PET–RAFT process was catalyzed here by Ir(ppy)₃ with blue light, and the cationic polymerization was catalyzed by oxidizing catalyst 2,4,6-tris(*p*-methoxyphenyl)-pyrylium tetrafluoroborate that can be activated with blue light and selectively activated with green light. A one-pot process in which the light source is changed from green to blue, to switch the mechanism in situ from cationic to radical, was shown to successfully polymerize PIBVE-*b*-PMA block copolymers. When the mixture was irradiated with only blue light, both radical and the cationic polymerization takes place producing diblock- or multiblock-copolymer depending on the amount of catalysts present. This process, however, does not allow for selectivity toward only the radical polymerization as the Ir(ppy)₃ catalyst absorbs light at similar wavelengths as the oxidizing catalyst. Following up on this work, Fors et al. have shown that the cationic and the radical processes could be stimulated orthogonally (Figure 18) from TTC and dithiocarbamate by controlling the cationic polymerization with an addition of ferrocenium salts and the radical process with a photocatalyst to synthesize multiblock copolymers.¹⁸²

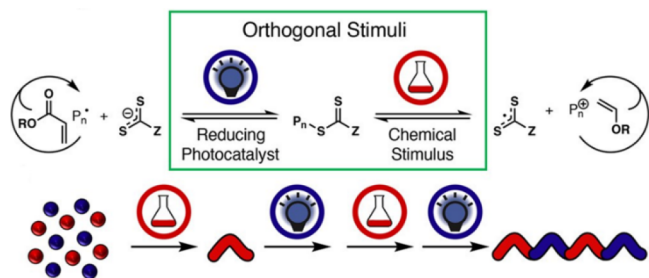


Figure 18. Interconversion of polymerization mechanisms via two orthogonal stimuli for the synthesis of block copolymers. Adapted from ref 182. Copyright 2018 American Chemical Society.

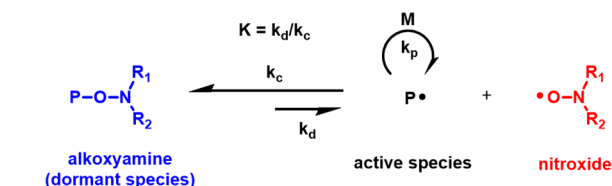
Showcasing the versatility of RAFT agents, monomers that require drastically different mechanisms can still be polymerized to access block copolymers. Utilization of mechanistic transformation with RAFT agents is an effective method to synthesize block copolymers as it does not require dual initiation site on the RAFT agent, eliminating the need to modify the RAFT agent pre- or post-polymerization. Additionally, even with a switch in mechanism, both techniques carry its unique control and quality over polymerization without any interference with one another. Although some conditions do not allow for complete orthogonality and rather rely on difference in kinetics of polymerization, adjusting external reagents or stimuli would provide better selectivity.

2.4.2. Outlook. The RAFT polymerization technique offers exceptional control over polymerization and variety of monomers. Benefiting from this process, countless types of block copolymers can be synthesized. Adding to this, coupling with other techniques through dual initiator, macro-CTA, coupling, or mechanistic switch approaches showcase the versatility of the RAFT polymerization technique. The most common technique combined with RAFT polymerization has been ROP, offering block copolymers with extended array of properties and characteristics. As the two techniques have different polymerization mechanisms, both can take place sequentially or simultaneously using number of stimuli. The RAFT polymerization can also be combined with cationic polymerization requiring no modification on the RAFT agent itself. Combining RAFT and ATRP techniques provide well-defined block copolymers from LAMs and MAMs.

2.5. Nitroxide Mediated Polymerization

The first report of initiators used to afford control over radical polymerization was demonstrated by Tobolsky et al. with methyl methacrylate and styrene in 1955.¹⁸³ The dithio initiators yielded ill-defined polymers, yet the seminal work laid the foundation for radical polymerization techniques we use today. The application of inifers was first reported in 1982 by Solomon et al. for styrene polymerization.¹⁸⁴ Once control was achieved through the use of these radical initiators, studies soon following that investigated multiple stable radical species for controlled radical polymerizations.¹⁸⁵ In 1983, CSIRO officially filed a patent detailing the use of nitroxides in radical polymerization, deemed nitroxide mediated radical polymerization (NMP).¹⁸⁶ The polymerization of styrene and acrylic monomers was found to proceed in a more controlled manner. The control of this polymerization lies in the homolytic cleavage of the C–O bond that yields a stable radical in the form of a nitroxide from alkoxyamines (Scheme 4).

Scheme 4. General Scheme for Nitroxide Mediated Polymerization, Where Dissociation of an Alkoxyamine (Blue) Leads to an Active Species and a Stable Nitroxide (Red)



NMP is now regarded as a very attractive RDRP technique for many reasons. The system is metal-free, encompasses a broad range on monomers with various functionalities, produces colorless and odorless polymers which demand no purification, and the system has been thoroughly discussed in the literature.^{187,188} Thermolysis of a well-defined unimolecular initiator is the dominant approach for NMP, as both the initiating radical and nitroxide are created simultaneously in a 1/1 molar ratio. Control of the NMP process proceeds by the reversible capture of the propagating species by nitroxides to form dormant polymer chains (Scheme 4). The minimization of termination during NMP arises from what has been termed the “persistent radical effect,” which describes the occurrence of the cross reaction of a reactive radical with a stable radical in preference to the homocoupling of reactive radicals.^{189,190} For this section of the review, the development of NMP as a platform will be evaluated in terms of the mechanism, scope of reactions, and compatibility with other polymerization techniques to afford robust block copolymers. Additionally, only focus on synthetic advancements to produce block copolymers will be given; there are many excellent examples of graft and brush copolymers that are not considered.

2.5.1. Mechanistic and Kinetic Features. Herein, we provide a general understanding of the NMP mechanism for nonexperts and summarize suitable conditions for the technique. We note that for the purposes of this review, focus is given to monomer and initiator combinations, which afford controlled polymerization to provide the reader with a succinct scope of polymers that can be synthesized utilizing NMP. For more detailed discussions of the NMP mechanism,¹⁸⁸ the chemistry involved in polymer synthesis for NMP,¹⁹¹ and the development of NMP,¹⁸⁷ the reader is encouraged to consult the excellent review articles which have previously been published.

2.5.1.1. Persistent Radical Effect. NMP as a polymeric system takes advantage of the aforementioned persistent radical effect. As chains undergo termination, transient radicals are removed from the system and the concentration of persistent species builds.¹⁸⁹ The persistent species in this case is the nitroxide, which does not go on to generate new polymer chains, and only cross-couples with transient radical species. Unlike typical radical polymerizations where the radical concentration is essentially constant, steady-state approximations are not possible for NMP due to the buildup of stable radicals in combination with early cross-termination exhibited by transient radicals. Access to nitroxides from a variety of sources can be credited to the prompt success of NMP as a polymerization platform, thus a variety of methodologies are available to synthesize the stable radicals (Figure 19).

Although NMP is now extremely efficient for the preparation of a variety of well-defined (co)polymers, availability and cost of nitroxides and/or alkoxyamines remain a concern. In typical

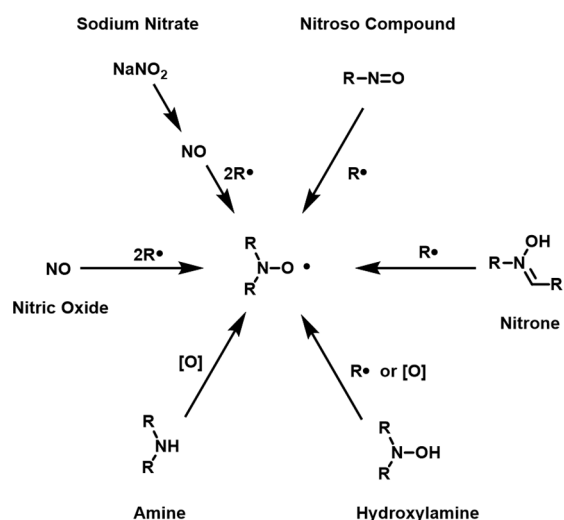


Figure 19. Common approaches for the synthesis of nitroxides.

NMP, suitable carbon centered radicals are combined with a nitroxide to form alkoxyamines.^{192–194} The rate constants of the cleavage of the dormant chains into radicals (activation) and of the reverse coupling (deactivation) influence the degree of livingness and control of the resulting polymer and the monomer conversion rate. To obtain living and well controlled radical polymerizations, these rate constants must favorably interrelate with the propagation constants k_p and the termination constants k_t of a particular monomer system at a given temperature, as well as with the applied initiator (regulator) concentration $[I]_0$ and the rate r of an additional radical generation. For systems involving reversible bond cleavage, the activation and deactivation parameters are denoted as k_d and k_c , while their ratio ($k_d/k_c = K$) is the equilibrium constant. Thermolysis of the C–O bond in alkoxyamine active sites at elevated temperatures results in the formation of carbon-centered radicals that predominantly follow one of two major reaction pathways to enable controlled polymerization: (1) recombination with nitroxide radicals to regenerate a dormant alkoxyamine end-group or (2) addition to the alkene group of a monomer molecule to extend the reactive chain by one repeating unit, which creates a new polymer radical that can again either react with nitroxide or with the monomer (Figure 20).¹⁹⁵ NMP has recently been described as a three-stage polymerization process, which is extensively covered by Tordo et al.¹⁹⁶

The three-stage polymerization is segmented into initiation, propagation, and termination (Figure 20) and the major findings are summarized here. **Initiation:** The faster the homolysis of the initiating alkoxyamine, the better the control of the polymerization.¹⁹⁷ Thus, alkoxyamines with high k_d can be used for initiation only when the H-transfer reaction cannot compete with the first addition of the initiating alkyl radical onto the monomer. **Propagation:** For kinetic equations used to predict the behavior of the polymerization, it was discovered that $k_{c,ds}$ and $k_{c,ds}$ of the dormant species must be applied instead of the k_d and k_c of the alkoxyamine model.¹⁹⁸ Additionally, the effect of the chain length is partly accounted for by the “penultimate unit effect”.¹⁹⁹ **Termination:** In general, for the case of styryl radicals, the H-transfer is negligible and does not hamper the polymerization. The H-transfer is more favored in the case of acrylyl radicals, and not all nitroxides can provide controlled polymerization of this type of monomer. H-transfer in the case of

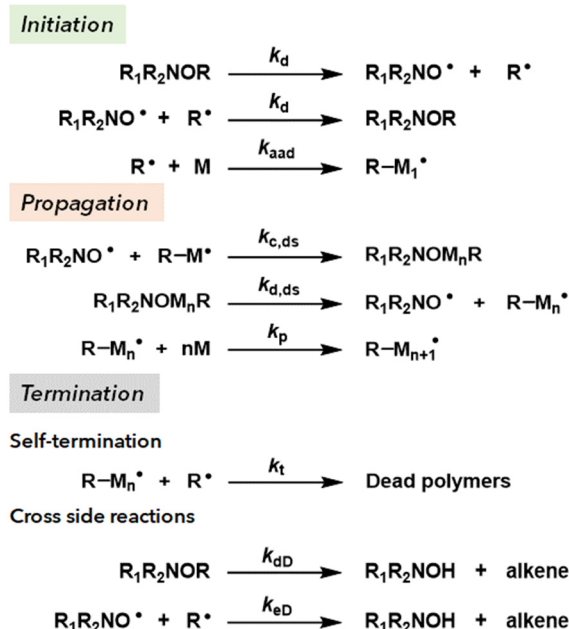


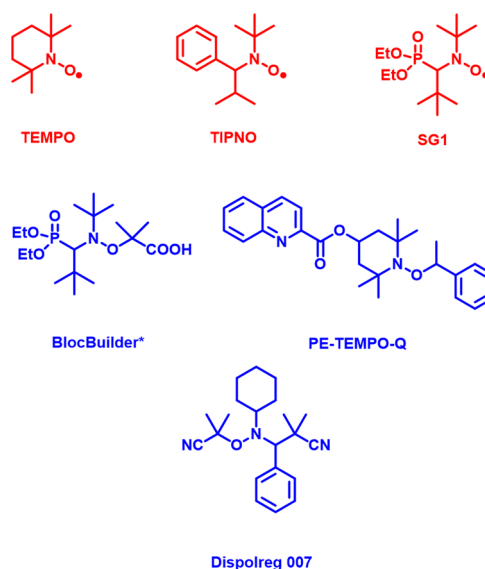
Figure 20. Overview of initiation, propagation, and termination pathways typical for NMP. Adapted with permission from ref 195. Copyright 2011 Taylor & Francis.

methacryl radicals occurs for most of the nitroxides, which is a reason why NMP of methacrylic monomers remained a challenge for many polymer chemists until recently.

2.5.2. Alkoxyamines/Nitroxides: Conditions for NMP.

NMP as a technique can be studied in a variety of chemical environments in order to gain greater control in polymerization by understanding factors which influence C–O bond homolysis. The dependence of k_d on the nitroxide structure has been addressed by Moad et al.²⁰⁰ They found the order of reactivity for C–O bond homolysis follows five-membered ring < six-membered ring < open chain nitroxides. These findings are represented in the development of nitroxides which have moved toward open chain structures (Chart 1). Studer et al. have

Chart 1. NMP Initiators Both As Stable Nitroxides (Red) and Alkoxyamines (Blue)



additionally investigated the effect that hydrogen bonding has on C–O bond homolysis, and nitroxides which are capable of intramolecular H-bonding exhibit faster rates than those that do not.²⁰¹ As such, polar solvents can be employed in reactions conditions to increase the rate of polymerization if H-bonding is possible in the nitroxide structure. Gryn'ova et al. have studied the effect that pH has on stable radicals, such as aminoxyl, peroxy, and aminyl derivatives. From their studies, it was discovered that radical stability could be affected by 3–4 magnitudes of order using pH-induced orbital conversion.²⁰² Aside from investigations which probe the initiation and propagation of NMP, work has also been made to elucidate the termination. The majority of side-reactions that affect a successful polymerization in NMP is disproportionation and concerted alkoxyamine decay.^{203,204}

NMP has been used with great success in the preparation of a wide variety of significant polymer structures and has key advantages in its simplicity, monomer compatibility, and polymer purity. However, it has been known to suffer from three main challenges. One of the first challenges is the slow polymerization kinetics that require high temperatures and lengthy polymerization times, especially when compared to other RDRP techniques such as ATRP and RAFT. Another common issue which had been associated with NMP was their inability to easily control the polymerization of methacrylate monomers, owing to side reactions and/or slow recombination of the polymer radical with nitroxide. This preconceived notion, however, has finally seen great advancements, as recent work has shown that modern nitroxides are able to overcome this once challenging monomer family.^{205–210} Finally, synthetic difficulties associated with nitroxide and alkoxyamine synthesis have generally limited studies to a few commercially available systems or to those carried out by synthetically focused research groups.

2.5.3. NMP Monomer Scope. Since its patenting in 1983, the scope of monomers capable of nitroxide mediated polymerization had remained limited, with many recent advances expanding and improving the controlled polymerization of other monomers. The general structure of monomers which have been successfully polymerized in a controlled manner for NMP are shown in Figure 21.

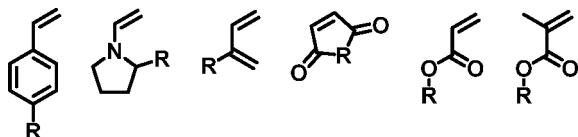


Figure 21. Monomers suitable for nitroxide mediated polymerization.

The most ubiquitous monomer polymerized by NMP is styrene, which had driven research to incorporate functionality into polymers utilizing functionalized styrenics. A common derivative, styrene sulfonic acid sodium salt (SSNa), has been incorporated/polymerized in aqueous media with a variety of nitroxides^{211–214} as well as 4-acetoxystyrene.²¹⁵ Another particularly effective monomer family for NMP includes 1,3 dienes such as isoprene,²¹⁶ myrcene,²¹⁷ and farnesene.²¹⁸ The initial focus on styrene and 1,3 diene polymerization had solidified NMPs inclusion into combined polymerization approaches where a styrenic or diene block copolymer was desired. Although NMP was the first reported RDRP technique, with ATRP and RAFT following in the 1990s, it was quickly outpaced by the other techniques, which were shown to readily

polymerize acrylic monomers as well as vinyl esters. NMP finally broke away from styrenic monomers and again came to the forefront with other RDRP techniques with the key development of TIPNO²¹⁹ and SG1,²²⁰ which allowed for controlled acrylate and acrylamide polymerizations in the 2000s. The most challenging monomer sought after for NMP remained methacrylic monomers which were only copolymerized in small amounts employing either TIPNO or SG1 and failed at crossover to other monomers like styrene. It was not until 2018 that a new alkoxyamine, Dispolreg 007, was shown to achieve polymerization of methacrylic monomers in a controlled manner while allowing for crossover to other monomers.²²¹ Although the scope of monomers suitable for NMP is now understood to be broad in scope (Figure 21), the implementation of NMP into combined approaches has still largely been focused on polymerization of styrene. This partiality can ultimately be attributed to the early narrow use of styrenic monomers for NMP, while other RDRP techniques became hallmarks for acrylic-based monomers.

2.5.4. NMP Block Copolymerization. As stated previously, NMP had only been effective for styrenics; however, the recent advances in initiator design have broadened the scope of obtainable block copolymers. Initially, Hawker et al. established conditions with α -hydrido nitroxide derivatives that were capable of polymerizing acrylates,²¹⁹ and 1,3 dienes, such as isoprene,²²² in a controlled manner. Polyacrylate-*b*-polyisoprene and polystyrene-*b*-polyisoprene diblock copolymers were successfully prepared with low polydispersity ($\text{Đ} < 1.2$) and molecular weights up to 140 kDa (Figure 22A). The authors note the reinitiation from polyisoprene macroinitiators was controlled with styrene but not acrylates.²²² Additionally,

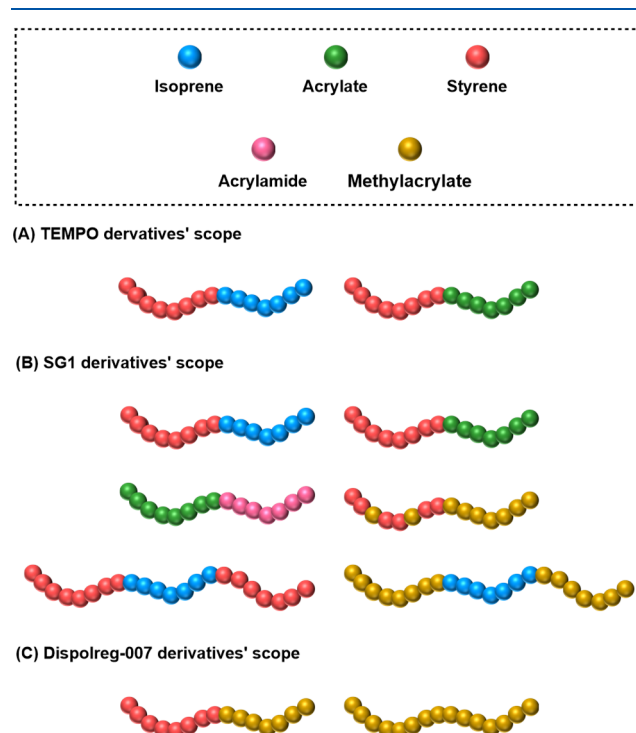


Figure 22. Scope of block copolymers capable of being synthesized utilizing solely NMP. (A) Block copolymers constructed with TEMPO and similar derivatives. (B) Block copolymers constructed with SG1 and similar derivatives. (C) Block copolymers constructed with Dispolreg-007 and similar derivatives.

reinitiation of acrylates was not possible from polystyrene macroinitiators,²¹⁹ detailing that monomer crossover from acrylate initiators is possible but crossover to acrylates is not. More complex block copolymer architectures became available with the development of newer initiators such as SG1 and Dispolreg 007. SG1-based initiators were successful in expanding the scope of block copolymers that were achievable solely with NMP (Figure 22B).

In 2013, Marić et al. synthesized water-soluble block copolymers of acrylic acid and carbazole functionalized styrene monomers.²²³ Low molecular weight poly(acrylic acid) was first polymerized, yielding a macroinitiator with a molecular weight of 3.3 kDa and low dispersity ($\bar{D} < 1.2$). Subsequent extension with 9-(4-vinylbenzyl)-9H-carbazole (VBK) yielded a poly(acrylic acid-*b*-poly(VBK)) diblock copolymer with molecular weights as high as 50 kDa and dispersity ($\bar{D} < 1.4$). Marić et al. also demonstrated that block copolymers made with acrylate and acrylamide monomers was possible with an SG1-based initiator.²²⁴ Poly(phenyl acrylate) macroinitiators were synthesized with a low molecular weight (4 kg/mol) and low dispersity ($\bar{D} < 1.2$). Subsequent extension with diethyl acrylamide was demonstrated, yielding poly(phenyl acrylate)-*b*-poly(diethyl acrylamide) block copolymers with higher molecular weights (22 kg/mol) and broader dispersities ($\bar{D} \sim 1.9$).

While successful block copolymer extensions were demonstrated, control over acrylamide polymerization was limited. More recently, SG1-based initiators were shown to successfully polymerize methacrylic and styrenic block copolymers by Lessard et al. This approach relied on a statistical copolymerization to incorporate the methacrylic monomer in a controlled fashion for the first block, followed by subsequent extension with a styrenic monomer.²²⁵ Statistical copolymerization of chloromethylstyrene (CMS) and methyl methacrylate (MMA) yielded poly(CMS-*r*-MMA) macroinitiators with molecular weights <20 kDa and dispersity $\bar{D} < 1.8$. The reactivity ratios of the monomers ($r_{\text{CMS}} > r_{\text{MMA}}$) led to favorable addition of the styrenic controlling comonomer compared to MMA. Successive extension with CMS led to poly(CMS-*r*-MMA)-*b*-poly(CMS) block copolymers. Post-transformation of the polymers CMS units into ionic liquid monomer 1-(4-vinylbenzyl)-3-butylimidazolium bis (trifluoromethylsulfonfyl)imide (VBBI⁺ TFSI⁻), yielding ionic liquid copolymers. Most recently, double headed SG1 initiators were demonstrated to prepare triblock copolymers.²²⁶ Dispolreg-007's development allowed for controlled methyl methacrylate polymerization, overcoming the prior need to incorporate comonomers into the polymerization.^{227,228} The synthesis of polystyrene-*b*-poly(*n*-butyl methacrylate) ($\bar{D} < 2.2$) and poly(methyl methacrylate)-*b*-polystyrene ($\bar{D} < 1.8$) block copolymers was demonstrated, highlighting effective monomer crossover for the system (Figure 22C).²²⁸ Currently, NMP as a technique excels at polymerizing styrene and 1,3-dienes. Similar control exists for acrylates, however, crossover to this monomer exhibits challenges. To a lesser extent, NMP has demonstrated limited control with acrylamide and methacrylic monomers. As a result, there still exists a need for approaches that overcome the challenges of crossover and limited control for certain monomer families, while also increasing the scope of other suitable monomer species.

2.5.5. NMP First: Combined Approaches for Block Copolymer Synthesis. In this section, we separate methods which have been recognized to combine NMP with alternative polymerization techniques into two key approaches, as depicted in Figure 23. (1) The first approach performs NMP, followed by

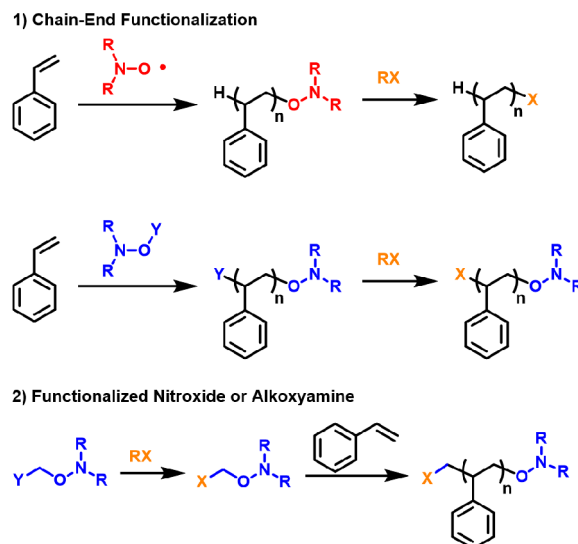


Figure 23. Common methodologies in NMP to incorporate orthogonal polymerization approaches. X refers to a reactive functional handle that is suitable for postpolymerization via alternative polymerization techniques.

chain-end functionalization which installs a reactive handle for subsequent polymerization. This approach undergoes single-site functionalization, allowing for successive block copolymer synthesis. The nitroxide is either sacrificed or preserved (α,ω chain-ends) in this process. (2) The second approach also allows for block copolymer synthesis by functionalizing an alkoxyamine or nitroxide before polymerization and then undergoing NMP. Similar to the first approach, single-site functionalization is again achieved, yet the alkoxyamine is always preserved in this approach yielding α,ω chain-end functional polymers. Additionally, this section of the review provides three archetypal examples of NMPs combination with ATRP, RAFT, and ROP, respectively. A comprehensive examination of block copolymers that are synthesized by first performing NMP and subsequently undergoing the other polymerization processes is detailed.

2.5.5.1. NMP Combined with ATRP. NMP first approaches which combine NMP and ATRP techniques largely employ asymmetrical difunctional alkoxyamines or nitroxides which contain a terminal bromine handle (Figure 24A). This approach is advantageous because of the ability to perform NMP without loss of the terminal bromine unit. The stability of the bromine handles allows initial synthesis of initiators with high α,ω functionalization that is retained during NMP.

An early example of this tactic was demonstrated in the 2000s by Hizal et al. with a difunctional alkoxyamine (Figure 24A, left).^{229,230} The initiator was synthesized in mild conditions over a two-step reaction, in an overall yield of 45%. NMP was then performed with the initiator in styrene at 125 °C, yielding α,ω macroinitiators containing a terminal alkoxyamine and bromine handle. Diblock and triblock copolymers were constructed with successive ATRP of *tert*-butyl acrylate, followed by methyl methacrylate, respectively. The authors investigated both NMP first and ATRP first approaches and discovered that starting with NMP provided a more efficient block copolymerization platform. The authors attribute the loss of TEMPO-end functionality during the ATRP reaction as a reason for the loss of efficiency with respect to ATRP first approaches. Block copolymers with molecular weights ranging from 30 to 70 kDa and $\bar{D} < 1.3$ were synthesized with percent composition of

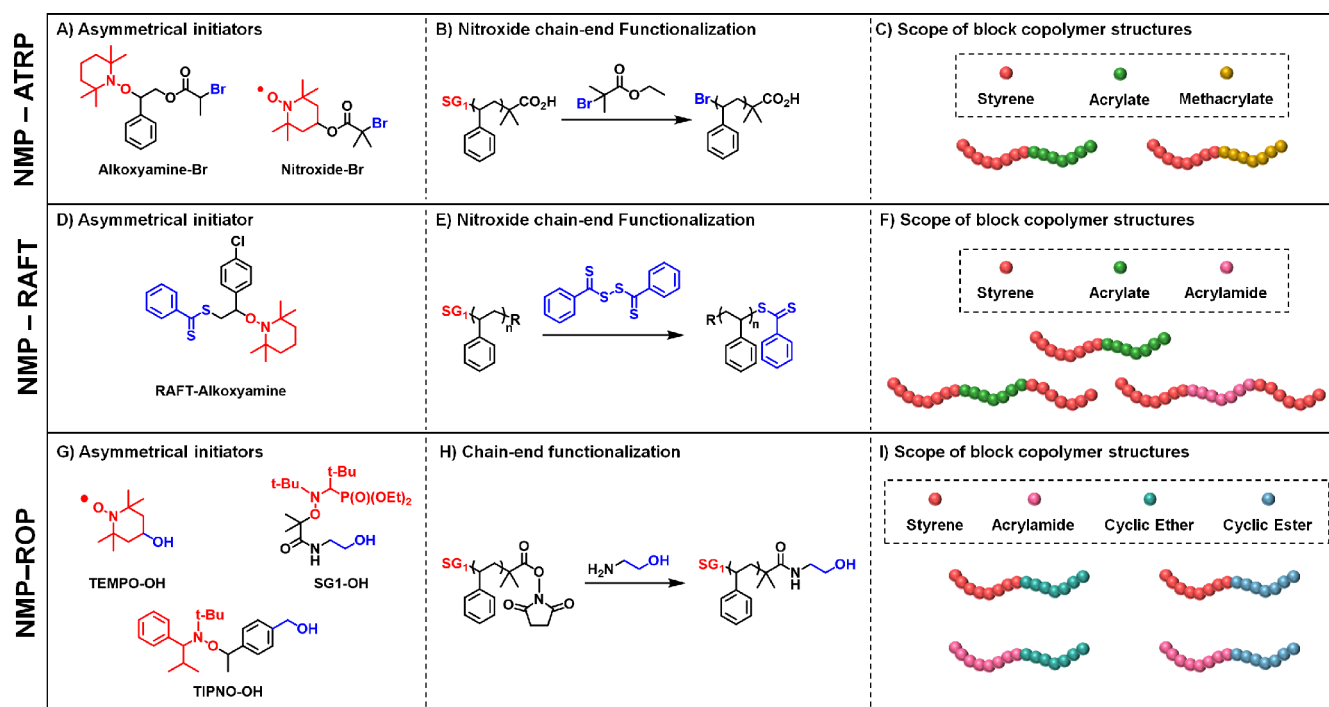


Figure 24. (A) Examples of asymmetrical difunctional initiators. The NMP handle is highlighted in red, while the ATRP handle is highlighted in blue. (B) Approach to swap a nitroxide with a terminal bromine handle. (C) Scope of monomers and polymers made with NMP-ATRP combined approaches. (D) Example of an asymmetrical difunctional initiators. The NMP handle is highlighted in red, while the RAFT handle is highlighted in blue. (E) Approach to swap a nitroxide with a RAFT agent. (F) Scope of monomers and polymers made with NMP-RAFT combined approaches. (G) Examples of asymmetrical difunctional initiators. The NMP handle is highlighted in red, while the ROP handle is highlighted in blue. (H) Approach to install a terminal hydroxyl unit while preserving the alkoxyamine. (I) Scope of monomers and polymers made with NMP-ROP combined approaches.

styrene ranging from 10 to 40%. In 2006, Yang et al. synthesized a TEMPO-Br stable nitroxide (Figure 24A, right) in a one-pot reaction in high yield (>90%).²³¹ Similarly, this difunctional initiator first undergoes NMP, generating polystyrene macroinitiators for subsequent ATRP. Methyl and ethyl acrylate were both polymerized via ATRP, yielding diblock copolymers with molecular weights as high as 30 kDa and $\bar{D} < 1.4$. It is notable that NMP first approaches are obligatory to achieve orthogonal polymerizations when employing functional nitroxides, as the ATRP mechanism would be greatly influenced by the presence of stable radicals which could cross-couple with propagating species.

Less common approaches undertake chain-end functionalization of alkoxyamines to install terminal bromine functionality postpolymerization (Figure 24B). Bertin et al. demonstrated radical chain-end functionalization of low molecular weight SG1-polystyrene macroinitiators.²³² The transformation was accomplished over the course of 6 days by reacting the macroinitiator with ethyl 2-bromoisobutyrate at 75 °C, replacing the SG1 moiety with a halogen end group with up to 90% functionalization. Subsequent polymerization was demonstrated with MMA via ATRP. Similar approaches were established by Du Prez et al. that show CBr₄ was also capable of installing a terminal halogen at the end of SG1-polystyrene macroinitiators.²³³

In the early 2000s, NMP first approaches combined with ATRP overcame the inherent limited control that NMP had over (meth)acrylic monomers, allowing the synthesis of narrow dispersity block copolymers containing styrenic segments (Figure 24C). ATRP in turn benefited from the control that NMP exhibited over a large family of functionalized styrenes. It is notable that the continued development of both platforms

eventually led to a greater overlap in their monomer scope, and this progress ultimately obviated their continued combination.

Nevertheless, the compatibility between the two platforms is accomplished by the chemical inertness exhibited by the terminal bromine handles during the NMP mechanism. As such, asymmetrical difunctional initiators remained the ubiquitous approach to combine NMP and ATRP.

2.5.5.2. NMP Combined with RAFT. As opposed to ATRP, combination of NMP and RAFT techniques have a larger body of work that explores chain-end functionalization as opposed to difunctional asymmetrical initiators (Figure 24E).^{216,234,235} This focus on chain-end functionalization is a result of the fact that RAFT agents operate under a chain-transfer mechanism. Orthogonality for these two techniques has largely remained inaccessible, as the NMP mechanism can activate RAFT agents, effectually overlapping the two processes. Bertin et al. first demonstrated their exchange of substituents between (macro)-alkoxyamines and (macro)RAFT agents approach, denoted as ESARA.²³⁴ Exchange of the nitroxide was performed for both dithiobenzoates and trithiocarbonates. One drawback for this approach is that it is heavily dependent on the nature of the alkoxyamine and RAFT agent as well as the reaction conditions. First, the authors state that the R group of the RAFT agent should exhibit a lower but sufficiently good leaving group ability compared to the A substituent stemming from the alkoxyamine and the dissociation rate of the initial alkoxyamine should be significant, whereas that of the resulting alkoxyamine should be very low at the chosen temperature. By fulfilling these conditions, a high yield of chain-end functionalization was demonstrated for the ESARA approach with dithiobenzoate RAFT agents (>95%) and, to a lesser extent, TTCs. While their work shows an in-depth approach for effectively swapping a

RAFT agent with a nitroxide, chain extension studies were only shown with styrene. Guerrero-Santos et al. took an alternative approach and synthesized NMP–RAFT iniferters through functionalization of an alkoxyamine (Figure 24D).¹⁴⁰ As mentioned above, traditional NMP polymerization at 120 °C with the difunctional initiator showed that the dithiobenzoate moiety underwent chain-transfer, producing side reactions where the RAFT process was concurrently activated. As such, NMP first approaches were not orthogonal, as both sides of the α,ω initiator polymerized styrene. A living polymerization was still achieved for styrene polymerization with high molecular weights and $\bar{D} < 1.4$. Because of both polymerization processes being activated with NMP conditions, RAFT first approaches were employed as opposed to NMP, and their results can be found in section 2.4 of this review.

NMP first approaches when combined with RAFT overcame the inherent limited control that NMP had over acrylic monomers, allowing the synthesis of narrow dispersity block copolymers (Figure 24F). RAFT and NMP are not entirely orthogonal, however, as the presence of a RAFT agent can act as a chain transfer agent under typical NMP conditions. As such, asymmetrical initiators (Figure 24D) are susceptible to both processes being activated, and chain-end functionalization (Figure 24E) offers an orthogonal approach that prevents dual activation of both NMP and RAFT. The continued advancement of RAFT polymerization has lessened the scope of monomers which NMP excels at. As such, combined approaches are no longer common between the two techniques for the development of block copolymers.

2.5.5.3. NMP Combined with ROP. The most ubiquitous combined approaches with NMP first techniques are ring-opening polymerization (ROP). This is attributed to the chemical inertness of hydroxyl units during the NMP process, as well as the abundance of chain-end functionalization methodologies which can install a terminal hydroxyl unit. As such, orthogonal polymerizations are available, utilizing both asymmetrical initiators and chain-end functionalization. Early work by Huang et al. showed that chiral diblock copolymers could be synthesized by NMP and ROP.²³⁶ Styrene polymerization was initiated in the presence of 4-hydroxy-TEMPO, yielding hydroxyl terminated polystyrene. Subsequently, ROP of L-lactide with a lithium alkoxide catalyst yielded PS-*b*-PLLA block copolymers. The chirality afforded by the lithium alkoxide catalyst led to nanohelices which adopted a left-handed helical sense, consistent with the fact that the PLLA blocks also possess an L-chiral center. Molecular weights as high as 80 kDa and $\bar{D} < 1.3$ were achieved, which exhibited self-assembly in the bulk. Similar approaches by Hedrick et al. synthesized an asymmetrical difunctional initiator, which is a derivative of TIPNO with a hydroxyl functionalization.^{237,238} NMP was first performed for both styrene and *N,N*-dimethylacrylamide, yielding hydroxyl chain-end polymer chains low molecular weight (<10 kDa) and $\bar{D} < 1.1$. Subsequently, ROP of lactide led to PS-*b*-PLA and P-(NIPAm)-*b*-PLA block copolymers with molecular weights up to 36 kDa with $\bar{D} < 1.1$. Similar work with the hydroxyl functionalized TIPNO was also shown in subsequent work.^{239–241} Bertin et al. synthesized a *N*-hydroxysuccinimide (NAS) derivative of MAMA-SG1.²⁴² The NAS functional handle is compatible with NMP techniques and, upon treatment with ethanolamine, installs a terminal hydroxyl unit at the chain-end of polystyrene polymers. This chain-end functionalization is unique to above techniques in that the alkoxyamine is not

destroyed, affording α,ω macroinitiators. ROP of lactide and propylene oxide from the polystyrene-hydroxy macroinitiators lead to PS-*b*-PLA and PS-*b*-PPO block copolymer formation, respectively. Molecular weights up to 25 kDa and $\bar{D} < 1.3$ were achieved.

NMP first approaches when combined with ROP greatly expands the diversity of block copolymers that are capable of being synthesized (Figure 24I). As opposed to the combination of NMP with other RDRP techniques, the monomer scopes of NMP and ROP have not exhibited overlap in their continued development. In this context, the continued combination of each technique did not succumb to eventual obsolescence.

2.5.6. Outlook. The body of research which is based around combining NMP with other polymerization techniques is immense, yet only a fraction of that work is based upon NMP first techniques. One reason that NMP is normally introduced in later stages of block copolymer development, and not initially, is due to the unique stability of nitroxides. All other RDRP techniques discussed in this review exist as dormant species where there is no radical present. This is also true for alkoxyamines, whose dormant form exists in the C–O bond, but nitroxides are distinctive in that their dormant form exists as stable radicals. As a result of this, radical chain-end functionalization of polymers is ubiquitous with nitroxides, as they can effectively act as radical traps for carbon centered radicals whose reaction generates stable alkoxyamines. Another reason that NMP is favored for later block development is that alkoxyamines exhibit a broad tolerance to other polymerization techniques which are photochemically or redox driven. Lastly, the high temperatures required for NMP are not tolerant for many other systems, thereby requiring their use after the more sensitive platform.

2.6. Organometallic-Mediated Radical Polymerization (OMRP)

Organometallic-mediated radical polymerization (OMRP)²⁴³ is based on the temporary deactivation of a growing radical chain by a transition metal complex and a reversible formation of a carbon–metal covalent bond.²⁴⁴ Wayland^{245,246} and co-workers reported the first controlled radical polymerization using cobalt species as controlling agents. While acrylic, MAM monomers were first investigated, the first polymerization of a nonacrylic, LAM VAc was reported by Jerome et al.²⁴⁷ Vinylacetate generates highly active propagating radicals because of the lack of stabilizing substituents caused by an electron-rich double bond.²⁴⁸ NMP is incapable of polymerizing LAMS's and ATRP polymerization methods do only offer fair results. The fact that OMRP next to RAFT/MADIX with xanthates and dithiocarbamates and iodine transfer polymerization (ITP)²⁴⁹ is capable of polymerizing challenging monomers has been one of the reasons to investigate this polymerization method further.

Of particular importance to the OMRP reaction is the ability of the transition metals to work as spin traps and not just only transferring a halogen to the propagating radical (ATRP), which makes the chemistry of these complexes related to the “persistent radical effect effect”. Specifically, the cobalt complexes have been exploited in organic chemistry and radical polymerization. Depending on the experimental conditions, two different mechanisms have been identified. One, the reversible-deactivation (RD) mode, in which the transition metal complex reversibly caps the radical polymer chains and functions as persistent radical. The reactivation occurs by the homolytic cleavage of the metal–carbon bond through thermal or

photolytic treatment. Second is the degenerative transfer mode (DT) mode, in which the transition metal complex transfers one polymer chain for another (Figure 25).

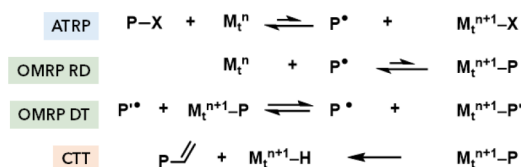
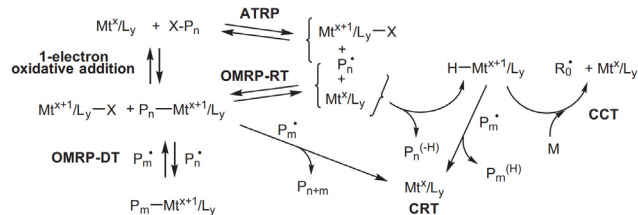


Figure 25. Transition-assisted polymerization mechanisms. Adapted with permission from ref 244. Copyright 2011 Taylor & Francis.

The OMRP RT equilibrium can abstract an H atom, leading to an intermediate hydride complex which can start a new chain by transferring the H to a new monomer molecule, generating a catalytic chain transfer (CTT).²⁵⁰ The catalytic chain transfer must be limited to preserve the livingness of the radical polymerization. In addition, the same hydride complex can also transfer the H atom to another radical chain, leading to a catalyzed radical termination (CRT). All of these mechanisms can potentially compete and interplay with each other. For example, the OMRP RT/CTT equilibrium can be carefully controlled by the metal coordination sphere but is not completely understood.²⁵¹ If the radical initiator is in excess and the coordination sphere allows it, the continuous radical injection leads to associative and degenerative radical exchange (OMRP DT). When transferable halogen groups are present, an interplay between OMRP-RT and ATRP can be maintained by simultaneously moderating the radical concentration to yield both dormant species. The radical concentration of chain carrier radicals can be controlled in ATRP by OMRP processes but can also trap radical chains irreversibly (Scheme 5).^{251,252}

Scheme 5. Interplay of the One-Electron Transition Metal Reactivity²⁵¹



2.6.1. OMRP Block Copolymerization. OMRP has been proven to be responsive toward changes in the carbon–metal energy driven by the chosen metal and temperature changes. Because OMRP is related to other mechanisms such as ATRP and CCT, the polymerization conditions must be chosen carefully. The fact that the CMRP process can be applied to monomer families such as acrylic esters, acrylic acid, vinyl esters, and acrylonitrile, unprotected acrylic acid has motivated the synthesis of block copolymers that include these monomer families which are difficult to be polymerized by other mechanisms. These monomers can be polymerized at low temperature ranging from 0 to 60 °C in high molecular weights ($M_n > 200\,000$) and is usually controlled by one specific cobalt complex. Therefore, the modulation of the cobalt complex when polymerizing a range of monomers at the same time with one complex is of utmost importance when preparing block copolymers and the introduction of coordinating molecules as

well as polymerization conditions such as temperature and solvents are critical. Obtaining experimental conditions for monomers of similar reactivity is relatively straightforward but more challenging when the polymerization of monomers of significantly different reactivity needs to be controlled. The monomer sequence and initiation strategy are very important when polymerizing these monomers. Table 3 summarizes the most representative block copolymers resulting from vinyl monomers.

The first known block copolymers were derived from acrylic monomers and PMA-*b*-PnBuA block copolymer ($M_n = 131\,400$ g/mol, $M_w/M_n = 1.29$) and PEA-*b*-PnBuA block copolymer could be prepared by photolytic activation. An exception is block copolymers in which a PMA is end-capped with a Co(TMP) complex and VAc was added as second block with low conversion. Debuigne et al.²⁵³ prepared double thermoresponsive di- and triblock copolymers based on *N*-vinylcaprolactam (NVCL) and *N*-vinylpyrrolidone (NVP) to serve the need for water-soluble polymers with tunable thermal response in water. Poly(*N*-vinylcaprolactam) (PNVCL) is a valuable alternative to PNIPAm with an LCST of ~ 36 °C, close to body temperature, and does not produce toxic low molecular weight amines during hydrolysis and does not form interchain hydrogen bonds in the collapsed state as the result of the hysteresis phenomenon in the coil-to-globule-to-coil transition. The PNVCL-*b*-P(NVP-*stat*-NVCL) were prepared using Co(acac)₂ as mediating species with high control over polymerization in which the statistical block was only performed at low monomer conversions to ensure well-defined NVP/NVCL statistical copolymers. PNVCL-*b*-P(NVCL-*stat*-NVP)-*b*-PNVCL triblock copolymers are the result of the addition of one isoprene unit at the copolymer chain-end and does not propagate. Instead the allyl radicals terminated chains are dimerizing to form the triblocks (Scheme 6, Table 3).²⁵³ All polymers displayed a double thermoresponsive behavior with two T_{cps} , which varied depending on the architecture and composition of the blocks.

Ameduri et al. reported on well-defined poly(vinyl acetate-*alt*-*tert*-butyl-2-trifluoromethacrylate)-*b*-poly(vinyl acetate) copolymers in which two electronically distinct monomers were combined in a one-pot technique: VAc as donor and *tert*-butyl-2-trifluoromethacrylate (MAF-TBE) as acceptor, with low dispersity ($\mathcal{D} \leq 1.24$) and molar masses up to 57 000 g/mol. These copolymers had a precise 1:1 alternating structure over a wide range of comonomer feed compositions. The poly(VAc-*alt*-MAF-TBE)-*b*-PVAc copolymer exhibited two T_g s at 43 and 67 °C, which correspond to PVAc homopolymers and poly(VAc-*alt*-MAF-TBE) alternating copolymers (Table 3). These sequence specific polymers are investigated as high-valued materials for optics and lithography to capitalize on their low dielectric properties and unique surface properties.²⁵⁴

Polymerizations with either α -olefins or ethylene have been tested in block copolymerization. PVAc-*b*-PO block copolymers were synthesized from isolated PVAc macroinitiators end-capped by a Co(acac)₂ complex ($M_n = 5000$ g/mol).²⁵⁵ After the addition of octane, only a small octane block could be formed, consisting of four octene units, and could be explained by degenerative chain transfer to the α -olefin with the formation of allyl radicals, which are too slow to reinitiate the polymerization and leads to termination. A block copolymerization with ethylene showed as well a low incorporation of ethylene initiated by the macroinitiator and led to a complex structure of PVAc-*b*-(PVAc-*grad*-PE).²⁵⁵

Table 3. Block Copolymers from OMRP

monomers	transition metals	main group metals	block copolymer	ref
acrylates	(TMP)CO—CH(CO ₂ CH ₃)CH ₃		P(MA- <i>b</i> - <i>n</i> BA)	246
	(Br ₈ TMP)Co			246
	(TMP)Co(II)			258,259
	4-methoxy substituted Co(acac)bpi			260
	(TMP)CO(II)		P(MA- <i>b</i> -Vac)	261
vinyl esters	Co(acac) ₂		P(PVAc- <i>b</i> -AN)	262,263
			P(VAc- <i>b</i> -St)	264
			P(VAc- <i>b</i> -NVP)	265
			P(VAc- <i>b</i> -AN) P(VOH- <i>b</i> -AA)	262
			P(VAc- <i>b</i> -NVCL)	235
			P(VAc- <i>b</i> -Oct)	253
			P(VAc-co- <i>n</i> BA)- <i>b</i> -P _n BA	266
			P(VAc- <i>b</i> - <i>n</i> BA)	266
			P(VAc- <i>b</i> -vBz) P(VAc- <i>b</i> -vPv)	267
			P(VAc- <i>b</i> -ethylene)	268
styrenes		methyl-2-methyl-2-methyltellanyl-propionate	P(St- <i>b</i> -NVP)	269
		methyl 1-phenylethyltelluride	P(St- <i>b</i> -4-MeOSt)	270
			P(St- <i>b</i> -MMA)	271
			P(St- <i>b</i> -tBA)	271
		organostibine	P(St- <i>b</i> -NVP)	272,273
		EMA-TeMe	P(St- <i>b</i> -MMA)	274
		EMA-TeBu	P(St- <i>b</i> - <i>n</i> BA)	275
			P(St- <i>b</i> -MMA)	275
MMA		methyl 1-phenylethyltelluride	P(MMA- <i>b</i> -St)	271
			P(MMA- <i>b</i> -tBA)	271
		EMA-TeMe	P(MMA- <i>b</i> -St)	274
		EMA-Te-Bu	P(MMA- <i>b</i> -St)	275
		organostibine	P(MMA- <i>b</i> -NVP)	272,273
NVP		methyl-2-methyl-2-methyltellanyl-propionate	P(NVP- <i>b</i> -St)	269
		organostibine	P(NVP- <i>b</i> -MMA)	272,273
NIPAm		EMA-TeBu	P(NIPAm- <i>b</i> -NVP)	276
NVCL	Co(acac) ₂		PNVCL- <i>b</i> -P(NVP-co-NVCL)	277
MAF-TBE	Co(acac) ₂		P(VAc- <i>alt</i> -MAF-TBE)- <i>b</i> -PVAc	252

2.6.2. OMRP First: Combined Approaches for Block Copolymer Synthesis. In this section, we discuss block copolymerization in which the first block is generated by an OMRP pathway, and the second block is produced either by CRP through NMP, ATRP, and RAFT. End-capping of polymer–metal complexes with radical trapping entities is the most typical strategy. A second block can be also generated by ROP through end functionalization with OH groups to form the basis for lactone polymerization. Other recent strategies include the insertion of O₂ to switch the polymerization from OMRP to ROCOP, giving polycarbonate blocks.

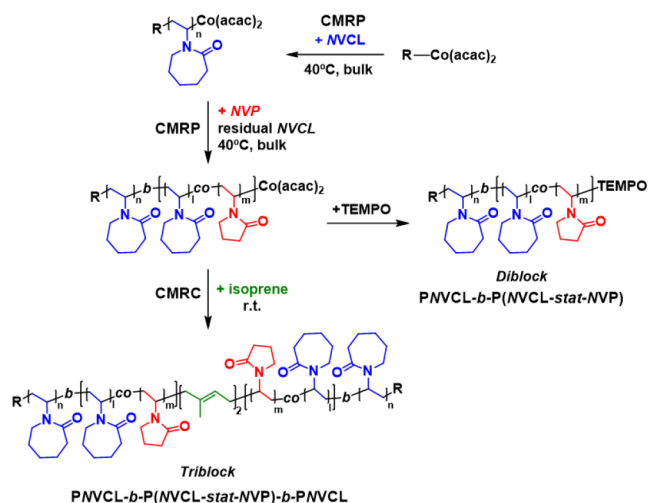
2.6.2.1. OMRP Combined with CRP. Parallel to the development of OMRP and investigation of metal complexes to polymerize challenging monomers such as MMA and styrene combined approaches were developed. To combine a range of different acrylic monomers, polymer–Co(acac)₂ are end-functionalized with nitroxide derivatives.²⁵⁷ However, the resulting PVAc-Co(acac)₂ TEMPO derivatives are not suitable

for reinitiation as the C–ON bonds of the alkoxyamines are stable up to 180 °C.

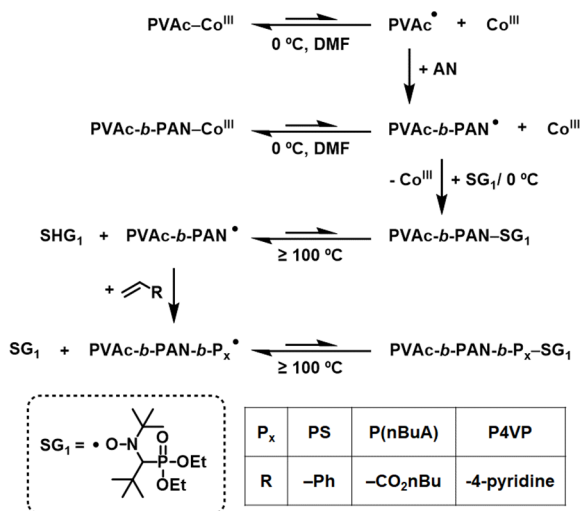
ABC triblocks are realized by preparing a PVAc-*b*-PAN-Co(acac)₂ macroinitiator and performing an *N*-tert-butyl-*N*-(1-diethylphosphono-(2,2-dimethylpropyl)) nitroxide (SG1) radical coupling to give a PVAc-*b*-PAN-SG1 (AB block), which then was used to form a series of ABC triblocks with various acrylic monomers (Scheme 7).^{256,278}

The TEMPO coupling strategy and the stability of the C–ON bond can be advantageous when preparing functionalized nitroxide derivatives containing bromo-ketones or bromo-esters to perform ATRP reactions.²⁸⁰ Well-defined PVAc-*b*-PS, PVAc-*b*-PEA, and PVAc-*b*-PMMA block copolymers were then synthesized. A subsequent methanolysis of the PVAc block of PVAc-*b*-PS diblocks led to the formation of the corresponding amphiphilic PVOH-*b*-PS copolymers of well-defined structure and composition (Scheme 8). A different coupling strategy was employed when OMRP and RAFT polymerization is combined to prepare well-defined poly(vinyl acetate)-*block*-polystyrene

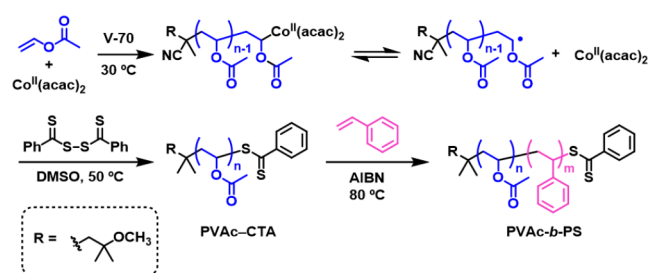
Scheme 6. Di- and Triblocks from NVCL and NVP Monomers by OMRP²⁵³



Scheme 7. ABC Triblock Copolymers by Combining OMRP and NMP Polymerization²⁵⁶



Scheme 8. Poly(vinyl acetate)-polystyrene Diblock Copolymers via Sequential OMRP and RAFT Polymerization²⁷⁹



(PVAc-*b*-PS) block copolymers.²⁷⁹ The ω chain ends were modified into a phenyl dithioester group by reacting with bis(thiobenzoyl) disulfide, producing PVAc-CTA and PVAc-PS-CTA. The RAFT polymerization of styrene with PVAc-CTA or PVAc-PS-CTA gave PVAc-*b*-PS block copolymers with $M_n = 21\,000$ g/mol, $\bar{D} = 1.28$ starting from a polymer of ~ 10 K. The hydrolysis

to amphiphilic PVA-*b*-PS block copolymer was conducted under basic conditions.

2.6.2.2. OMRP Combined with ROP. Diblock poly(vinyl acetate)-*b*-polycarbonate can be realized by OMRP polymerization of vinyl acetate monomers followed by a mono oxygen insertion in the Co-C bond, leading to the formation of (salen)Co^{II}-O-R. This active species then can initiate a ring opening polymerization of CO₂/epoxides (ROCOP) as reported by Poli and Wang.²⁸¹ The switchable polymerization can proceed in a one-pot process, and O₂ functions as an external stimulus to switch the mechanism from OMRP mediated by (salen)Co^{III}-R [salen = *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2 cyclohexanediamine; R = alkyl] to the ring-opening copolymerization (ROCOP) of CO₂/epoxides. (salen)Co^{III}X (X = Cl, Oac, etc.) complexes were first employed by Coates, and the reversible formation and dissociation of polar Co-O bonds are crucial for the chain propagation process. The insertion of the mono oxygen insertion into CoIII-C bonds, which generates (salen)Co^{III}-O-R as an active species for the ROCOP of CO₂/epoxides is key in the mechanism and sequential block copolymer formation (Figure 26).

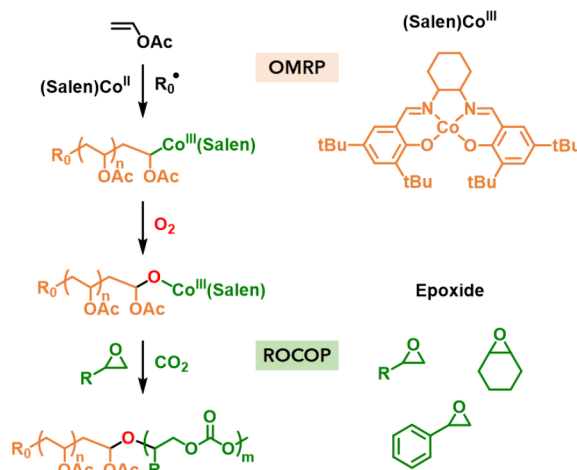


Figure 26. Polyacrylate-polycarbonate block copolymers by combining switching from OMRP to ROCOP. Adapted with permission from ref 281. Copyright 2019 Wiley.

Combining OMRP with ROP can be conducted by endfunctionalization of polymer-Co(acac)₂ using ethanol VA-086 to form an OH-functionalized polymer end-group which can perform ring opening polymerizations with caprolactones to give PVP-*b*-PCL.²⁸² Another possibility to create PNVP-*b*-PCL and PCL-*b*-PNVP-*b*-PCL engages ω -chain-end modification and α -functionalization. The α -functional and α,ω -telechelic PNVPs when polymerized with hydroxy-functional VA-086. When α -hydroxy-PNVP-Co(acac)₂ is treated with isoprene, it leads to the almost quantitative coupling of the chains to give α,ω -hydroxy-telechelic PCL-*b*-PNVP-*b*-PCL.

2.6.3. Outlook. OMRP has been successfully applied to the synthesis of block copolymers, especially with the ability to polymerize LAM's and has to numerous block copolymer architectures which generally start from the LAM segment followed by other acrylic monomers. The choice of the metal complex can be used to govern the block copolymer composition by sequential additional of the monomer or by changing the OMRP complex. The combination of OMRP with

CRP can accomplish the formation of block copolymers with styrene such as RAFT and ATRP. End-capping and radical trapping of the first block are the most important strategies to extend by insertion or ring-opening polymerization. Here, isoprene has been found to be a very useful end-capping reagent to specifically couple polymers to form triblock architectures. The interest in switchable catalysis and accessible radical macroinitiators will be the future driving force to develop block copolymers with other monomer combinations.

2.7. Degenerative Chain Transfer (DT) Reagents for CRP

In this section, we discuss how the degenerative transfer mechanism in controlled radical polymerization can be tuned to optimize block copolymer formation of acrylates and specifically with monomers of low activity such as α -olefins and ethylene. The copolymerization of α -olefins and ethylene is not trivial through radical methods as the intrinsic reactivity is low and high temperatures and pressures are required.

2.7.1. DT in RAFT. In early attempts to copolymerize α -olefins or ethylene with acrylates via the free radical pathway, only low incorporation of the olefins was achieved. CRP such as RAFT has been shown to be the first method to polymerize ethylene. It has been found that nonactivated monomers such as ethylene benefit from solvents that are used in free radical polymerization reactions such as dimethylcarbonate (DMC) to minimize chain-transfer reactions. Monteil et al. were the first to report the successful RAFT polymerization of ethylene using xanthate as a chain-transfer agent under rather mild conditions (200 bar, 70 °C) in DMC.⁹⁰ The chain extension was realized with ethylene to prove the living character of the process, allowing the synthesis of PE-*b*-PE. The process gave access to low molar mass polymers ($M_n < 2000 \text{ g}\cdot\text{mol}^{-1}$), with dispersities in the range of $1.4 < M_w/M_n < 2.3$. A RAFT/MADIX method was used by Zhou and You et al. to copolymerize polar monomers such as *N*-vinyl lactams, with ethylene reaching $10^4 \text{ g}\cdot\text{mol}^{-1}$ with a relatively narrow molar masses distribution ($M_w/M_n < 1.5$). The polar monomer arrangement can be tuned to give block copolymer structures in which the polar block (*N*-vinylpyrrolidone) is synthesized first ($P^\circ < 75 \text{ bar}$, 70 °C) and extended with ethylene.²⁸³ The key for the success of this process is attributed to the use of a xanthate RAFT reagent with the electron donating group in the Z position. It is thought that the destabilization of the RAFT-adduct results in an increase of the fragmentation rate of PE and might contribute to the increased control of polymerization of the two adverse monomers (Figure 27). However, it was found that PE• is a rather unstable radical species, and a side fragmentation along the stabilizing Z or L group can be observed which continuously decreases the livingness of the chains and diminishes chain

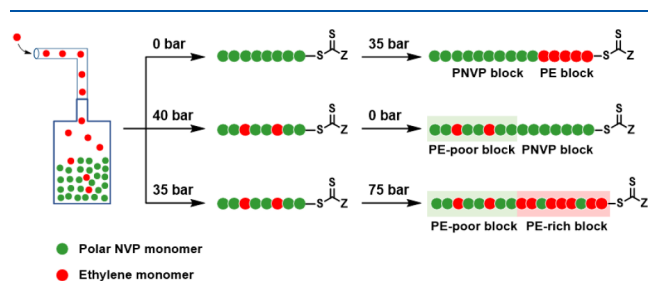
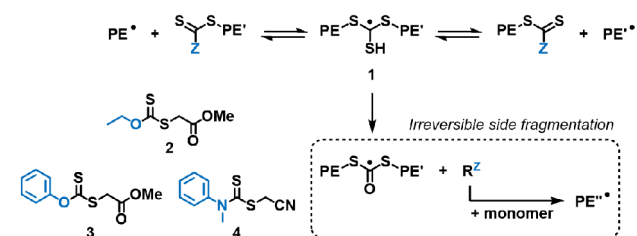


Figure 27. PNVP-*b*-PE and PE-*co*-PNVP copolymers by tuning the pressure. Adapted with permission from ref 283. Copyright 2017 Royal Chemical Society.

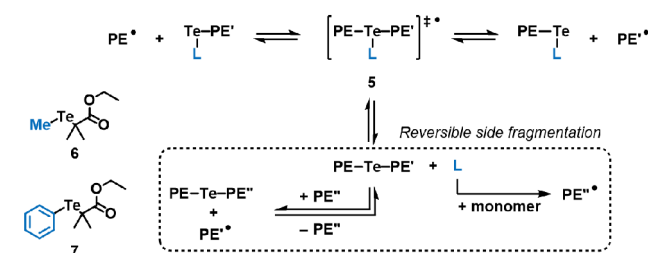
extension and rate retardation in the RAFT process. In related organotellurium-mediated radical polymerization (TERP) processes similar trends of side reactions of the intermediate radical species was observed.

2.7.2. DT in TERP. Chain transfer reagents (DT) generated in situ from organoditelluride compounds are oxygen-stable in contrast to organomonotelluride compounds (MTs). Binary azo initiators and DT lead to the synthesis of ultrahigh molecular weight copolymers but also block copolymers containing polar repeating units with properties highly desirable for the use as dismantlable adhesive materials. The degenerative chain transfer mechanism allows for the synthesis of block copolymers, starting with a synthesis of acrylate and α -alkene, 6-methyleneundecane (6MU) copolymers under TERP conditions and 2-methyl-2-methyltellanylpropionate as the CTA, to form a macro-CTA. This macro-CTA can then be used to chain extend with styrene or *N*-vinylpyrrolidone (NVP) to form poly[(MA-*co*-6MU)-*b*-St] and poly[(Ma-*co*-6MU)-*b*-NVP] with a copolymer block of a molecular weight of 4–31 kDa by adding fluoro alcohols as a Brønsted acid.²⁸⁴ The incorporation of olefin is 0.49% mole fraction in the first block and the final block with dispersities in the range of 1.19–1.41 and molar masses as high as 31 000 g/mol. TERP proceeds by the DT mechanism like RAFT, but it does not involve a stable intermediate radical during the DT process and is therefore ideal for olefin polymerization, moreover, as the P–Te–P' might still serve as an effective CTA and prevent the formation of dead chains (Figure 28). Polyethylene can be formed by TERP with narrow dispersities between 1.3 and 2 and molecular weights up to 5000 g/mol as shown by Monteil, D'Agosto, and Yamago et al.²⁸⁵

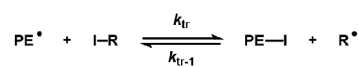
A) Degenerative chain transfer (DT) in RAFT polymerization (main equilibrium)



B) Degenerative chain transfer (DT) in TERP (main equilibrium)



C) Reversible chain transfer (DT) in ITP (pre-equilibrium)



Degenerative chain transfer (DT) in ITP (main equilibrium)

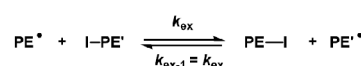


Figure 28. Use of DT in CRP for the polymerization of ethylene. Adapted with permission from ref 291. Copyright 2020 Wiley.

2.7.3. DT in Iodine Transfer Polymerization (ITP). ITP is another CRP based on reversible degenerative chain transfer.²⁸⁶ The terminal iodine functionality offers a platform for postpolymerization modifications and possibility to switch to other polymerization techniques.^{286,287} The technique is mostly reported for the controlled polymerization of fluoroalkene and specifically vinylidene fluoride (VDF) with an iodinated compound as chain-transfer agent.²⁸⁸ The process is commonly applied in the industrial setting to synthesize fluorinated thermoplastics elastomers.^{289,290} The side fragmentation at transition radicals is not favored as the ITP mechanism involves the transfer of one iodine atom only. Monteil and D'Agosto found that $C_6F_{13}-I$ used as alkyl iodine CTA could polymerize ethylene without any significant side reactions. Molar masses of up to 7 g/mol^{-1} were reported. Block copolymers were formed from PE-*co*-EVA copolymers as first block containing up to 16% EVA with the second block being a pure PE block copolymer (EVA 16%-*b*-PE) with molecular weights ranging from 9 to 20 g/mol⁻¹ and dispersities ranging from 1.52 to 1.89.²⁹¹

2.7.4. Outlook. The degenerative chain transfer mechanism offers the possibility to polymerize monomers with poorly stabilized radicals, and here specifically olefinic monomers have been investigated to generate block copolymer structures. Usually using this radical pathway, the olefin is either copolymerized with the acrylate, and then an acrylic block follows, or a purely acrylic block is first prepared, and the olefin block follows. So far, it is not possible to start the polymerization in a reversed pathway.

2.8. Living Cationic Polymerization

Studies of cationic polymerization were reported as early as in the 18th century. Since its discovery, the technique has been studied extensively; thus by the early 20th century, an elemental understanding on the scope of monomers, different initiator systems as well as the kinetics of cationic polymerization have been established.^{199,292} A particular emphasis was given to the development of controlled cationic polymerization, especially after the discovery of living anionic polymerization by Szwarc et al. in 1956.²⁹³ However, living cationic polymerization proved to be a difficult challenge. The propagating cationic species' inherent natures of high chemical activity and low stability make it highly susceptible to side reactions, which ultimately results in chain transfer as well as chain termination. Chain termination, which often occurs via facile ion collapse, is difficult to avoid. On the other hand, chain transfer to monomer occurs via β -proton elimination, whose process can be slowed down rather than eliminated. As a result, the requirements for a living cationic polymerization are (1) controlled initiation, (2) reversible chain termination, and (3) retardation of the rate of chain transfer (Figure 29).

There are three different possible terms when discussing cationic living polymerization: (1) long-lived species, (2) quasi-living, and (3) ideal living. For long-lived species in polymerization, a continuous increase in molecular weight (MW) along the conversion of monomers is observed, but the molecular weight distribution (MWD) is usually broad because of heavy side reactions. Quasi-living polymerization, defined by Kennedy, successfully eliminates chain termination and achieves reversible chain transfer, but its MWD can still be broad given its relatively slow initiation rate. Ideal living polymerization requires that all three criteria above are achieved. It allows the formation of well-defined polymers as well as block copolymers with well-controlled molecular weight and molecular weight distribution.

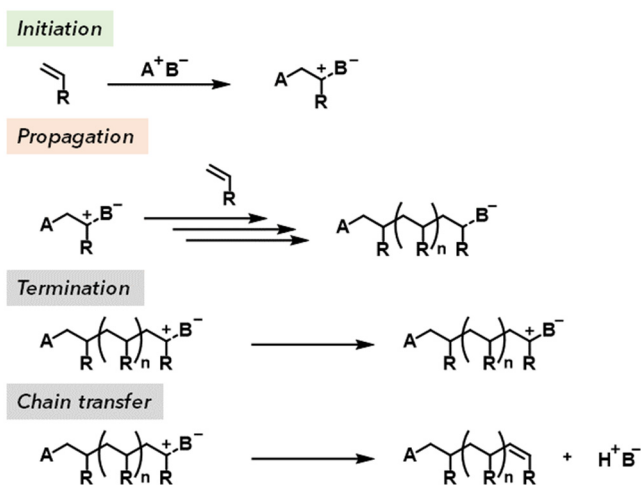
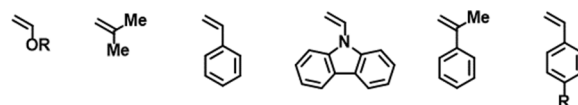


Figure 29. Initiation, propagation, termination, and chain-transfer pathway typical for cationic polymerization.

A breakthrough was reported in the late 1970s, when Higashimura and Kishiro first published their study of living polymerization of *p*-methoxystyrene by using iodine as the initiators.²⁹⁴ However, it was later claimed by Kennedy et al. that it is rather a long-lived species given that chain transfer to monomer was still observed during polymerization.²⁹⁵ Kennedy and Faust then reported the discovery of the first quasi-living cationic polymerization of isobutene. In 1984, the major obstacle was finally overcome when Higashimura and Sawamoto reported the true living cationic polymerization of isobutyl vinyl ether using hydrogen iodide/iodine system.^{296,297} Two years later, Kennedy and Faust successfully achieved living polymerization of isobutene through an initiator system consisting of cumyl acetate (CumOAc), 2,4,4-trimethylpentane-2-acetate (TMPOAc), and BCl_3 .^{298,299} Following these crucial findings, living cationic polymerization has been rapidly developed, and a plethora of new initiator systems and polymeric materials has arisen.

2.8.1. Monomer Scope. During cationic polymerization's course of development, vinyl ethers and isobutene have been among the most vigorously studied monomers because of their relatively good stability and reactivity as propagating species (Chart 2).

Chart 2. Monomers Suitable for Cationic Polymerization



Living cationic polymerization of isobutene is especially of great interest, as polyisobutylene has shown to be an excellent class of elastomer while being exclusively capable to polymerize via cationic polymerization. Polystyrene, another prominent industrial polymer, has also been investigated with this technique. However, styrene is more difficult to polymerize in comparison to vinyl ethers and isobutene due to the lack of good electron donating substituents. Styrene's growing cationic species are less stable and reactive, thus becoming more prone to chain termination and chain transfer to monomer processes. On the other hand, *p*-alkoxy styrene, or any other styrene derivatives with moderately good electron donating substituents

on the phenyl ring, are great monomers for cationic polymerization. In particular, *p*-alkoxy styrene's behavior in reactions are considered to be similar to those of vinyl ethers. α -Methylstyrene has also been examined, but its polymerization is more challenging to control because of greater steric hindrance at α -position from the methyl group. Moreover, this extra methyl group also has three additional β -protons, which results in a greater chance of β -elimination. Lastly, *n*-vinylcarbazole is one of the most reactive monomers for cationic polymerization due to its highly conjugated substituent group. Living polymerization of *n*-vinylcarbazole by hydrogen iodide/iodine was first reported by Sawamoto and Higashimura in the 1980s.^{300,301}

2.8.2. Initiator Scope. The initiation mechanism was first demonstrated by Kennedy and co-workers when the polymerization of isobutene using different Ziegler–Natta catalyst was studied.³⁰² Kennedy discovered that isobutene can only be polymerized by Et_2AlCl under the presence of a cationogens such as HCl or H_2O . He postulated that Me_2AlCl acted as a co-initiator, which then reacted with the cationogen to release the true initiator for cationic polymerization, the proton. A different system consisting of *t*-butyl chloride (tBuCl) and Et_2AlCl was used, and rapid (sometimes explosive) polymerization of isobutene was achieved. The mechanism involved the generation of the highly stable carbocation $(\text{CH}_3)_3\text{C}^+$ from the abstraction of the chloride from *t*-BuCl by Et_2AlCl . This finding has helped introduce the strategy for the control of the initiation step and overall polymerization as well as the use of the cationogens for headgroup functionalization.

As discussed earlier in this section, possible formation of living cationic polymerization of *p*-methoxystyrene via I_2 as the initiator was first observed by Higashimura et al. in 1977.²⁹⁴ *p*-Methoxystyrene was targeted as the monomer due to its ability to form a stable carbocation to avoid β -proton elimination and thus chain transfer to monomer as a nondissociated propagating species. Iodine was the initiator because it could produce a counterion with good nucleophilicity. It was reported that the molecular weight increased as the monomer was consumed, and nondissociated propagating species was observed to be long-lived at 0 °C in CCl_4 . This system was subsequently employed to generate long-lived propagating species for the polymerization of isobutyl vinyl ether and *n*-vinylcarbazole.^{300,303,304} However, the I_2 -catalyzed initiation was slow, which resulted in a broad dispersities. Around the same time, Kennedy and Faust reported the quasi-living cationic polymerization of isobutene induced by BCl_3 in the presence of H_2O at -78 °C under high vacuum.^{295,302,305} It was discovered that this system would eventually lead to chain termination with chloride being the end group regardless of quenching methods. This terminated polymer chain would further react reversibly with BCl_3 to form the carbocation propagating chain and BCl_4^- as the counterion. Kinetic studies using Mayo plot ($1/\text{DP}_n$ vs $1/[\text{M}]$) showed a linear line through the origin without intercepts, which indicated the absence of chain transfer. Nonetheless, this system was not capable of fully eliminating chain transfer to monomer.

In 1984, Higashimura and Sawamoto successfully modified the I_2 -catalyzed system by employing equimolar amount of hydrogen iodide (HI) as the co-initiator to achieve the first true cationic living polymerization of isobutyl vinyl ether (IBVE).²⁹⁶ The HI/I_2 initiating system overcame the initiation barrier because of HI 's reasonably high dissociation constant. Using this system, the polymerization of IBVE at -15 °C in *n*-hexane resulted in nearly monodisperse poly(IBVE) ($\text{Đ} \leq 1.1$). The

molecular weight increased proportionally to the conversion of monomer and inversely to the initial HI concentration. Kinetic studies showed the complete absence of chain termination and chain transfer while the initiation of HI/I_2 was faster than propagation, thus satisfying the necessary conditions of living polymerization. For the BCl_3 -based system, the main objective was to identify suitable counterions, which is sufficiently stable to suppress chain transfer and termination while promoting initiation and chain propagation (Figure 30).

Initiators for Vinyl Ethers:



Vinyl Ethers Living Polymerization using HI/I_2 :

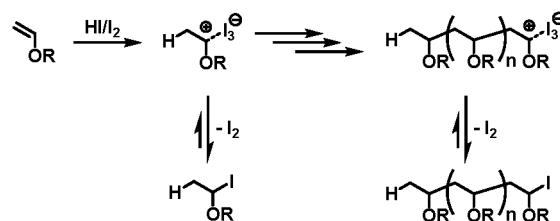
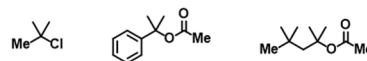


Figure 30. Initiator scope and mechanism of living cationic polymerization of vinyl esters.

In 1987, Kennedy and Faust solved this problem by introducing the system of BCl_3 and tertiary esters, which are cumyl acetate and 2,4,4-trimethylpentane-2-acetate.^{298,299} BCl_3 and the tertiary esters were able to form stable zwitterionic complexes, which then initiate the polymerization of isobutene rapidly. Polyisobutylene with narrow dispersities ($\text{Đ} = 1.17$ – 1.3) could be obtained at low temperature from -50 °C to -10 °C in a variety of solvents such as CH_2Cl_2 , and a mixture of chlorinated solvent with *n*-hexane. Kinetic studies demonstrated a linear relationship between M_n and W_{polymer} (grams of polymer formed). The monomer conversion and initiator efficiency were also roughly 100% (Figure 31). Further

Initiators for Isobutene:



Isobutene Living Polymerization using BCl_3 /Cumyl Acetate:

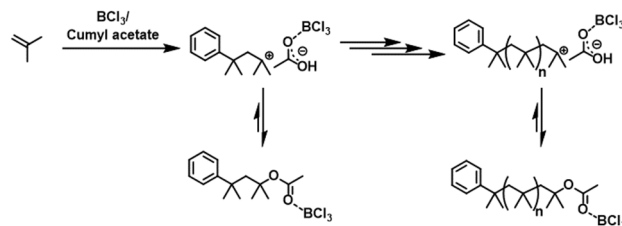


Figure 31. Initiator scope and mechanism of living cationic polymerization of isobutene.

modifications have been made for the HI/I_2 system for the polymerization of vinyl ethers. Higashimura et al. combined HI with various Lewis acids and observed a number of different results.³⁰⁶ The binary system of HI and ZnX_2 , a weak Lewis acid, produced a living polymerization of vinyl ethers as well as *p*-methoxystyrene at room temperature 25 °C in toluene. In

particular, ZnI_2 generated the most stable counterion, thus being the best co-initiator. The propagating species' stability followed the order of $\text{ZnI}_2 > \text{ZnBr}_2 > \text{ZnCl}_2$. Other weak Lewis acids like SnX_2 could also produce living polymerization at low temperature of -40°C in CH_2Cl_2 .

On the other hand, strong Lewis acids like TiCl_4 , SnCl_4 , or Et_2AlCl failed to facilitate a living polymerization. However, the addition of tetraalkyl ammonium salts (nBu_4N^+) or phosphonium salts (nBu_4P^+) with nucleophilic counterions such as I^- , Br^- , or Cl^- aided to yield living polymerization with narrow MWD ($M_w/M_n \approx 1$) for the SnCl_4^- system.³⁰⁷ Moreover, strong Lewis acids in combination with a weak base (ethers, esters) could produce living polymerizations for IBVE.^{308,309} The system of EtAlCl_2 and 1-(isobutoxy)ethyl acetate ($\text{CH}_3\text{-CH}(\text{O-}i\text{-Bu})\text{OCOCH}_3$), which is the adduct of IBVE with acetic acid could produce living polymerization of IBVE with the addition of ethers such as 1,4-dioxane, tetrahydrofuran (THF), and diethyl ether at 0 to 40°C in *n*-hexane. The optimal amount of ether depended on the basicity, which followed the order of THF (1–2 vol %) > 1,4-dioxane (5–10 vol %) > Et_2O (70 vol %). Aoshima et al. also reported fast living polymerization of IBVE by adding SnCl_4 into the EtAlCl_2 /base system.³¹⁰ The dual Lewis acids system resulted in rapid polymerization with narrow dispersities ($\bar{D} = 1.02\text{--}1.08$), which was 10^3 times faster than that of the conventional EtAlCl_2 system in the presence of ethyl acetate at 0°C in toluene. In addition, this system polymerized O- and N-containing monomers $10^3\text{--}10^5$ times faster than compared to the $\text{Et}_x\text{AlCl}_{3-x}$ system. On the basis of the hard soft acid base (HSAB) theory, esters, considered as hard bases would interact strongly with a hard acid like EtAlCl_2 . On the other hand, SnCl_4 is a rather soft acid, and thus it would not interact with the ester groups as strongly. Instead, it would attack the soft chlorine group at the polymer chain end more readily to form a stable hexa-coordinated tin anion complex as counterion. Another system consisting of a soft Lewis acid FeCl_3 , IBVE/ HCl adduct, and 1,4-dioxane also led to fast polymerization of IBVE in 15 s in toluene at 0°C .³¹¹

The BCl_3 /tertiary ester system for isobutene (IB) polymerization has also seen several improvements over the years. Puskas and Kaszas showed that TiCl_4 functioning as co-initiator worked well in tandem with either esters or ethers.³¹² More importantly, they demonstrated that an improved controlled living polymerization could be achieved by adding a strong Lewis base to the system. Traditional systems such as $\text{CumCl}/\text{BCl}_3$, $\text{CumOH}/\text{BCl}_3$, or $\text{TMPCl}/\text{TiCl}_4$ could only initiate the nonliving polymerization of isobutene, which resulted in a broad MWD. However, the presence of dimethyl sulfoxide (DMSO) or dimethylacetamide (DMA) permitted the living polymerization of the three systems above and gave well-defined narrow MWD.³¹³ Similarly to the base-assisted living systems for vinyl ethers, these Lewis base played an important role in controlling the activity of the Lewis acid as well as the stability of the carbocation species, thus avoiding any unwanted side reactions. Faust et al. also reported controlled living polymerization of isobutene with improved MWD in the presence of 2,6-di-*tert*-butylpyridine (DTBP) as a proton trap.³¹⁴ In these systems, DTBP would solely scavenge protic impurities without interacting with the propagating species because excess amount of DTBP did not affect the rate of polymerization.

Although living polymerization of isobutene primarily utilizes BCl_3 and TiCl_4 , there are a few examples of other Lewis acids used for those systems. Cheradame et al. was the first to report that Et_2AlCl could achieve living polymerization of isobutene.

Compared to previous methods, this system did not require an additional Lewis base (DMSO, DMA) or a halogenated cationogen.³¹⁵ Instead, it was shown that a system of Et_2AlCl and a tertiary azide was able to achieve living polymerization with reasonable dispersities ($\bar{D} = 1.3\text{--}1.5$) at -50°C in CH_2Cl_2 . Moreover, the azide end group could allow for further modification postpolymerization. Shaffer et al. later reported a similar system of EtAlCl_2 and a conventional tertiary alkyl chloride co-initiator, which also did not require an added Lewis base or a proton trap.³¹⁶ This system could yield living polymerization with narrow dispersities ($\bar{D} = 1.2$) at low temperature from -80°C to -75°C in a 60/40 mixture of *n*-hexane/ CH_2Cl_2 .

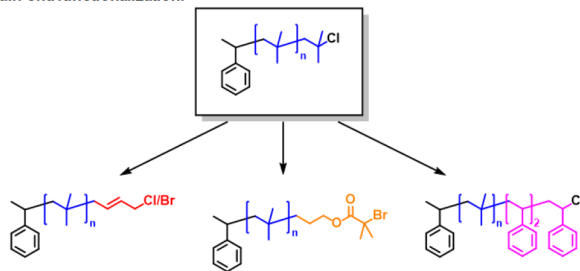
2.8.3. Kinetics of Cationic Polymerization. It is important to recognize that all living cationic polymerizations are not ideally living but rather quasi-living polymerizations. For every initiating system, reversible chain termination is present, but chain transfer to monomer is completely absent, which still results in monodisperse polymers with narrow dispersities. Reversible chain termination is achieved through the manipulation of the equilibrium between the dormant species (covalent) and the active species (carbocation). The rates for these steps are much faster than that of propagation. However, ideal living and quasi-living polymerization are kinetically indistinguishable, thus bearing little effects on the outcome of the polymerization. Sawamoto and Kennedy's kinetic studies both showed that their systems had fast initiation, and the polymerization rates were rapid as well.^{296,299} Both the HI/I_2 and $\text{BCl}_3/\text{CumOAc}$ systems also demonstrated that the molecular weight increased continually as the monomer was consumed, and a linear relationship between the conversion of monomers and the number-average molecular weight (M_n) was established. In addition, the number of polymer molecules (N) produced per unit initiator remained constant as the monomer conversion increased to near 100%. The formula follows $N = [\text{M}]_{\text{consumed}}/\text{DP}_0[\text{I}]_0$, where $[\text{M}]_{\text{consumed}}$ is the real time concentration of the monomer, DP_0 is the number-average degree of polymerization, and $[\text{I}]_0$ is the initial concentration of the initiator. The polymer dispersity of these systems was also relatively narrow and well-defined in comparison with their precedents I_2 and $\text{BCl}_3/\text{H}_2\text{O}$ systems as discussed in the earlier section.

2.8.4. Cationic Polymerization First: Combined Approaches for Copolymer Synthesis. Compared to their homopolymer counterparts, block copolymers have proved to exhibit interesting and superior properties due to the ability to combine a wide array of monomers. Although living cationic polymerization has laid out, the major groundwork for the development of many block copolymers, the monomers scope is rather limited, as cationic polymerization is not successful, with several industrial monomers like methacrylate (MA), methyl methacrylate (MMA), or acrylonitrile (ACN). The electron-rich nature of these monomers as well as the tendency of common initiators (BCl_3 , AlCl_3 , TiCl_4) to be easily poisoned by polar groups, rendering cationic polymerization to be ineffective. As a result, it is important that these problems are bypassed by combining cationic polymerization with other polymerization techniques.

2.8.4.1. Cationic Polymerization Combined with FRP. Prior to the discovery of controlled free radical polymerization techniques (ATRP, RAFT), attempts of combining cationic and classical free radical polymerization (FRP) to yield block copolymer resulted in moderate success. Nuyken et al. reported

the preparation of block copolymer of IBVE and methacrylonitrile (MAN) using a pseudobifunctional azo-based initiator for the cationic polymerization.³¹⁷ Specifically, the initiating system consisted of HI, $n\text{Bu}_4\text{NClO}_4$, and 2,2'-azobis[2-methyl-4-(2-vinyl-2-oxoethyl)butyronitrile] 1 (Figure 32), which

A) Chain-end functionalization:



B) Scope of block copolymer structure:

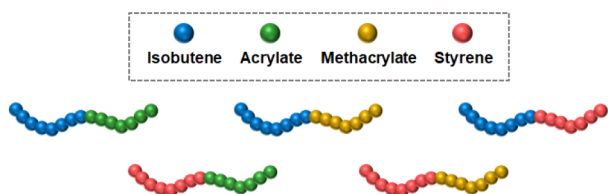


Figure 32. Polyisobutylene blocks with end functionalization for subsequent ATRP to form block copolymers.

could be easily synthesized from commercially available 4,4'-azobis(4-cyanovaleic acid). This system first induced well-controlled living cationic polymerization of PIBVE- R_x -PIBVE macroinitiator with narrow dispersities ($\bar{D} = 1.2$). The azo-macroinitiator then underwent homolysis at 60 °C to generate the macroinitiator free radical, which further polymerized the MAN monomer to form the AB diblock copolymer. GPC results showed a left-shifted peak with no tailing, which indicated the absence of homopolymer. However, the polymerization of the MAN block was not controllable due to the nature of radical polymerization, leading to a not well-defined final polymer with a relatively broad dispersities ($\bar{D} = 1.4$ – 1.6).

2.8.4.2. Cationic Polymerization Combined with ATRP.

Upon the discovery of ATRP, the technique was quickly adapted to be combined with living cationic polymerization to produce block copolymers due to the similarities of the two propagating chains' end groups. As discussed in earlier in the section, living cationic polymerization that used MX_n (BCl_3 , TiCl_4) as catalyst would always result in halogenated chain ends of domain species irrespective of quenching methods, thus suggesting that sequential ATRP polymerization was possible with the living cationic propagating chain as the macroinitiator. Indeed, Matyjaszewski et al. first demonstrated one-pot sequential copolymerization of styrene (via living cationic polymerization) with MA and MMA (via ATRP) without any further chain end functionalization.³¹⁸ PS was first polymerized by the initiating system of (1-chloroethyl) benzene/ SnCl_4 / $n\text{Bu}_4\text{NCl}$ at -15 °C in CH_2Cl_2 . MA was added to deactivate the catalyst, and the remaining ester, Lewis acid, and CH_2Cl_2 were removed under vacuum. The mixture of CuCl /bipy in toluene along with the second monomer was then added at 100 °C. GPC results showed a peak shift with for both PS-*b*-PMA and PS-*b*-PMMA and M_w/M_n values of 1.20 and 1.57, respectively. Sequential copolymerization was further demonstrated via the use of prefunctionalized initiator for the living cationic ring-opening

polymerization of THF followed by ATRP of PS, MA, or MMA.³¹⁹ This method allowed for the preparation of either AB or ABA block copolymers depending on the initiators. For AB block copolymers, ring-opening polymerization of THF was initiated by the 2-bromopropionyl bromide/ AgOTf system at 25 °C. Once the polymerization was completed, it was quenched with H_2O , and the bromine-terminated chain end became the macroinitiator for the ATRP of the second segment. The resulting block copolymers were well-defined and exhibited narrow dispersities ($\bar{D} = 1.2$ – 1.5). For ABA blocks, the polymerization of THF used the sodium 2-bromopropionate/ $\text{O}(\text{OTf})_2$ system, which yielded bifunctional PTHF for the sequential ATRP of styrene, MA, and MMA.

For PIB-based block copolymers, however, it proved to be more challenging for the sequential ATRP without functionalization of chain ends due to the low reactivity of tertiary chloride PIB-Cl in the redox reaction. Capping the propagating chain with more reactive intermediates has been shown to improve the efficiency for the synthesis of this type of block copolymer. As discussed above, block copolymer of PS and MA/MMA could be easily obtained via a seamless sequential polymerization from cationic to ATRP, so it was a logical step to transform the PIB-Cl chain end to a PIB-St-Cl intermediate for the subsequent ATRP.³²⁰ Specifically, PIB would be polymerized under standard conditions of cumyl acetate/ TiCl_4 /DTBP in CH_2Cl_2 /hexane at -80 °C, then 3 equiv. of styrene would be added to cap the chain. This macroinitiator was now sufficiently reactive for the polymerization of MA/MMA via ATRP under the condition of CuCl /dNbipy in toluene at 100 °C. This approach was used to synthesize a thermoplastic ABA triblock of PMA-*b*-PIB-*b*-PMA, as the GPC result showed unimodal curve with narrow molecular weight distribution. In another approach, the cationic alkyl chain end was transformed into an allyl halide macroinitiator for ATRP. Faust et al. reported a straightforward synthesis of PIB-allyl-halide terminated chain by adding either 1,3-butadiene/ $\text{Me}_{1.5}\text{AlBr}_{1.5}$ or 1,3-butadiene/ TiCl_4 to the living PIB chain.³²¹ Matyjaszewski et al. investigated the efficacy of this allyl halide macroinitiator in ATRP with various monomers, including St, MA, and MMA.³²² Polymerization of St using an allyl-Cl initiator showed well-controlled molecular weights but a rather broad molecular weight distribution. However, polymerization of MMA using the same initiator resulted in a molecular weight which was four times higher than anticipated, which indicated poor control of the polymerization. The allyl-Br initiator analogue showed great control for the polymerization of styrene, but MMA polymerization was still not controlled, as the resulting molecular weight was 2 times higher than targeted. The polymerization, however, could be improved by incorporating 10% of styrene into the reaction as the resulting MMA-*co*-St demonstrated great molecular weight control and distribution. Kennedy et al. also demonstrated the synthesis of 3-arm PIB-*b*-PMMA star polymer by a series of chain end manipulations from the chloride end group to the standard 2-bromoisobutyryl end group for the subsequent ATRP of MMA.³²³ This approach required more complex transformations, but in return the polymerizations of both IB and MMA were better controlled with narrow molecular weight distributions. The inherent disadvantages of these approaches of sequential polymerizations are that there is usually a trade-off between relative monomer activities for the two techniques. Additionally, chain end functionalization might prove overly complex, thus affecting the overall efficiency of the reaction (Figure 32).

The polymerizations of both homo and copolymer were in line with previous results, as the GPC results showed a unimodal trace as well as reasonably narrow dispersities of $\bar{D} = 1.5$. Another improvement of this metal-free cationic RAFT polymerization over the first discussed approach is the possibility of a one-pot transformation from a cationic to a radical pathway without one hindering the other (Figure 33).

With the emergence of photoinduced electron/energy transfer (PET) RAFT,^{119,330} Satoh et al. demonstrated a new strategy to combine cationic polymerization with RAFT via a switchable cationic/PET-RAFT polymerization mechanism triggered by visible light.³³¹ While this strategy was also used to copolymerize IBVE with MA, the designed initiating system for the cationic segment were modified differently compared to the standard cationic RAFT polymerization. Specifically, unlike cationic RAFT polymerization's requirement for a Brønsted acid, this system instead used a Lewis acid such as EtAlCl_2 , ZnCl_2 , and $\text{B}(\text{C}_6\text{F}_5)_3$ to mediate the cationic chain addition—fragmentation of IBVE as well as ZnTPP , a photoredox catalyst, along with CTA 5 or 9 to induce PET-RAFT polymerization of MA. This method was also capable of promoting interconvertible copolymerization of IBVE and MA at the same time as the reaction was radiated by visible light. As a result, this method was highly versatile because it was possible to synthesize either statistical copolymer or block copolymer via switchable one-pot synthesis triggered by light. However, the molecular weight distribution for these copolymers were not as narrow as one would expect for a true living system as the M_w/M_n values were in the range between $\bar{D} = 1.5$ and 1.6.

2.8.4.4. Cationic Polymerization Combined with Anionic Polymerization. Chain-end functionalization followed by lithiation to generate anionic species is a common and highly effective approach which can produce thermoplastic elastomers (TPE), block copolymers of IB, and acrylates with narrow molecular weight distribution. Kennedy et al. demonstrated a straightforward scheme by using Friedel–Crafts alkylation of toluene by the precursor dihalogenated polymer chain Cl-PIB-Cl obtained from the standard cationic polymerization procedure.³³² The resulting ditolyl-PIB ($\text{CH}_3\text{Ph-PIB-PhCH}_3$) underwent lithiation and further reacted with diphenylethylene (DPE) to form the suitable dianion species for the anionic polymerization of MMA in THF at -78°C to yield PMMA-*b*-PIB-*b*-PMMA thermoplastic elastomer triblock copolymer. The livingness was maintained throughout both polymerization steps, as evidenced by clear left-shifted GPC peaks as well as narrow dispersities ($\bar{D} = 1.2$ –1.3). In a similar fashion, Hatada et al. functionalized OH-PIB-OH via esterification to form diisobutylate-PIB, which was then lithiated by LDA to obtain the dianionic macroinitiator for the subsequent polymerization of acrylates to yield the final triblock copolymer.³³³ Looking to bypass the chain-end functionalization steps, Muller et al. directly end-capped the living PIB-Cl/Cl-PIB-Cl chains with DPE and further terminated the cationic species using MeOH, which yielded either a diphenyl vinyl or diphenyl methoxy end-group depending on the reaction conditions.³³⁴ Metalation of both species were achieved using Na/K alloy in THF. Li metal and Cs metal were also capable of cleaving the methoxy group to yield the anionic macroinitiator for the synthesis PIB-acrylates block copolymers. However, metalation of DPE end-capped PIB was rather slow and thus not quantitative. Thus, thiophene was demonstrated to be a better alternative, in which it can directly end-cap the PIB chain as well as undergo lithiation quantitatively.³³⁵ Notably, this method could also produce

star-shaped PIB by reacting 4 equiv of lithiated PIB—thiophene with SiCl_4 . This approach of site transformation is also viable for ring opening anionic polymerization to synthesize PIB-*b*-PEO^{336,337} and PIB-*b*-lactones³³⁸ block copolymers. Another methoxy-free approach was developed by Faust et al., in which they employed *para*-double diphenyl ethylene (PDDPE) 1,4-bis(1-phenylethenyl)benzene in combination with Bu_3SiH as the hydride source instead of methanol to end-cap the polymer chain quantitatively (Figure 34).³³⁹

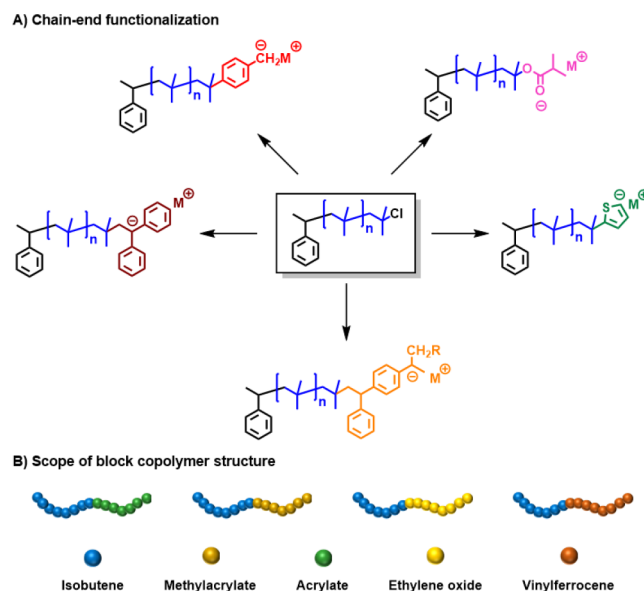


Figure 34. Polyisobutene's chain-end functionalization for anionic polymerization.

Alternatively, block copolymers of IB with anionic-compatible monomers could be synthesized via chains coupling of homopolymers synthesized by cationic and anionic polymerization individually. Specifically, Faust et al. successfully synthesized block copolymers of IB and vinylferrocene (VFc) by coupling vinyl halide end-capped PIB-allyl-X chains with nonterminated LiPVFc chains.³⁴⁰ This method exhibited a high coupling efficiency at 85% for the PIB-*b*-PVFc diblock. However, a similar attempt for triblock PVFc-*b*-PIB-*b*-PVFc formation resulted in a high amount of side products due to the undesired lithium–halogen exchange. Coupling efficiency of both diblocks and triblocks were well improved to 94% by transforming the vinyl halide end-capped PIB-allyl-X to the halosilyl end-capped PIB-SiX as the coupling partner with LiPVFc. Following this method, the resulting polymer exhibited uniformity close to the expected molecular weight with extremely narrow dispersities ($\bar{D} < 1.1$).

2.8.4.5. Cationic Polymerization Combined with Coordination Polymerization. Grubbs et al. combined ring opening metathesis polymerization (ROMP) with cationic polymerization via end-group functionalization using a chain transfer agent.³⁴¹ Polynorbornene and poly(exodicyclopentadiene) were synthesized using bis(cyclopentadienyl)titanacyclobutane catalysts via ROMP. Terephthalaldehyde, as the chain transfer agent, reacted with the living polymer chains in a Wittig-like transformation to introduce the aldehyde end-group to the polymer chain, which then acted as the initiator for the cationic polymerization of *tert*-butyldimethylsilyl vinyl ether to yield block copolymer with low dispersities ($\bar{D} < 1.6$) (Figure 35).

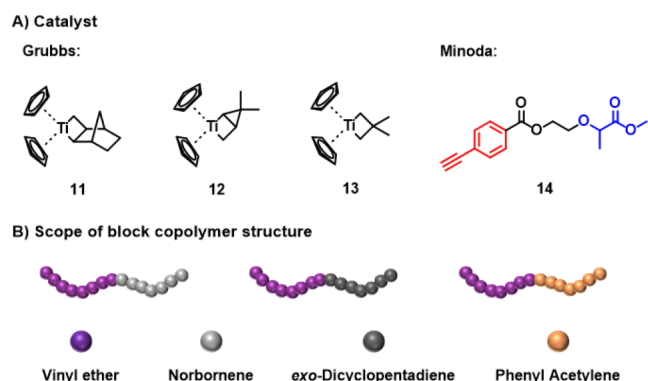


Figure 35. Employed catalysts for combining cationic polymerization with coordination insertion polymerization.

Alternatively, Minoda et al. employed a bifunctional initiator **14**, which contained a phenylacetylene (PA) and 1-(acetoxymethoxy)ethoxy end groups.³⁴² The PA initiator site could polymerize alkynes like PA using a rhodium alkylidene catalyst to generate conjugated poly(phenylacetylene) (PPA). On the other hand, the 1-(acetoxymethoxy)ethoxy end-group, along with EtAlCl_2 , initiated living cationic polymerization of IBVE. The polymerization could be first initiated from either end, which resulted in well-controlled polymerizations using optimal reaction conditions.

2.8.5. Outlook. Cationic polymerization has had a long history of development, with an extensive library of initiators and monomers. With one of the major breakthroughs in 1984, when Higashimura and Sawamoto first demonstrated a true living polymerization of isobutyl vinyl ether block copolymers based on poly(isobutene) as well as poly(isobutyl vinyl ether), which had been synthesized and designed with various architectures and topologies. Cationic polymerization's versatility is further demonstrated as the first building block for block copolymer synthesis in combination with other techniques including ATRP, RAFT, anionic polymerization, and insertion polymerization. The nature of halide chain end resulted from cationic polymerization allows for simple chain end transformation into different functional groups for further copolymerization via different polymerization techniques. Additionally, the simplicity of the initiators also enables a straightforward integration into other systems' initiators/catalysts with respect to the approach of bifunctional initiators.

2.9. Living Anionic Polymerization

Within the method of ionic polymerization, there are two different routes of polymerization that can be used, anionic and cationic, as discussed in the previous section. These methods vary in their compatibility with certain monomers, solvents, polymerization conditions, and mechanistic pathways.^{343,344} Since 1956,²⁹³ pioneering work with radical anions led to the polymerization of styrene with exhibited negligible chain transfer or termination reactions and is termed as living anionic polymerization.³⁴⁵ It revolutionized the field of ionic polymerizations due to the technique's ability to form stereoregular and stereospecific polymerizations and provides conditions which inhibit free radical polymerization.³⁴⁶ Specifically, styrene and conjugated dienes are the most prominent monomers used in this type of polymerization. According to the mechanism, a carbanion is formed during propagation first by a sodium naphthalenide initiator, which was later replaced by alkyl-lithium.³⁴⁷ The carbanion can undergo nucleophilic addition to the monomer and is supported by a stabilization by resonance or

induction. Therefore, monomers having stabilizing groups, such as styrene,^{348–350} dienes,³⁵¹ acrylates,³⁵⁰ acrylamides,³⁵² methacrylates,³⁵³ acrylonitriles,^{354,355} vinylpyridine,³⁵⁶ and vinylferrocenes,³⁵⁷ were the first ones which were investigated. Here the carbanion stability is achieved under stringent, inert conditions where oxygen and moisture as well as other protic impurities are removed.³⁴⁷ The monomer scope could be expanded to lactones, isocyanates, hexamethylcyclotrisiloxane, functional ester groups, and metal-containing monomers through newer methodology.

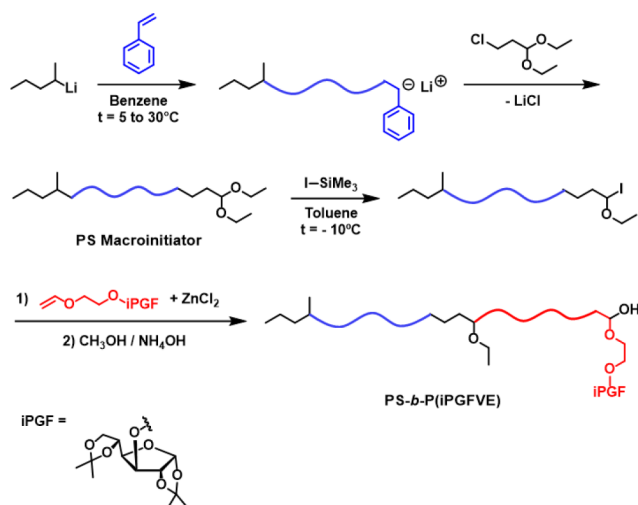
2.9.1. Anionic Block Copolymerization. As a general consideration for block copolymer formation with anionic polymerizations is to avoid all impurities or conditions which lead to a termination or chain transfer, which makes the experimental conditions quite demanding. A sequential addition of monomers to yield AB block copolymers has been widely used, and a high nucleophilicity of the macroanion is required in order to initiate efficiently the polymerization of the second monomer and has a higher rate of propagation. The order of addition is chosen therefore to be styrene > dienes > vinylpyridines > (meth)acrylates > oxiranes > siloxanes. Additionally, the initiation rate of the second monomer must be much higher than the propagation rate. The livingness of the chain-end and a quantitative consumption of the first monomer is a requirement to guarantee a successful formation of block copolymers. AB, ABA, and ABC triblocks, ABCD tetrablocks, and also multiblocks are commonly prepared by this method. These can be formed by the sequential addition of monomers or by the combination of functionalized chains prepared by anionic polymerization pathways. Block copolymers from nonpolar monomers, such as styrene and dienic monomers such as isoprene and 1,3-butadiene or 1,3-cyclohexadiene, vinyltrimethylsilane, and trimethylsilylstyrene, represent the greatest body of work prepared by sequential addition. Usually $n\text{-BuLi}$ or sec-BuLi and N,N,N',N' -tetramethylethylenediamine, TMEDA, or 1,4-diazabicyclo[2, 2, 2]octane, DABCO, are used as the initiation system. ABA triblocks such as PS-*b*-PI-*b*-PS can either be prepared from living PS-*b*-PI- Li^+ by adding TMEDA to create solvent free anions to continue with the polymerization of the second A block. Another approach includes the use of a linking reagent such as chlorosilanes, which can be a time-consuming process. ABC triblock copolymers are usually prepared through the sequential addition of monomers and the monomer reactivity sequence is playing a crucial role. Multiblock copolymers such as ABCD and ABABA can be prepared through the sequential addition or mostly through postpolymerization chemical modification reactions by avoiding chain scission or degradation to give quantitative conversions. Hydrosilylation, hydrolysis, hydrogenation, and quaternization reactions are the most applied methods.³⁵⁸

2.9.2. Anionic Polymerization First: Combined Approaches for Block Copolymer Synthesis. When these methodologies are not sufficient to generate block copolymers as desired, other techniques are required. Over the years, the most common strategies to combine polymerization techniques for the formation of block copolymers involve macroinitiators, chain transfer agent functionalization, or coupling of polymer segments, for instance, via “click” reactions. In this section, we will summarize the different approaches used to combine living anionic polymerizations with other vinyl polymerizations such as cationic polymerization, NMP, ATRP, and RAFT polymerization, combination with ring-opened polymers and polyolefins via either ring-opening metathesis polymerization (ROMP),

metallocene, and post-metallocene chemistry and will conclude with an assessment of the current methods.

2.9.2.1. Anionic Polymerization Combined with Cationic Polymerization. Deffieux et al., synthesized amphiphilic block copolymers of styrene and hydrophilic glycosidic vinyl ether by a combination of living anionic and cationic polymerization.³⁵⁹ In this work, the PS segment synthesized by living anionic polymerization was transformed into a macroinitiator that could initiate the living cationic polymerization of the hydrophilic segment. The synthesis of the macroinitiator was carried out by reaction of the polystyryl lithium with chloroacetal derivatives that yield acetal-PS. The acetal-PS was then derivatized in the presence of trimethylsilyl iodo to iodo ether-PS that can initiate the cationic polymerization of glycosidic vinyl ether (Scheme 9).

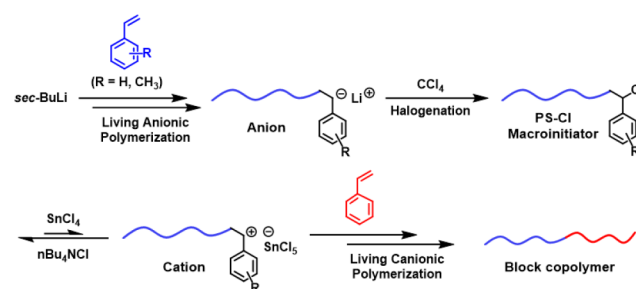
Scheme 9. Amphiphilic Block Copolymer of PS-Glycosidic Vinyl Ether by Combining Living Anionic with Cationic Polymerization³⁵⁹



A mechanistic transformation study was conducted by Satoh et al.,³⁶⁰ in which PS done from living anionic polymerization is transformed to a macroinitiator capable of undergoing either controlled radical polymerization or living cationic polymerization by direct halogenation of PS. The living anionic polymerization was conducted with typical conditions, inert environment, and *sec*-BuLi as initiator, however, the resulting polymer in this case was involved in direct halogenation by CCl₄. The carbon–halogen terminal can then undergo living cationic polymerization to form block copolymers with 4-methylstyrene, with SnCl₄/*n*-Bu₄NCl as the catalyst (Scheme 10). The resulting block copolymers were well characterized, and unprecedented gradient block copolymers were also studied.

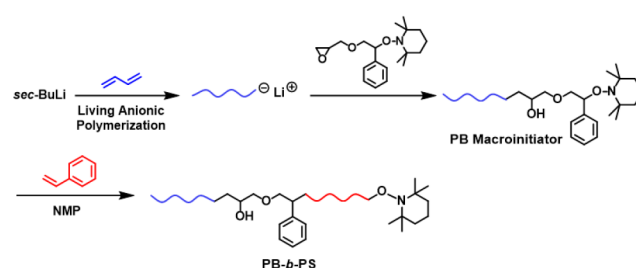
2.9.2.2. Anionic Polymerization Combined with NMP. Nitroxide-mediated polymerization (NMP) is a technique that has been first developed for styrenic monomers. In 1987, Rizzardo et al. presented a work where alkoxyamines initiate NMP for radical polymerization.³⁶¹ The macroinitiator is prepared by using living anionic polymerizations, as for example in the work by Endo et al.³⁶² The PS was synthesized using living anionic conditions with *sec*-BuLi and via one-electron-transfer and radical-coupling reaction with TEMPO and 1-oxo-4-methoxy-2,2,6,6-tetramethylpiperidinium salt, the PS was end-capped to give the C–O-alkoxy linkage. In 1998, Priddy et al.³⁶³ synthesized a block copolymer of butadiene and styrene,

Scheme 10. Terminal Halogenation of Styrene for Living Cationic Polymerization³⁶⁰



combining living anionic and NMP using the described macroinitiator approach. Although both monomers, butadiene and styrene, can undergo formation of block copolymers via sequential anionic polymerization, costly purification steps should be avoided. Hence, in this work, the living anionic polymerization of butadiene in cyclohexane with *sec*-BuLi as initiator for 24 h at room temperature was carried out. The resulting poly(butadiene) (PB) was terminated using an epoxy-functionalized alkoxyamine that was used to initiate the NMP of styrene (Scheme 11). GPC results indicated that almost all of the PB macroinitiator was converted to block copolymers and those were monodisperse.

Scheme 11. Poly(butadiene-*co*-styrene) Block Copolymer Obtained from Sequential Living Anionic Polymerization and Nitroxide-Mediation Polymerization³⁶³



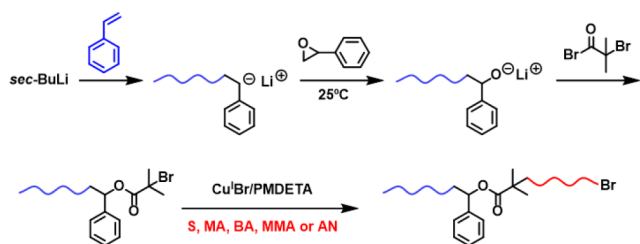
A following paper by Kobatake and Priddy et al.³⁶⁴ developed other macroinitiators to combine living anionic polymerization and NMP. Here, two different halogen-containing benzyloxyamines, one chlorine and one bromine, were used as terminating reagents of the PS segment, and it emphasizes that the termination needs to be conducted at low temperature. Similar work was conducted by Yamada et al.,³⁶⁵ where butadiene and hexamethylcyclotrisiloxane (D₃) polymerized by living anionic polymerization and the chain ends were terminated by using 4-formylphenylalkoxyamine to give a functionalized PB and PD₃ that were used for NMP of styrene in high yields.

2.9.2.3. Anionic Polymerization Combined with ATRP. Immediately after the discovery of ATRP in the mid-1990s, ways to combine this new technique with living anionic polymerization became popular to form block copolymer with interesting architectures. The seminal work from Matyjaszewski³⁶⁶ in 1998 involved a macroinitiator approach to combine living anionic polymerization with ATRP to form block copolymers of styrene and isoprene/styrene with styrene, methyl acrylate, butyl acrylate, methyl methacrylate, and styrene/acrylonitrile.

The living anionic polymerization took place under common conditions with *s*-BuLi as initiator in benzene at room

temperature. From the living anionic polymerization, a styrene homopolymer and styrene–isoprene copolymer was formed, and the chain was extended with styrene oxide to be later terminated with 2-bromoisobutyl bromide (BriBBR). The PS and PS-*b*-PI containing the bromine end-groups were used as efficient macroinitiators for ATRP with a variety of monomers as mentioned above with the CuBr/PMDETA catalyst system (Scheme 12). Characterization via FT-IR showed the

Scheme 12. ATRP Macroinitiator Generation from PS Anionic Polymerization³⁶⁶

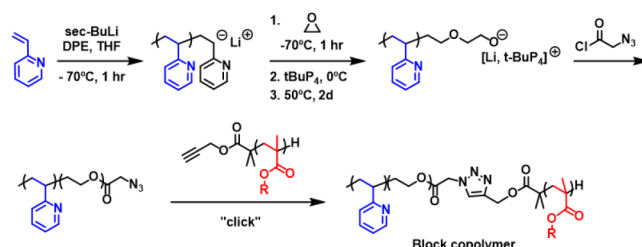


incorporation of the 2-bromoisobutyl in the anionic chain end, and SEC traces of the block copolymers indicated an increase of molecular weight, corroborating the formation of blocks with dispersities of less than 1.34. Finally, synthesis of ABA triblocks were studied using the PS-*b*-PI block made by sequential anionic polymerization using *s*-BuLi in toluene at $-30\text{ }^{\circ}\text{C}$ and undergoing the same termination transformation to yield bromine terminated chain ends. ATRP was preformed using the same catalyst system and styrene to yield the resulting PS-PI-PS triblock with a dispersity of less than 1.2. Similar work was carried out by Winnik et al.,³⁶⁷ where a PS-*b*-PI block containing a single fluorescent dye molecule at the junction was required but could not be accomplished by living anionic methods, and hence a combination of techniques was necessary. The approach initially synthesized the PI via living anionic polymerization with *s*-BuLi and was terminated by a reaction between the carbanion and the dye, 1-(9-phenanthryl)-1-phenylethylene (9-Ph). The resulting polymer is labeled with a single fluorescent dye at the junction that can be treated with α,α' -dibromo-*p*-xylene to form a macroinitiator for ATRP. This macroinitiator is very efficient because of the benzylic halide function, which is more favorable for ATRP, and hence the polymerization of styrene with CuBr/bPy could be accomplished to prepare the PI-*b*-PS block copolymer. Dhamodharan³⁶⁸ and his group presented similar work preparing block copolymers of styrene and 2-vinylpyridine using a macroinitiator approach. First, the styrene segment was made using common living anionic conditions with *s*-BuLi followed by termination with ethylene oxide because the resulting PS-OH can be converted to PS-Cl using a simple displacement reaction with thionyl chloride. The macroinitiator was then used to initiate ATRP of 2-vinylpyridine using a CuCl/bPy catalyst system, and the formation of block copolymers was confirmed by GPC. Both examples achieved the desired block copolymers using both bromine and chlorine catalyst systems and a macroinitiator approach. Using a macroinitiator approach to combine living anionic polymerization and ATRP of other monomers such as MMA and poly(ethylene glycol) methyl ether methacrylate have also been studied. In 2000, Liu et al.³⁶⁹ presented the preparation of block copolymers composed of PS or PS-*b*-PB via living anionic polymerization and PMMA made via ATRP. The macroinitiator was synthesized by termination with

trichloroacetoxy to initiate ATRP with MMA using CuCl/bPy and resulted in blocks with high yield. In addition, Paik et al.,³⁷⁰ reported using a macroinitiator approach to obtain PS-*b*-PB block copolymers with poly(ethylene glycol) methyl ether methacrylate to be used as a silica dispersant. The PS-*b*-PB block was prepared following living anionic polymerization with termination using α -bromoisobutyl bromide that serves as initiator for ATRP of poly(ethylene glycol) methyl ether methacrylate using a CuBr/PMDETA catalyst system.

Although utilizing a macroinitiator approach to combine living anionic and ATRP techniques have been widely studied, there are a few publications that focus on coupling polymer segments synthesized from both approaches separately, particularly utilizing “click” chemistry. In 2011, Schmalz et al. presented the synthesis of a triblock terpolymer made of 2-vinylpyridine-*block*-ethylene oxide (2VP-PEO) via living anionic polymerization and *N,N*-dimethylaminoethyl methacrylate or oligo(ethylene glycol) methacrylate via ATRP.³⁷¹ Initially, the P2VP-*b*-PEO was obtained via sequential living anionic copolymerization and end-functionalized by esterification with an azido-functionalized acid chloride to yield the azido group required for the click reaction. The ATRP segment was synthesized using propargyl 2-bromoisobutyrate as the initiator which places the alkynyl end-functionalization in the polymer segment. The coupling reaction to obtain the final triblock terpolymer was conducted via 1,3-dipolar Huisgen cycloaddition of the azide and alkyne groups using a copper(I) catalyst characteristic for this type of “click” reaction (Scheme 13). It is worth noting that this work initially studied a

Scheme 13. Formation of Triblock Terpolymers via “Click” Coupling to Combine Segments from Anionic and ATRP Polymerizations³⁷¹



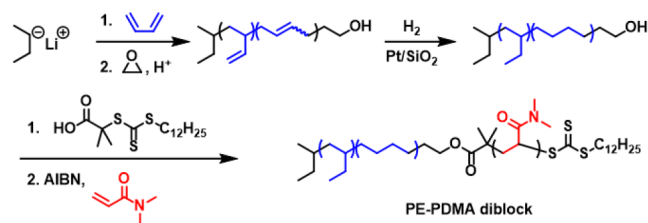
macroinitiator approach by terminating the living anionic polymerization with 2-bromoisobutyl bromide, however, the P2VP block has shown to disturb the ATRP by chelating with the Cu(I) catalyst, hence the coupling approach is more favorable.

2.9.2.4. Anionic Polymerization Combined with RAFT Polymerization. Given that the synthesis of block copolymers by living anionic polymerization might be limited to the range of monomers, combination with RAFT polymerization expands the number of monomers capable of forming blocks. As described above, when combining living anionic polymerization with other CRP techniques, the most common approach is to terminate the anionic polymerization with functionalities which can serve as a macroinitiator for the CRP techniques such as macro-chain transfer agent (macro-CTA) for RAFT. He et al.³⁷² reported the direct switching between living anionic and RAFT polymerization to obtain a polydiene-*block*-2-hydroxyethyl acrylate (HEA) or polydiene-*block*-*N*-isopropylacrylamide (NIPAm). The approach involved conducting a living anionic polymerization of isoprene or styrene with *sec*-BuLi and then

reacting it with 1,1-diphenylethylene (DPE). The resulting anionic chain ends undergo nucleophilic addition to the carbon disulfide followed by a reaction with alkyl bromides to form the thiocarbonylthio moiety. Once the macro-CTA was formed, it was used for RAFT polymerization of HEA or NIPAm with 2,2'-azobis(isobutyronitrile) (AIBN) as the initiator. The RAFT polymerization of NIPAm presented a few challenges with slow initiation and hence resulted in broader distribution, yet the HEA blocks showed low polydispersities with monomodal distributions.

Similar work where disk-like micelles were formed was presented by Hillmyer et al.³⁷³ In this work a polyethylene-*block*-*N,N*-dimethylacrylamide (DMA) was formed using a macro-CTA approach. The first block segment was achieved by either isoprene or butadiene living anionic polymerization and terminated using ethylene oxide. The PI or PB was further modified to ω -hydroxyl-functionalized polyolefin via heterogeneous catalysis with Pt/SiO₂. And finally, the RAFT agent was attached to the polyolefin chain via reaction with the hydroxyl end; the resulting macro-CTA undergoes RAFT polymerization of DMA (Scheme 14).

Scheme 14. Amphiphilic Polyolefin-*b*-DMA Copolymers Using a Macro-CTA Approach³⁷³

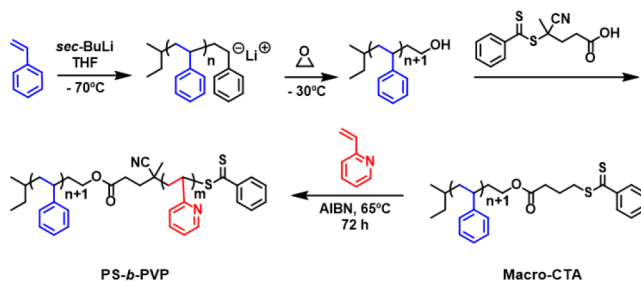


Hillmyer and Lodge³⁷⁴ also reported micellization and micellar aggregation of a very similar block copolymer polyolefin-NIPAm synthesized by a similar approach of living anionic and RAFT polymerization as described above. The polyolefin formation was achieved in similar steps by living anionic polymerization of isoprene with the sequential addition of ethylene oxide and hydrogenation with Pd/CaCO₃ to the polyolefin, and finally, the hydroxyl groups at the chain ends were reacted with the CTA to form the macro-CTA capable of aiding in the RAFT polymerization of NIPAm. Finally, Reineke and Hillmyer et al.³⁷⁵ also reported a similar approach for the synthesis of glucose-functionalized micelles. In this work, living anionic polymerization of isoprene and hydrogenation with Pt/SiO₂ was obtained and terminated with ethylene oxide to integrate hydroxyl groups to the chain ends. The terminated polyolefin was transformed into an ester with a trithiocarbonate to afford a macro-CTA for RAFT polymerization of DMA and a synthesized trimethylsilyl-protected 2-deoxy-2-methacrylamido-glucopyranose monomer (TMS-MAG). The resulting block copolymer self-assembled into micelles, and further micelle characterization was conducted.

Other reports for the combination of living anionic and RAFT polymerization for the formation of block copolymers using a macro-CTA approach involve work from Patrickios et al.³⁷⁶ and Barner-Kowollik and Gallei et al.³⁷⁷ Patrickios et al. reported the block copolymer formation of styrene and 2-vinylpyridine or 4-vinylpyridine with high molecular weight. The approach used is quite similar to the living anionic polymerization of styrene terminated with ethylene oxide to achieve a hydroxyl group at

the chain end that reacted with the 4-cyanopentanoic acid dithiobenzoate CTA to form the macro-CTA (Scheme 15).

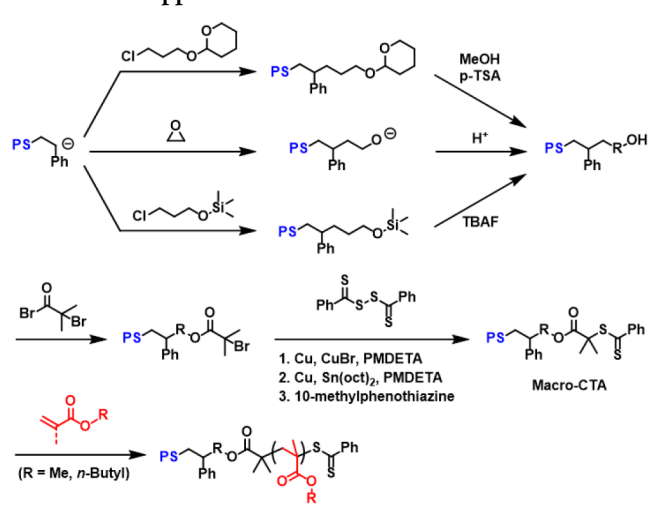
Scheme 15. Synthesis of Styrene and 2- or 4-Vinyl Pyridine Diblock Polymers of High Molecular Weight Using a Macro-CTA Approach³⁷⁶



The resulting diblock polymers are of high molecular weight and show dispersities of less than 1.39. Barner-Kowollik and Gallei et al., on the other hand, presented block formation of vinylferrocene (VFc) and *N,N*-diethylacrylamide (DEA) using a hydroxyl-end-functionalized metallopolymer. Similar to the previous examples, PVFc was synthesized using living anionic conditions with *n*-BuLi followed by a reaction with *N,N*-dimethylformamide (DMF), where the resulting aldehyde in the chain end was converted to a hydroxyl dimethyl amino group that can react with 2-(dodecylthiocarbonothioylthio)propionic acid RAFT agent to form a macro-CTA. The final block copolymers were obtained via RAFT polymerization of DEA using the macro-CTA and AIBN as initiator and displayed a dual-stimuli-responsive character (thermo- and redox-responsive block segments). A more recent work presented by Cochran et al. in 2019 claims to be the most efficient combination of living anionic and RAFT polymerization especially when considering industrial applications. In this report, the synthesis of PS under common living anionic polymerization in *sec*-BuLi was conducted and then underwent end-capping modifications via three options: (a) ethylene oxide, (b) acetal capping, or (c) silyl capping.³⁷⁸ The resulting hydroxyl-end functionalized PS was then modified by reaction with 2-bromo-2-methylpropanoyl bromide to further react with bis(thiobenzoyl)disulfide to form a macro-CTA. The macro-CTA was used to perform ARGET ATRAF and photocatalyzed metal free ATRAF but also RAFT polymerization of *n*-BA, MA, and MMA with AIBN as initiator (Scheme 16).

2.9.2.5. Anionic Polymerization Combined with Ring-Opening Polymerization. The combination of living anionic polymerization and ring opening polymerization (ROP) have been mainly developed in the 1970s by a series of seminal work by Richards et al.^{379,380} The advantage of combining both anionic polymerization and cationic ROP is the livingness of both polymerization pathways and hence facilitating the synthesis of block copolymers. Block copolymers of PS and tetrahydrofuran (THF) were prepared by termination of the polystyryllithium with bromine to carry out an anion-to-cation transformation. The PS segment was achieved under common living anionic conditions and terminated using excess bromine for direct reaction with the PS anionic chain end. The bromine-PS was further reacted with silver salts, which generated very reactive carbenium ions that attack THF to form oxonium ions that are more stable and polymerize the PTHF segment. However, at the conditions studied, β -elimination occurred and

Scheme 16. Diblock Copolymer of Styrene and *n*-Butyl Acrylate, Methyl Acrylate, or Methyl Methacrylate Using a Macro-CTA Approach³⁷⁸

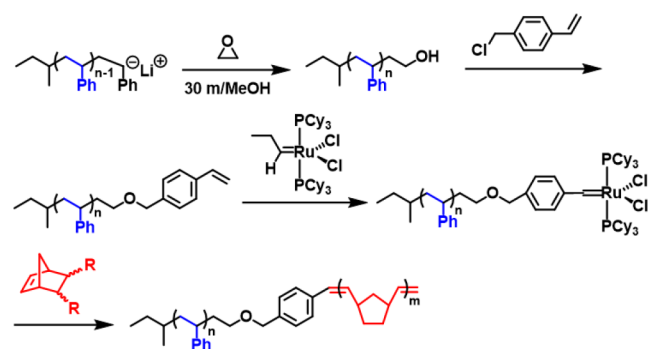


therefore limited the block copolymer formation efficiency. To limit the β -elimination and increase the block formation, the use of xylene dibromine as termination reaction of the PS was employed but no quantitative formation was observed.³⁸⁰

2.9.2.6. Anionic Polymerization Combined with ROMP. A commonly used strategy for this combination is to utilize the polymer obtained from living anionic polymerization, followed by postmodification as a macromonomer. A report for the synthesis of PEO-*b*-PNB employing this approach was described by Hutchings and Khosravi et al. in 2004. The termination of propagating PEO chain by 4-vinylbenzyl chloride yield PEO, bearing a terminal unsaturated functionality. Subsequent reaction with Grubbs catalyst afforded a macroinitiating Ru complex that enabled ROMP of NB to attain diblock copolymers with a wide ranges of molecular weight and compositions ($M_n = 10.0\text{--}63.1$ kg/mol), while dispersities remains reasonable ($\bar{D} = 1.1\text{--}1.32$).³⁸¹

Not so long after the initial report, Khosravi and Hutchings, and co-workers applied the similar strategy to prepare PS-*b*-PNB. In this study, anionic propagating PS chains were end-capped by ethylene oxide/MeOH to produce a hydroxyethylated PS that underwent Williamson coupling reaction with 4-vinylbenzyl chloride. In a similar manner, ruthenium PS macroinitiator was synthesized and used to initiate ROMP of NB (Scheme 17).³⁸²

Scheme 17. Macroinitiator Approach to Combine Living Anionic Polymerization and ROMP³⁸²



In another approach, Bates and Hillmyer, and co-workers carried out a living anionic block copolymerization of styrene and 1,4-butadiene (BD) to obtain PS-*b*-PBD-*b*-PS triblock.³⁸³ Selective hydrosilylation of the terminal vinyl group that from via 1,2-addition was then performed to prevent grafting and depolymerization side reactions in the next step. Subsequent ROMP with cyclooctene (cOE) using Grubbs second catalyst eventually afforded ABA-type triblock copolymers of PE-*b*-PcOE-*b*-PS that exhibited microphase separation in TEM studies.

2.9.3. Outlook. Living anionic polymerization has been recognized as a robust method, but the stringent polymerization conditions present limitations. To extend the versatility of this technique, a mechanistic transformation from living anionic into a different polymerization mechanism has been employed to allow for new monomers to be incorporated into blocks. All of the mechanistic transformations are conducted by deactivation or termination of the living anionic chain end with a functional group initiating the new polymerization technique. Few examples are coupling reactions, mostly “click” reactions, to ligate two polymer segments polymerized by living anionic polymerization and another technique, however, this approach is not as popular and further development is necessary. Among the polymerization techniques, other vinyl polymerization techniques, such as living cationic, ATRP, or RAFT polymerization, are extensively studied with ROP and coordination-insertion being more limited. In the case of NMP, although some progress has been made achieving macroinitiators, very little work has been focused on the actual synthesis of block copolymers that combine both techniques as well as studying the scope of block copolymer synthesis. The combination of living anionic polymerization and ROMP has produced only a few reports using a macroinitiator approach including some successful results from Khosravi and Hutchings et al.,³⁸² where different monomers could be studied using this approach.

3. BLOCK COPOLYMERS FROM RING-OPENED POLYMERS

Catalytic ring-opening polymerization has been a valuable method to prepare some of the most important classes of polymers. Other than vinyl polymers, the polymer backbones contain heterofunctionality to give raise to degradability and crystallinity and chain–chain interactions. Polyesters, polyamides, and polyoxazolines, which are carrying functional groups along their backbone, are highly polar polyethers; polysiloxanes (silicones) in contrast are elastomeric and nonpolar. The electronic characteristics of the involved cyclic monomers have governed the development of several ring-opening methods. The individual methods are either organic- or metal-based and have the goal to prepare tailored, low, and high molecular materials, which can be also stereospecific. In contrast to polycondensation, the ring-opening polymerization is a chain reaction and higher molecular weights with narrow polydispersities can be reached. Metal-based complexes can lead to an anionic or a coordination mechanism. Enzymatic and small molecule initiators are also very effective. With ongoing refinement of these methods, these polymers can work as ideal precursors to form block copolymers in combination with other polymerization methods. In this part of the review, we will first discuss ring-opening and block copolymer formation from polar monomers, such as lactones, lactams, and oxazolines, and last, nonpolar monomers such as glycidols/epoxides and silicones are discussed.

3.1. Block Copolymers from Polyesters

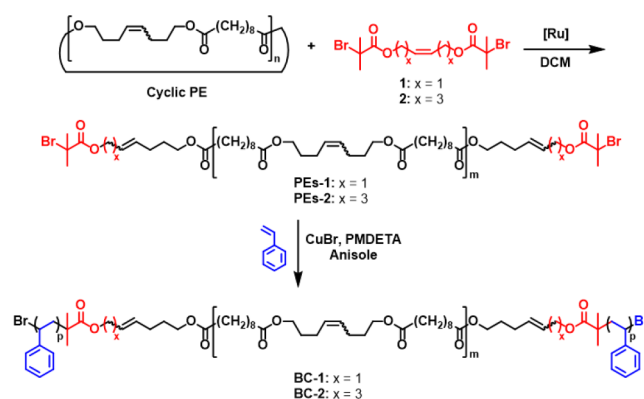
Anionic ROP from cyclic esters is initiated by alkoxide, for example, potassium methoxide or lithium/potassium *tert*-butoxide through an attack of the carbonyl groups to generate the propagating species. But for several lactones like, for example, L-lactides, this mechanism is not ideal, and therefore stannous octanoate and triflate are used for the coordination–insertion process and the propagation of a metal alkoxide species.³⁸⁴ Enzymatic or organocatalysis³⁸⁵ operating by a different mechanism of enchainment than metal oxides. Electrophilic monomer activation of the carbonyl facilitates a nucleophilic attack by the initiating or propagating alcohol by protic acids (catalytic) or methylating agents (stoichiometric). A nucleophilic monomer activation by pyridines, imidazoles, phosphines, and *N*-heterocyclic carbene can lead to more activated chain-carrying intermediates. Protonation of the zwitterionic alkoxide by the alcohol carrying chain end and acylation leads to the formation of a ring-opened alcohol. In another classical mechanism, the chain ends are activated such as by bases as in anionic polymerization. Bifunctional activation of monomer and initiator/chain end is proposed in metal alkoxide catalysts in which an electrophile and general base are working together to activate the monomer and the initiator/chain end. Organic acids, pyridine bases, and phosphine and carbene bases or strong neutral bases such as phosphazenes are other possible activators in organocatalysis.

An example of how these initiation reactions can be used to form polyester block copolymers is demonstrated in work from Irvine, Alexander, and Taresco.³⁸⁶ Here, 2-hydroxyethyl-methacrylate (HEMA) is used as initiator that provides at the same time a methacrylate termination for postmodification purposes. The acrylic alcohol in combination with triazabicyclodecene (TBD) and their ratios has an influence on the final reaction rate and molecular architecture by circumventing transesterification reactions. Block copolymers from poly(lactic acid) (PLA) and polycaprolactone (PCL) or poly(trimethylene carbonate) (PTMC) are highly desired in pharmaceutical and environmental applications due to their biodegradability and lost cost. End-terminalized block copolymers from polyesters will give another opportunity for postfunctionalization or further polymerization. Another way to use the idea of end-group functionalization of polyester blocks was accomplished in the work of Munoz-Guerra,³⁸⁷ in which a metal-free, enzymatic catalysis was applied to polymerize ω -pentadecalactone (PDL) by ring-opening polymerization (ROP) with several amino-terminated initiators, namely hexylamine, allylamine, and *O,O'*-bis(3-amino-propyl)diethylene glycol. Diblock copolymers were prepared by using polymeric amine carrying PEG macroinitiators. Triblock copolymers were synthesized by using difunctionalized PEG amine polymers, forming triblocks with a soft PEG-center block (PPDL–PEG–PPDL).³⁸⁷ A ROP of cyclic esters/carbonates and *N*-carboxyanhydride results in polyester-*b*-polypeptide and polycarbonate block copolymers via a one-pot sequential ROP. Sequential polymerizations are conducted in a one-pot process of monomers of the same type and which are initiated by the same initiators. However, when the monomers requiring different initiating/catalytic systems in a sequential one-pot synthesis, these must be differently planned. For example, for the preparation of polypeptide-based hybrid block copolymers, a cyclic ester or carbonate monomer (CL or TMC) is polymerized using 3-phenyl-1-propanol and methanesulfonic acid. Methanesulfonic acid is a good organocatalyst for both monomer families with con-

versions of over 97%. Then the *N*-carboxyanhydride, β -benzyl-L-aspartate is added together with *N*-ethyl-diisopropylamine as base to deprotect the ammonium groups which starts the propagation step of the carboxyanhydride. With this, the diblock copolymer can be formed in a one-pot process with high conversions of the monomers.³⁸⁸

Polyester–polystyrene block copolymers in a triblock copolymer fashion of PS-*b*-PE-*b*-PS (BAB type) was prepared by producing telechelic polyesters through the synthesis of cyclic polyesters containing carbon–carbon double bonds (C=C) by using unsaturated diols and dicarboxyl acid chlorides, which underwent cross-metathesis with a symmetric olefin with two functional groups as an exchange reagent, resulting into polyesters with functional groups at both ends. In this way, triblocks PS-*b*-PE-*b*-PS can be prepared initiated from a PEST–ATRP macroinitiator (Scheme 18).³⁸⁹

Scheme 18. Synthesis of PS-*b*-PE-*b*-PS Triblock Copolymer via Cross-Metathesis with a Macroinitiator for ATRP³⁸⁹



Polyester–polyether block copolymers of a (AB)_nB_m type structure have been prepared by a tunable bicomponent catalyst in one synthetic step (Figure 36).³⁹⁰ The involved ring-opening

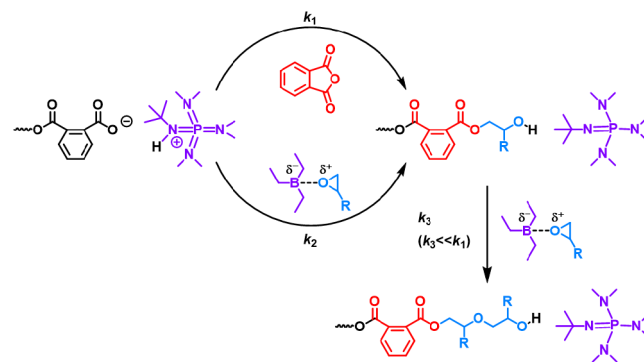


Figure 36. Mechanistic pathway for sequence-selective copolymerization of phthalic anhydride and epoxide. Adapted from ref 390. Copyright 2019 American Chemical Society.

alternating copolymerization (ROAP) with various nonhomopolymerizable compounds has established itself as a method which can provide a large number of diverse polycarbonates, polyesters, and specifically as pioneered by Coates, from a mixture of cyclic anhydride, epoxides, and CO₂.³⁹¹ By using this method, block copolymers can be prepared by the addition of a third monomer to form (AB)_nC_m by, for example, a sequence-selective terpolymerization of phthalic anhydride, epoxide, and

rac-lactide.³⁹² Here, cyclic anhydrides react with ring-opened epoxides faster than CO₂ or cyclic esters. However, Zhao et. al used an excess of the epoxide as a third monomer in which a homopolymerization of the epoxide is possible after the anhydride is consumed. A mild phosphazene base (*t*-BuP₁) and triethylborane (Et₃B) achieves a full conversion of the anhydride when polyether is not formed. The mild basicity and reduced nucleophilicity of the hydroxyl group activated through the *t*-BuP₁ and interaction with Et₃B enables the absence of transesterification. A fixed loading and increasing amount of Et₃B leads to the higher reactivity of the polyether and self-propagation is possible.³⁹⁰

Polyester block copolymers that combine controlled radical polymerizations such as ATRP and RAFT are commonly prepared by “end-functionalization” methods, “click” chemistry, and dual initiation methods.³⁸⁴ In the end-functionalization method, the polyester is prepared first and then the functionality of the other technique is added in the form of the initiating unit. For example, poly(CL)-*b*-poly(HPMA) are prepared by ROP of CL by benzyl alcohol, and the RAFT reagent is conjugated through its COOH group via DCC mediated esterification. The RAFT polymerization can be performed in pseudo-first-order kinetics and allows the formation of block copolymers with narrow distributions.³⁹³ Using this approach, the polyester chain can be either attached to the leaving (R) group or the stabilizing group (Z). When attached to the leaving group, some termination products can be observed. An attachment to the stabilizing group has a destabilizing effect on the intermediate in the pre- and main equilibrium of the RAFT mechanism, and a loss over the control of the polymerization is the result. In the “click” chemistry approach to combine polyester ROP with RAFT, the two polymers are prepared independently and are then conjugated or “clicked” together. For example, poly(LA)-*b*-poly(vinyl-alcohol) block copolymers have been prepared with an alkyne bearing initiator for the ROP of the polylactide and a RAFT reagent carrying an azide on its leaving group. After polymerization of VAc, the two blocks are conjugated via 1,2 cycloaddition. In the “dual initiator method” the hydroxy group is usually located on the leaving group of a thiocarbonyl compound of the RAFT chain transfer reagent as, for example, in the work from Dove and O'Reilly.³⁹⁴ Here, the OH group was used for an ROP polymerization of L-lactide with organic thiourea/(−)sparteine catalysts. The subsequent polymerization of tetrahydropyran acrylate (THPA) with AIBN as initiator led to PLLA-*b*-PTHPA block copolymers which can be deprotected to lead to PLLA-*b*-PAA block copolymers. The same approach was used earlier by Youk et. al in a one-pot synthesis by first ROP of CL, followed by a polymerization of VP to form PCL-*b*-PVP block copolymers (Scheme 19).³⁹⁵

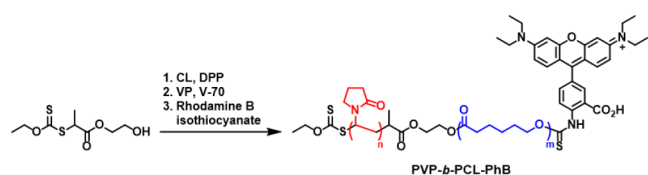
The method is successful without the intermediate purification of the polyester as the solubility of the monomer in the anisole solvent is compatible to both monomers and polymerization methods. The dual initiator method has also

been applied in an orthogonal strategy by Xu and Boyer et al., by which PCL-*b*-PMA block copolymers were prepared using PET–RAFT and DPP-catalyzed ROP. The modified chain transfer agent containing a hydroxyl group, 2-hydroxyethyl 2-(((butylthio)-carbonothioyl)thio)-propanoate (HEBCP), is used to initiate a ROP and PET–RAFT polymerization. The reaction can be conducted in one-pot by performing the PET–RAFT polymerization, first followed by ROP of CL, or by conducting ROP, first followed by the PET–RAFT reaction or by a simultaneous reaction engaging both pathways together.³⁹⁶ In an analogous approach with light-initiated ATRP, PLLA-*b*-PMMA block copolymers were produced in which 2,2,2-tribromoethanol (TBE) acted as a dual functional initiator, 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) was used not only as a catalyst for ROP but also the ligand for copper(I) bromide (CuBr) in UV light-induced ATRP. It was possible to first conduct the ATRP reaction in the light followed by the RAFT polymerization, as well as in reversed order, by first conducting the ROP and then the RAFT reaction. A simultaneous ATRP and ROP can be conducted as well.³⁹⁷ When combining ROP with ATRP methods, using a dual initiator with an OH group which is located on the alkyl halide, the ROP can be performed with the subsequent polymerization of the poly(methyl methacrylate) block. For example, in the work from Bo and Ji et al., PLLA-*b*-PDMAEMA block copolymers were prepared in this fashion with narrow dispersities.³⁹⁸ With the end-functionalization method, a lactone is polymerized with ROP, and after the conversion of the polyester OH end-groups into the ATRP initiator, CRP can be performed. In a classic approach from Matyjaszewski et al. a cationic ROP is conducted with tetrahydrofuran in the presence of AgOTf, which generates a polyTHF with a bromine chain end. PolyTHF-bromopropionate (pTHF-Br)³¹⁹ is then used to initiate the polymerization of styrene, MA, and MMA with ATRP. ABA triblock copolymers are prepared through the synthesis bifunctional polyTHF by initiation with triflic anhydride followed by a termination with sodium 2-bromopropionate. The triblock formation shows the best results with MMA.

3.2. Block Copolymers from Polyoxazoline

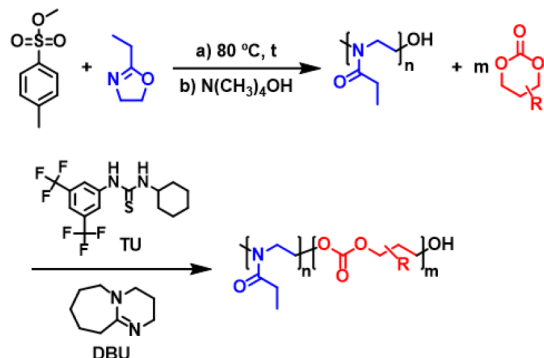
Polyoxazolines³⁹⁹ are pseudopeptides due to their structural relationship to polypeptides. The properties of polyoxazolines depend strongly on the substituents of the endoimino ether ring. Alkyl substituents of high molecular weight such as propyl or higher such as phenyl(perfluoroalkyl) have hydrophobic properties and are insoluble in water. However, alkyl substituents such as methyl and ethyl will provide polymers which are very soluble in water and are analogues of *N,N*-dimethylacetamide (DMAc) and display a strong hydrophilicity comparable to poly(vinyl alcohol). 2-Oxazolines (OX) can be ring-opened in a cationic pathway, with methyl *p*-toluenesulfonate as an initiator, which can then be terminated with ammonia to give an ω -amine-terminated poly(2-methyl-2-oxazoline), PMeOX. These polymers have been of interest because of their sensitivity to external stimuli (temperature and/or pH) and are therefore investigated in biotechnological applications. These polymers can be used as macroinitiators for the ROP, for example, poly(L-phenylalanine) and poly(γ -benzyl-L-glutamate).⁴⁰⁰ Polyoxazoline block copolymers with hydrophobic blocks are generally used for micellization and can contain PMeOX or PEOX together with polycaprolactone or polylactide. For example, Hoogenboom and Mespouille

Scheme 19. One-Pot Synthesis of RhB-Labeled PCL-*b*-PVP³⁹⁵



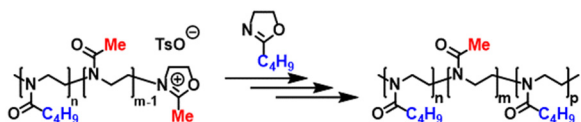
reported⁴⁰¹ on poly(2-alkyl-2-oxazoline)s (PAOx) that were combined with aliphatic polycarbonates (Scheme 20).

Scheme 20. Preparation of Block Copolymers Composed of 2-Oxazolines and Functional Six-Membered Cyclic Carbonate⁴⁰¹



The block copolymers were prepared via cationic ROP of 2-oxazolines, followed by the organocatalytic ROP of cyclic carbonate monomers. A termination step with methanolic KOH proceeded through an efficient OH nucleophilic attack to the 5 position and is used regularly for PEOx termination, yielding hydroxyl end-groups quantitatively. But for a milder conditions and to enhance the end-group fidelity, tetramethylammonium hydroxide was chosen as a terminating agent and used in stoichiometric amounts related to living polymer chains in methanol. The lower basicity of the $N(CH_3)_4OH$ ($pK_a = 9.8$) solution in comparison to the KOH ($pK_a = 13.5$) solution is attributed to the success of this termination reagent. It guarantees the highest end-group fidelity for the consecutive polyester formation. However, amphiphilic block copolymers can also be achieved by the sequential addition of hydrophobic and hydrophilic oxazoline monomers.⁴⁰² AB- and BA-type diblock and BAB triblock architectures were prepared in a “one-pot two-stage copolymerization” technique using living cationic polymerization (Scheme 21).⁴⁰²

Scheme 21. BAB Triblock Synthesis from 2-Oxazolines by the Sequential Monomer Addition Method⁴⁰²



A class of six-membered cyclic imino ethers, 5,6-dihydro-4H-1,3-oxazines (1,3-oxazines, OZI), have been employed for preparing block copolymers with a hydrophilic or lipophilic character of the chain. Also here a “one-pot two-stage copolymerization” is used to prepare first the hydrophilic, followed by a second hydrophobic monomer. Amphiphilic block copoly(2-oxazoline)s with a poly(2-perfluoroalkyl-2-oxazoline) hydrophobic block are other examples to demonstrate the range of block copolymers that are prepared with the intent to form micellar systems.⁴⁰³ ABA triblock copolymers containing the hydrophilic PMeOX as A block and a hydrophobic poly(dimethylsiloxane-co-methylhydrosiloxane) (P(DMS-MHS)) as B block were prepared to obtain vesicles upon self-assembly.⁴⁰⁴ Because the synthesis of 2-substituted oxazolines is straightforward, this class of polymers is quickly replacing some of the more

traditional polymers in the areas of drug delivery and novel material design.

3.3. Block Copolymers from Polyethers: Polyether–Polyester Block Copolymers

Ethylene oxide is the most prominent monomer to generate aliphatic polyethers, which in contrast to olefins and vinyl polymer has a high flexibility and a low glass transition below $-60\text{ }^\circ\text{C}$ and hydrophilicity. The high ring strain gave rise to several ring-opening methods such as oxo anionic, cationic, and by anionic coordination polymerization. The “activated monomer strategy” has been successfully developed for the synthesis of functional epoxides and has the advantage to an increased polymerization rate and limited transfer reactions compared to conventional AROP to give high molecular weight materials of 170 000 with low molecular weight distribution of below 1.35.⁴⁰⁵ Polyether–polyester block copolymers are thermoplastic elastomers and high performance materials which bridge the gap between cross-linked elastomers and rigid thermoplastics. One of their properties are exceptional toughness, impact resistance, load bearing capacity, and low temperature flexibility. The microphase separated structure and physicomechanical properties and blending with silicone resins has raised interest for applications as biomaterials.

Hadjichristidis et al. reported about a novel catalyst switch approach with rapid crossover characteristics and was developed for the one-pot synthesis of block co/terpolymers of cyclic ethers and esters. The combination of an optimized catalyst choice, (*t*-BuP4) for epoxide and (*t*-BuP2) for the cyclic ester polymerization yields (substituted polyether)-*b*-polyester di/triblock co/terpolymers such as styrene oxide (SO), PSO-*b*-PCL diblock copolymers, and PSO-*b*-PCL-*b*-PLLA (Figure 37).⁴⁰⁶

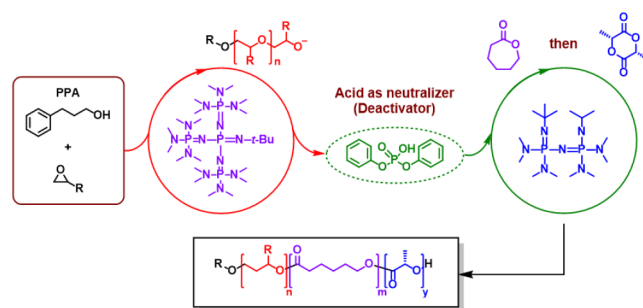


Figure 37. Substituted polyether-*b*-polyester di- and triblock co/terpolymers via an organocatalytic switching approach with a highly efficient crossover polymerization. Adapted with permission from ref 406. Copyright 2019 Royal Chemical Society.

Another class of polyether block copolymers with a broad range of applications are block copolymers composed of poly(ethylene oxide) PEO and poly(propylene oxide) PPO, known as poloxamers or pluronics. PEO-*b*-PPO-*b*-PEO copolymers are prepared via sequential anionic polymerization of PO and EO using potassium and sodium hydroxide as an initiator.⁴⁰⁷ Usually, the central PPO segment is synthesized and subsequently a chain is extended by the polymerization of EO. For side products such as PPO homopolymers and low molecular weight block copolymers, purification with chromatographic fractionation is employed. The variations of the block copolymers are so vast that there is an own nomenclature for these types of blocks established. Other block copolymers from

EO can be formed into a telechelic acetal–PEG–PEI by alkaline hydrolysis of the acetal group of each repeating unit of acetal–PEG–POz. The acetal–PEG–POz was prepared through the initiation of EO with potassium 3,3-diethoxypropanolate (PDP) to initiate the anionic polymerization to generate PEG with an acetal group at the R-chain end and a hydroxyl group at the R-chain end (acetal–PEG–OH). This macroinitiator is then used to initiate the polymerization of oxazoline after a conversion of the OH group into a sulfonate derivate by adding methanesulfonyl chloride. The ω -end modification to a methanesulfonic group allows the acetal–PEG–SO₃CH₃ to work as a macroinitiator to form the acetal–PEG–POz through ROP.⁴⁰⁸ In contrast to purely organic surfactants such as PEG–PPO, it is also desirable to generate different morphologies from polymers with inorganic backbones.

3.4. Block Copolymers from Polysiloxane

Polysiloxanes have a high biocompatibility, high flexibility, and excellent thermal stability like organic-based PEG–PPO materials. Polysiloxanes are obtained by ionic ring-opening polymerization of cyclosiloxanes. The formation of block copolymers has therefore to be achieved either by the formation of end-capped homopolymers followed by coupling reactions with other segments, or the living chain end is extended through the initiation of a polymerization with a second monomer. Through this method, a number of block copolymers composed of poly(dimethylsiloxane) (PDMS) and other segments such as polystyrene, polyisoprene, and poly(ethylene siloxane) can be prepared.⁴⁰⁹ However, when functionalities should be incorporated, the method shows little tolerance. Therefore, when hydrophilic properties are incorporated by the postfunctionalization, the block copolymers containing functional groups that do not interfere with the polymerization process. For example, Kickelbrink reported on the polymerization of 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane, a monomer with a high ring strain which is compatible with nucleophile/solvent combinations for anionic ring-opening polymerizations, and can achieve the synthesis of vinyl-functionalized polysiloxane–PDMS diblock copolymers. These polymers can then be postfunctionalized to give block copolymers with tunable hydrophilic functionalities.⁴¹⁰ Alternatively, polysiloxane- and poly(*tert*-butyldimethylsilyl methacrylate) PMASi-based block copolymers with marine bacterial antiadhesion properties are prepared in the form of AB diblock and ABA triblock copolymers (Scheme 22).⁴¹¹ PDMS-based block copolymers demonstrated a higher antiadhesive efficiency against a series of bacterial strains than coatings containing PMASi-based polymers. Moreover, diblock copolymers demonstrated higher antifouling performances than

the corresponding triblock copolymers. Macro-RAFT reagents from either mono- or dual functionalized PDMS precursors (5–10K) and were then extended with butyl methacrylate, MASi in various degrees of enrichment.

3.5. Block Copolymers from Polyamides

Polyamide containing block copolymers can find applications as lightweight thermoplastic elastomers based on polyester amide (PEA),^{412–414} polyether-esteramide (PEEA), or polyether-amide (PEBA) block copolymers. Besides, several polycondensation approaches PEA block copolymers can be prepared through the ring-opening of morpholine 2,5-dione derivatives. The monomers carry both ester and amide linkages in their structure and combine biodegradability and the excellent thermomechanical properties of polyamides. The peptide-based amide part adds preferential cell–polymer interactions. Although the ROP reaction form polymers with a molecular weight up to 20K, the harsh reaction conditions led to undesirable side reactions such as intra- and intermolecular transesterification. However, block copolymers could be formed from monomers with different amino acids and when the OH end group is used for the ROP of lactic acid. PEP-*b*-PLLA block copolymers were prepared as effective drug delivery systems for proteins without a burst release, attributed to the electrostatic interactions between the protein and the polymer.⁴¹⁵ Polyester amides can be prepared from the sequential addition of ϵ -CLA and CL by using an ω -aminated polyether macroinitiator and diblock copolymers with the composition of P(EO-*co*-PO)-*b*-PCLa-NH₂ are formed. The aminolytic ring-opening polymerization of CL was initiated by the terminal amine function of the previously synthesized polyamide block to form (P(EO-*co*-PO)-*b*-PCLa-*b*-PCL-*o*-OH).⁴¹⁶

3.6. Outlook

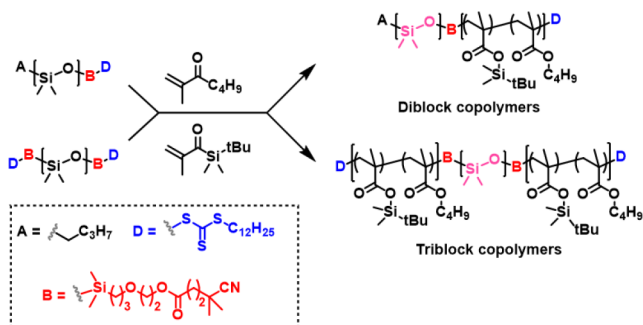
Block copolymers from ROP's are superior to polycondensation methods when sequential methods are applied to form diblocks and block copolymers that are combined that contain a block with copolymerized monomers. As documented above, ROP from polyesters, polyamides, polyoxazolines, and polysiloxanes give a multitude of highly versatile block copolymers that can implement switching mechanisms and a combination of strategies. We highlighted the most prominent strategies that will continue to provide block copolymers implementing blocks with heteroatoms.

4. BLOCK COPOLYMERS FROM POLYCONDENSATION

4.1. Nonconjugated Block Copolymers

In contrast to chain polymerization in which monomers are initiated by monomers and initiators, step polymerization is initiated by the reaction of monomers with each other. Here the propagation involves the reactions of monomers, oligomers, and polymers with themselves. This results in polymerizations in which the molecular weight is difficult to control, and broad molecular weight distributions are observed. However, polycondensation approaches have been successfully applied for the synthesis of ABA triblock copolymers, in which a telechelic macroinitiator is prepared by this method. Stimuli responsive amphiphilic ABA triblock copolymers were prepared from a telechelic macroinitiator using a step-growth polymerization between dithiol and diacrylate monomers in a work reported by Ghosh et al. (Figure 38).⁴¹⁷

Scheme 22. Polysiloxane and Polydimethyl Silyl AB and ABA Type Block Copolymers⁴¹¹



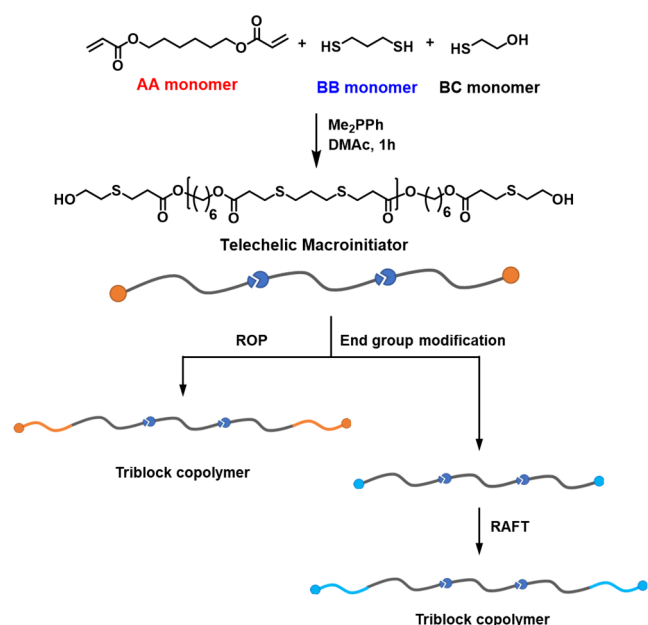


Figure 38. Telechelic macroinitiator for ABA type block copolymers. Adapted with permission from ref 417. Copyright 2014 Royal Chemical Society.

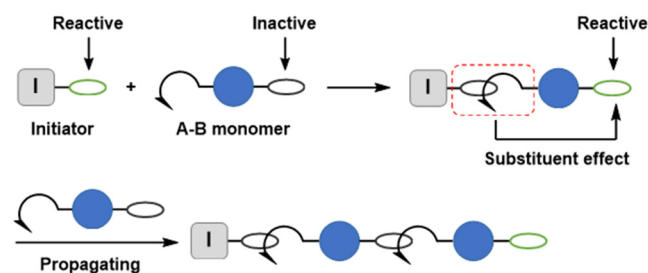
The following ROP with a lactide monomer generates the triblock. Functionalization of the OH group with CTA generates a macro-CTA, producing thermoresponsive ABA triblock copolymers. This end group transformation chemistry is typical for the preparation ABA triblocks in which the midblock B is derived from a traditional step-growth condensation polymerization of AA and BB type monomers. In general, these telechelics can be produced without using a chain stopper or with the addition of a chain stopper. Typically, aliphatic ester,^{418,419} aromatic polyesters,⁴²⁰ polycarbonates,^{421,422} poly(ether ketones),⁴²³ polyether sulfones,^{418,424} poly(sulfone ether ketones),⁴²⁵ fluorinated poly(arylene ether),⁴²⁵ and polyurethanes,⁴²⁶ are prepared by traditional step-growth condensation polymerization. The OH end functionality is ideal and common for polycondensates and can be transformed into RDRP functional groups.

The chain stopper can also already include the RDRP initiator and is therefore particularly useful for triblock copolymers which can contain all of the forementioned polymers as a middle block. For example, in work by Destarac et al.,⁴²⁰ poly(butylene terephthalate) were xanthate-terminated and triblock copolymers were prepared. Furthermore, a number of ABA triblock copolymers have been prepared with several combinations of middle-block and RDRP techniques such as ATRP,^{421,425,427} RAFT, RAFT/MADIX,⁴²⁰ and ARGET-ATRP. For example, Matyjaszewski and Lopez et al. reported on triblock copolymers, containing a polyketone (PEEK) or polysulfone (PAES) center block and PMMA, and poly(pentafluorostyrene), PPFS, or poly(ionic liquid) outer blocks. The center blocks were prepared by traditional step-growth polycondensation, giving the OH-difunctionalized macroinitiator which are then converted to 2-bromoisobutyryloxy haloester groups.⁴²⁷ The initiation was conducted under ARGET with MMA or normal ATRP for pentafluorostyrene. Multiblocks comprising both polycondensates and controlled free radical polymers can be accomplished by using a difunctional monomer and a difunctionalized monomer that contains the RDRP active site.⁴²⁸ The activation

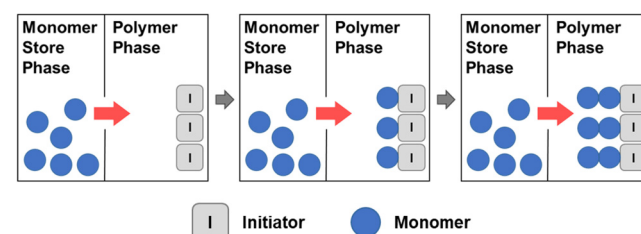
of the alkoxyamine through the addition and polymerization of styrene presents another possibility to prepare multiblock copolymers. In contrast to polycondensation, which is a step-growth process, chain-growth polycondensation is considered to be the “living” alternative as it proceeds through the chain growth mechanism⁴²⁹ and is made possible by: (1) The activation of a polymer end-group by substituent effects to turn an inactive group into a group that can conduct condensation and produces aromatic polyamides, polyesters poly(ether sulfones), and poly(ether ketones), (2) transfer of reactive species to the polymer end group and can be found in the polymerization of polymethylenes and polyphosphazenes, (3) phase-transfer polymerization in a biphasic composed of monomer storage phase and polymerization phase and is used with aliphatic polyesters, and (4) activation of the polymer end group by transfer of the catalyst and is applied in conjugated polymers and is discussed in a separate section.^{430,431} In particular, one approach highlights that the chain growth mechanism and monomers are of the AB-type in which one end is electrophilic and the other one is nucleophilic (Scheme 23).

Scheme 23. General Approaches for Block Copolymer Synthesis Using Chain-Growth Polycondensation⁴³¹

Approach 1: Substituent effect

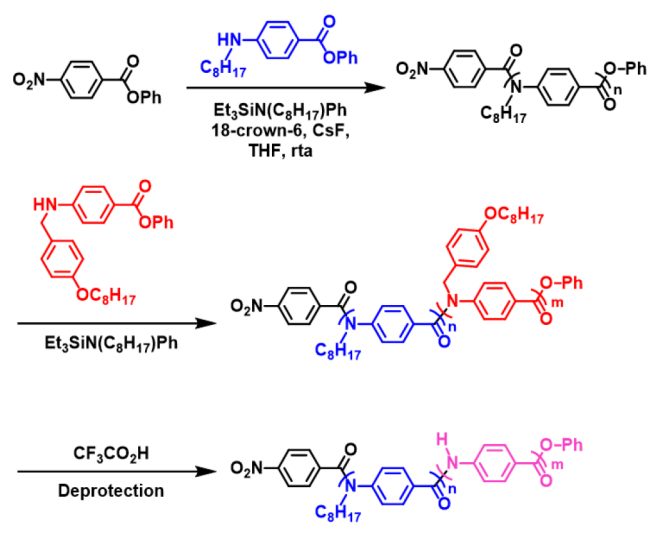


Approach 2: Biphasic system



The change in reactivity of approach 1 is attributed to the reactivity change of the end group by bonding of the monomer with the polymer. However, some of these polycondensation reactions do not lead to well-defined polymers because of the increasing insolubility of the polymers and side reactions of conventional polycondensation, but because of the living nature of this polycondensation, diblock copolymers from polyamides can be obtained in high control and the reaction is not challenged by transesterification reactions as in the case of polyesters. Scheme 24 is an example of a diblock copolymers generated of *N*-alkyl and *N*-H polyamides, called aramides. A prepolymer of *N*-octyl monomers is prepared and the second block is prepared by monomer addition. These block copolymers show self-assembly properties. Triblock copolymers are prepared by using a difunctional telechelic as an initiator, adding an AB monomer unit and BAB-type triblock copolymers

Scheme 24. Polyamide Diblock Copolymers by AB Monomer Chain-Growth Polycondensation⁴³¹



are formed such as PEG–polyamide–PEG triblock copolymers. In general, block copolymers using the first approach presents a practical method to prepare polyamide-based materials, which are known as aramides or Kevlar type materials and are one of the toughest organic materials.⁴³²

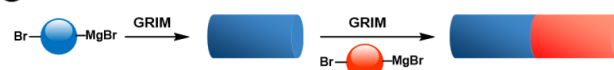
4.2. BCPs Containing Conjugated Polymers (CPs)

π -Conjugated polymers (CPs) have been an emerging interest due to their superior properties for electronic applications.^{433–437} Synthesis of CPs relies on metal-catalyzed cross-coupling reactions via either a step-growth (Suzuki, Yamamoto, Stille) or a chain-growth mechanism and has been discussed extensively in multiple specialized reviews.^{438–442} CPs synthesized using step-growth polycondensation (SGP) suffered from prolonged reaction times at high temperature ($>100\text{ }^{\circ}\text{C}$), poor control in molecular weight, and regioregularity. A breakthrough occurred in 2004 when Yokozawa⁴⁴³ and McCullough⁴⁴⁴ independently discovered a living chain growth polymerization method, namely, chain-transfer polycondensation/polymerization (CTP), to prepare regioregular poly(3-alkylthiophene) (P3AT) with low dispersities. This breakthrough quickly changed the landscape in CPs synthesis as it gave access to well-defined CPs with high chain-end fidelity as well as opportunities to develop complex architectures.

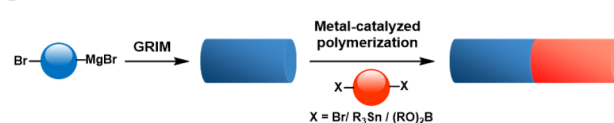
The performance of CPs was known to greatly depend on the morphologies in bulk/thin films. Thus, conjugated block copolymers (cBCPs), owing to their ability to self-assemble into highly ordered nanostructures, represent a great potential to tune and optimize the morphologies.⁴⁴⁵ Because of the extended and rigid chain conformation, CPs are commonly referred to as “rod” polymers to differentiate from conventional and flexible “coil” type polymers. cBCPs can be categorized into two main groups: “rod–rod” (or fully conjugated) and “rod–coil” types. The synthesis of “rod–rod” cBCPs remains challenging and heavily relies on “quasi-living” Grignard metathesis (GRIM) polymerization for poly(3-alkylthiophene) (P3AT) developed by McCullough and coworkers.^{446,447} On the other hand, enjoying the advancement in living/controlled polymerization techniques, the synthesis of the rod–coil diblock copolymer has been extensively explored. Two general approaches for the preparation of rod–coil cBCPs are shown in Figure 39.⁴⁴⁸ Grafting-from methods employ chain extension from macro-

A) Synthesis of “rod–rod” cBCPs

1 Sequential GRIM polymerization

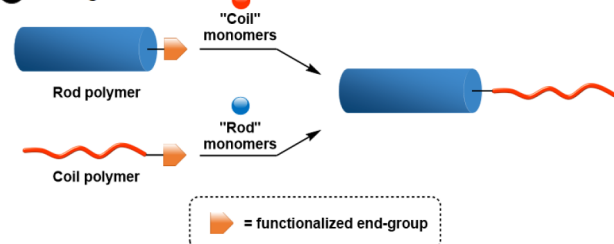


2 GRIM polymerization then then metal-catalyzed polymerization



B) Synthesis of “rod–coil” cBCPs

1 Grafting from



2 Grafting onto

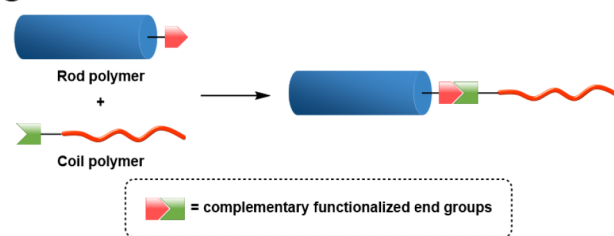


Figure 39. Synthetic strategies for “rod–coil” and “rod–rod” cBCPs.

initiators which can either be a rod or, to a lesser extent, a coil polymer. More commonly, the CP segments are prepared by a chain-end modification to achieve proper functionality for the subsequent controlled polymerization techniques. Alternatively, a rod block and a coil block with complementary functional end groups are synthesized separately via different polymerization techniques, followed by coupling reactions to obtain a “rod–coil” block copolymer in the “grafting-onto” approach.

4.2.1. CPs from Step-Growth Polymerization.

4.2.1.1. SGP and Living Anionic Polymerization. A procedure to prepare triblock copolymers with oligophenylenes as the rigid segment was described by Tsitsilianis et al.⁴⁴⁹ Suzuki cross-coupling reaction was employed to obtain telechelic bromo-functionalized oligophenylenes that were then treated with *sec*-BuLi/THF to generate a dual anionic site at the terminal chain ends. Anionic polymerization with styrene/2-vinylpyridine accomplished triblock copolymers with a coil–rod–coil architecture.

Mezzenga and Chen et al. reported the preparation of rod–coil diblock and coil–rod–coil triblock copolymers containing conjugated poly[2,7-(9,9-dihexylfluorene)] (PF6) and coil-like poly(2-vinylpyridine) (P2VP) segments.⁴⁵⁰ Mono- or divinyl terminated PF was first prepared using Suzuki or Yamamoto coupling methods, followed by the activation by *sec*-BuLi to obtain macroinitiators that are capable of initiating living anionic polymerization of 2VP monomers to afford PF6-*b*-P2VP and P2VP-*b*-PF6-*b*-P2VP block copolymers with 24–28% of PF incorporation. TEM imaging of the aforementioned block copolymers in the MeOH/THF mixture revealed that while

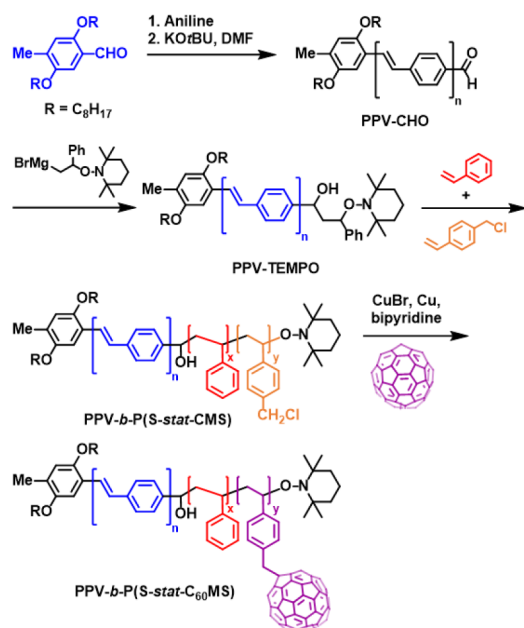
diblocks self-assemble in spherical structure, the triblock could readily aggregate in elongated cylinders. Because of the higher-ordered morphologies that favored the π - π interchain stacking, the solution of triblock copolymers exhibited a higher UV-vis absorption maximum compared to the diblock copolymer.

4.2.1.2. SGP and Ring-Opening Polymerization. A combination of Pd-catalyzed cross-coupling SGP with living anionic ring-opening polymerization was introduced by Mullen and co-workers in 1999.⁴⁵¹ The bromo-monofunctionalized poly(9,9-dioctylfluorene) (Br-PF8) with M_n of 3380 g/mol was first prepared via Suzuki coupling reaction followed by end-capping with bromobenzene. End-group transformation via tandem Suzuki coupling reaction with 4-formylphenylboronic acid and then reduction of the benzaldehyde moiety afforded OH-terminated PF8 (OH-PF8). Treatment of OH-PF8 with potassium naphthalenide yielded the required potassium-PF8 to initiate living anionic ring-opening polymerization of ethylene oxide, affording PF8-PEO diblock copolymer (M_n = 3380 g/mol). The resultant diblock copolymer displayed a more resolved fluorescence spectrum compared to PF8 homopolymer, which was attributed to the enhanced order of the “rod” structure when self-assembly in bulk.

4.2.1.3. SGP and Reversible Deactivation Radical Polymerizations (RDRP). As the earliest controlled radical polymerization technique, NMP has been extensively used for the synthesis of conjugated-nonconjugated block copolymers. Stalmach et al. reported chain-end modification of poly(*p*-phenylenevinylene) (PPV) bearing a terminal aldehyde unit that was prepared via Siegrist polycondensation, followed by chain-end modification to obtain the corresponding PPV-TEMPO macroinitiator (M_n = 2500 g/mol) (Scheme 25).⁴⁵²

Subsequent NMP with either styrene or styrene/4-chloromethylstyrene (CMS) generate PPV-*b*-PS (M_n = 3600–7000 g/mol) or PPV-*b*-P(*S*-stat-CMS) block copolymers. Postpolymerization of PPV-*b*-P(*S*-stat-CMS) via atom transfer radical addition with fullerene afford PPV-*b*-P(*S*-stat-C₆₀MS) as a donor/acceptor (DA), rod-coil diblock copolymers. In follow-

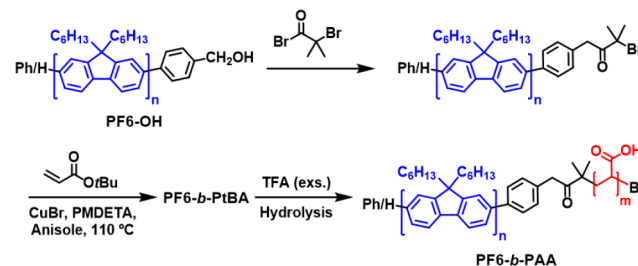
Scheme 25. Synthesis of PPV-Alkoxyamine Macroinitiator by Modification of Aldehyde Chain-End



up reports, the author broadened the scope of the coil polymer by introducing the TIPNO group on the PPV chain-end. By using PPV-TIPNO as a macroalkoxyamine, a variety of rod-coil diblock copolymers including PPV-*b*-P(nBA), PPV-*b*-(PnBA-*stat*-CMS), and PPV-*b*-(PnBA-*stat*-C₆₀MS) were prepared.^{453,454}

The Mullen protocol to prepare hydroxy-terminated PF enabled simple transformation to bromoester-functionalized PF macroinitiator via transesterification.⁴⁵⁵ Subsequent ATRP with *tert*-butyl acrylate (*t*BA), followed by hydrolysis of the poly(*tert*-butyl acrylate) (PtBA) segment yielded poly(dihexylfluorene)-*b*-poly(acrylic acid) (PF-*b*-PAA) diblock copolymers with different PAA block length (Scheme 26). The aggregation

Scheme 26. Synthesis of Poly(dihexylfluorene)-Poly(acrylic acid) Diblock Copolymer

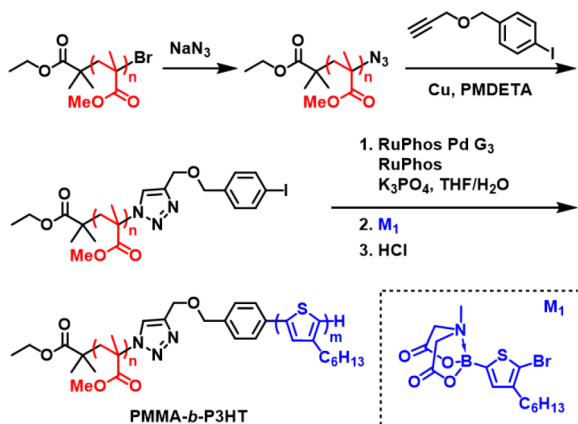


morphologies in a DCM/MeOH mixture of the resultant diblocks were investigated and found to greatly influence the photophysical properties of the materials in solutions. Adapting similar procedure, a variety of PF-based rod-coil block copolymers were prepared via combination of Suzuki cross-coupling SGP and ATRP, wherein the coil segment can be PNIPAm,⁴⁵⁶ PMMA,⁴⁵⁷ poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA),⁴⁵⁸ poly[3-(trimethoxysilyl)propyl methacrylate] (PTMSPMA),⁴⁵⁹ poly(methacryloxypropyl-trimethoxysilane) (PMPS),⁴⁶⁰ and poly(ethylene glycol) methyl ether methacrylate (PPEGMA).⁴⁶¹ More recently, Junkers and Michels et al. reported a procedure to prepare PF8 macroinitiator that is dual end-functionalized. Yamamoto cross-coupling was first employed to obtain distyryl-capped PF8 that subsequently react with 2-cyano-2-propyl ethyltrithiocarbonate (CPETTC) and AIBN to generate a bifunctional di-CPETTC-PF8 macroinitiator. Subsequent chain extension with styrene or MA afforded corresponding PF8-based diblock copolymers.⁴⁶²

Alternatively, end-functionalized coil blocks can be used as macroinitiators for the preparation of rod polymers. Cuendias et al. reported a synthetic approach wherein coil polymers were employed as the macroinitiator for the rod block.⁴⁶³ A thiophene-bromoester was used to initiate ATRP polymerization with *t*BA to generate corresponding thiophene-terminated coil polymers. Copolymerization of the coil blocks with 3-hexylthiophene using oxidative polymerization yielded P3HT-*b*-PtBA diblocks. Chang and co-workers employed methyl ketone-terminated PS/PMMA prepared from ATRP and 5-acetyl-2-aminobenzophenone monomers in a polycondensation reaction to obtain poly(phenylquinoline) (PPQ)-containing diblock copolymers. Lee and co-workers presented another “coil first” approach for the synthesis of P3HT-containing rod-coil block copolymers.⁴⁶⁴ Well-defined coil blocks of PS and P(M)MA were first synthesized via ATRP and underwent postpolymerization to introduce an aryl iodide as the

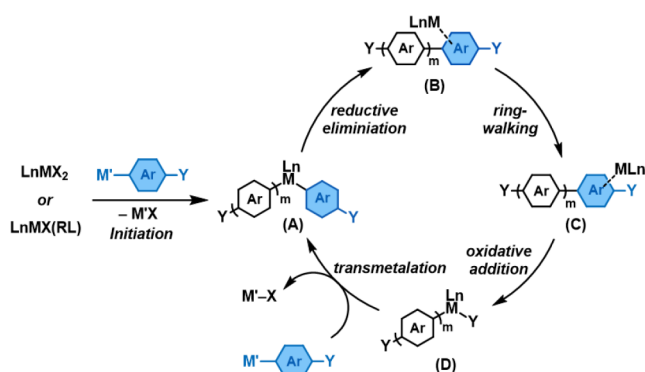
terminal unit. RuPhos Pd-catalyzed Suzuki–Miyaura CTP was then utilized for the block copolymerization with the *N*-methyliminodiacetic acid boronate-containing P3HT macro-monomer to afford diblock copolymers with various compositions, good control ($\bar{D} = 1.16\text{--}1.32$), and high yield (Scheme 27). The success of this approach also enabled the authors to combine widely used “rod first” and “coil first” approach to prepare ABC-typed rod–coil–rod triblock copolymers.

Scheme 27. Synthesis of PMMA-*b*-P3HT Using “Coil First” Approach⁴⁶⁴



4.2.2. CPs from Catalyst Transfer Polycondensation (CTP). Thanks to its living behavior, CTP has been demonstrated as the most efficient tool in the synthesis of cBCPs. However, the mechanism of CTP was not straightforward initially and required several years of accumulated studies.^{442,465–467} The mechanism of CTP was depicted in Scheme 28.⁴⁶⁸ The initiation step occurs with transmetalation

Scheme 28. CTP Mechanism⁴⁶⁸



between a $M(\text{II})$ precatalysts ($M = \text{Ni}, \text{Pd}$) and an AB-type organometallic monomer to afford the initiating complex (A). Subsequent C–C reductive elimination results in π -complex (B) wherein the catalyst is bound to the conjugated π -system of the monomer. The key mechanistic step that differentiates CTP and conventional SGP is ring-walking. In this step, the catalyst “walks” to the carbon–halogen (C–Y) chain-end while remaining associated with the polymer (C). Intramolecular oxidative addition at the C–Y bond yields $M(\text{II})$ complex (D) that can undergo successive transmetalation for further enchainment. This catalytic cycle continues until termination, which generally happens via the addition of a quenching agent

such as monofunctional transmetalating agent or acid. This mechanism allows for fine-tuning molecular weight, monomer sequences, as well as manipulate end-groups, while low dispersity can be obtained. As aforementioned, the ring-walking plays a critical role in successful propagation. Thus, it is important to pair the steric and electronic properties of the catalyst and the monomer well so that the π -complex is simultaneously stable (for catalyst association) and reactive (for transmetalation). To date, CTP is most successful in polymerizing electron-rich monomers such as thiophene derivatives.

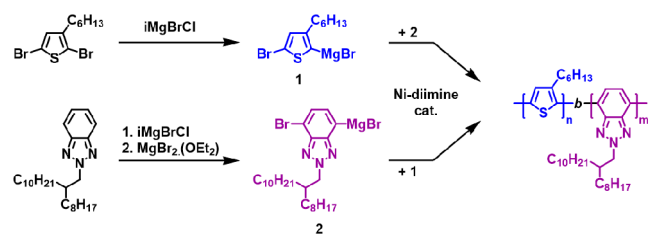
The first established method in chain-growth polycondensation for CPs is GRIM polymerization, which is also referred throughout literature as Kumada catalyst-transfer polycondensation.^{443,444,469,470} This technique was based on nickel-catalyzed Kumada crosscoupling reaction between aryl halides and Grignard reagents.⁴⁷¹ Although being widely used for the synthesis of P3AT-based polymer, the use of moisture-sensitive and reactive Grignard reagents greatly limits the degree of control and monomer scopes. Additionally, the preparation of nickel catalysts often involves multiple step under highly inert conditions. In an effort to overcome these problems, Yokozawa et al. developed an alternative CTP method based on Suzuki–Miyaura coupling reaction, wherein stable boronate monomers and a *t*Bu₃P-ligated Pd catalyst were employed. Compared to GRIM method, this technique offers more synthetic advantages, including mild reaction conditions, functional group tolerance, facile ligand modification, and broad monomer scope.^{472–476}

The section below will discuss the literature reports involving the uses of these two CTP methods in the synthesis of conjugated-based block copolymers.

4.2.2.1. Catalyst Transfer Block Copolymerization. The synthesis of rod–rod or fully conjugated block copolymers are largely governed by catalyst-transfer polycondensation (CTP) technique and is owing to its living nature. Several studies have successfully demonstrated the synthesis of P3AT-based diblock copolymers via GRIM polymerization. For example, Yue et al. reported the synthesis of well-defined poly(3-hexylthiophene-*b*-3-(2-ethylhexyl)thiophene) P3HT-*b*-P3EHT by monomer sequential addition with different compositions employing Ni(dppp)₂ as the catalyst.⁴⁷⁷ Thin film characterization revealed the self-assembly of the block copolymers in wormlike structures with P3HT segment packing in a high-ordered fashion. Similarly, Wu et al. synthesized the poly(3-hexylthiophene)-*b*-poly(3-cyclohexylthiophene) (P3HT-*b*-P3cHT) with relatively high molecular weight ($M_n = 156\text{--}211$ kg/mol, $\bar{D} = 1.45\text{--}1.57$).⁴⁷⁸

More recently, α -diimine nickel, a catalyst that has been long used in olefin polymerization, was employed for the synthesis of fully conjugated BCP. Homopolymerizations with 2,5-dibromo-3-hexyl thiophene and 4,7-dibromo-2-(2-octyldodecyl)-2H-benzo[*d*][1,2,3]triazole were initially performed to study the degree of control that can be achieved with this system. At 2% of catalyst loading, the molecular weight of P3HT and poly-benzotriazole (PBTz) can be controlled by varying the ratio of monomers to catalyst and dispersities remain fairly narrow ($\bar{D} < 1.30$), suggesting the good control in the polymerization of both electron-rich and electron-poor monomers. This facilitated the synthesis of DA block copolymers of P3HT-*b*-PBTz via sequential monomer addition as shown in Scheme 29.⁴⁷⁹

The preparation of fully conjugated block copolymers by successive monomer addition using well-established catalysts such as Ni(dppp)Cl₂ commonly requires a certain synthetic direction. To prevent the strong π -complexation between Ni

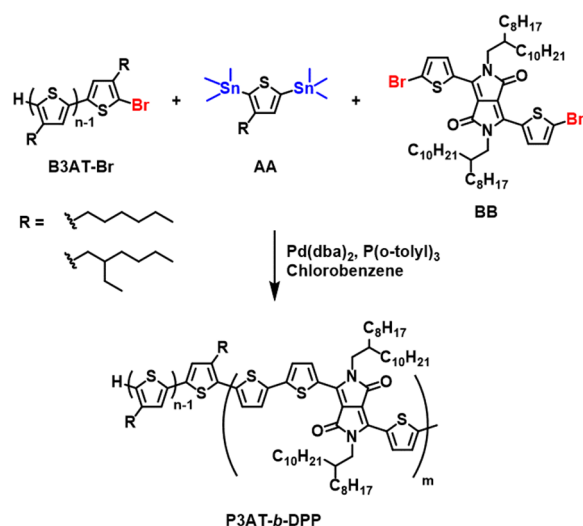
Scheme 29. Synthesis of P3HT-*b*-PBTz Block Copolymers by Ni-diimine Catalyst

center and monomer and facilitate initiation of the next monomer, there is a demand for the addition order of monomers with lowest binding affinity to highest binding affinity.⁴⁷⁶ Koeckelberghs and co-workers presented a more universal strategy that was based on the chain-growth polymerization of polyamides by Yokozawa.⁴⁸⁰ Here, the monomers were deactivated by a Zn–C bond to ensure the catalyst preferentially reacted with the polymer chain and oxidatively reinserted into the terminal C–Br of the polymer chain. Buchwald-type Ruphos-ligated Pd catalyst was shown as an efficient transfer catalyst thanks to its weaker π -complexation as well as solution stability. Negishi coupling protocol was applied for the preparation of di- and triblock copolymers with building blocks containing thiophene, selenophene, and fluorene.^{481,482}

Palladium catalysts bearing Buchwald-type ligand were also proved to be superior compared to the popular *t*Bu3P-ligated Pd in mediating living polymerization of thiophene monomers in the study by Choi and co-workers.⁴⁸³ Employing *N*-methylimidodiacetic (MIDA) boronate-protected thiophene to suppress protodeboronation side reaction in conjunction with RuPhos/SPhos Pd catalysts, excellent chain growth control was accomplished ($\bar{D} < 1.1$, yield >90%). The livingness of the system was demonstrated by the preparation of P3HT-*b*-P3EHT ($M_n = 9.2$ kg/mol, $\bar{D} = 1.18$) via sequential monomer addition. Furthermore, the thiophene diblock copolymer could also be synthesized via a one-pot manner thanks to the difference in coupling rate, which is dependent on the hydrolysis rate of boronate units.

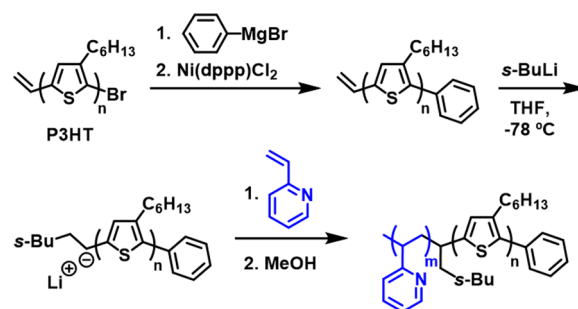
4.2.2.2. CTP and Cross-Coupling Polymerization. Scherf and co-workers prepared a series of DAD triblock copolymers comprising P3HT and cyano-substituted poly(phenylenevinylene) (CN-PPV) through two-step synthesis.⁴⁸⁴ Bromo-terminated P3HT macromonomers as the electron-donor block were first prepared via GRIM method and used as the end-cappers in Yamamoto cross-coupling reactions with dibromo cyanophenylenevinylene (acceptor) monomers. It was revealed that high molecular weight of the PPV segments can be obtained by introducing long chain alkyls on the phenylenevinylene monomers to enhance the solubility.

In 2012, Hawker, Chabynyc, and co-workers presented a novel pathway to prepare regioregular DA block copolymers of poly(3-hexylthiophene)-*b*-poly(diketopyrrolopyrrole-terthiophene) (P3AT-*b*-DPP). Bromo-terminated P3AT (P3AT-Br) obtained via GRIM polymerization was utilized as an end-capper in a Pd-catalyzed Stille cross-coupling reaction between 2,5-bis(trimethylstannyl)-thiophene and dibrominated-DPP monomers (Scheme 30). By varying the molecular weight as well as amount of P3AT, the authors were able to synthesize P3AT-*b*-DPP with various composition and molecular weight. Upon annealing above the melt temperature of individual homopol-

Scheme 30. Still Cross-coupling Polymerization of Br-Terminated P3AT and Difunctional Monomers⁴⁸⁵

ymers, the diblock copolymers were found to self-assemble into well-defined, semicrystalline domains.

4.2.2.3. CTP and Living Anionic Polymerization. Living anionic polymerization was one of the earliest methods that were utilized in “rod–coil” cBCP synthesis. In 2005, McCullough and co-workers developed a procedure for end-capping regioregular poly(3-alkylthiophene)s (P3AT) during CTP using a modified Grignard metathesis reaction.⁴⁸⁶ Dai et al. realized that the vinyl terminated-P3HT ($M_n = 7000$, $\bar{D} = 1.17$) can be activated by *sec*-Buli and employed as a macroinitiator for living anionic polymerization with 2-vinylpyridine (2VP) to produce rod–coil diblock copolymers with molecular weight ranging from 11.4 to 49.5 kDa with reasonable dispersity ($\bar{D} < 1.3$) (Scheme 31). The PH3T-*b*-P2VP were found to self-assemble into various morphologies (sphere, cylinder, lamellae, and nanofiber) depending on the P3HT weight fraction.

Scheme 31. Synthesis of P3HT–P2VP Diblock Copolymer

4.2.2.4. CTP and Ring-Opening Polymerization. A protocol featuring CTP, particularly the Grignard metathesis (GRIM) method, and ROP to generate amphiphilic conjugated block copolymer was described in a report by the Park group (Figure 40).⁴⁸⁷ Hydroboration/oxidation of the vinyl-terminated POT afforded hydroxy end-functionalized POT (OH-POT, $M_n = 3017$ g/mol, $\bar{D} = 1.24$) that undergo chain-extension with ethylene oxide via anionic ROP to accomplish POT-*b*-PEO ($M_n = 4700$ g/mol, $\bar{D} = 1.45$).

The amphiphilic nature of the resultant diblock allowed the authors to investigate the light-emission properties of the

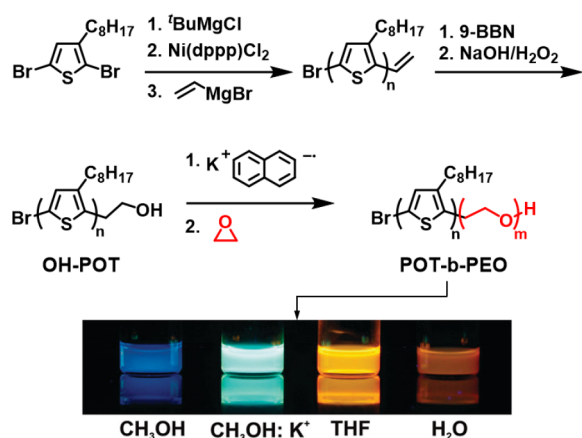


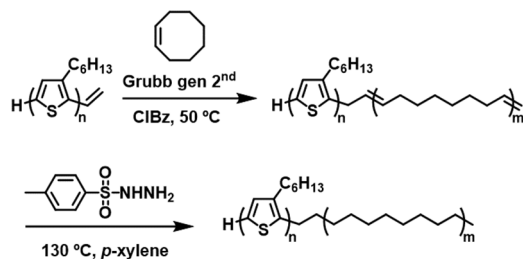
Figure 40. Synthesis of POT–PEO diblock copolymers and their emission colors in different solvents under UV light.

material in various solvents including THF, MeOH, and water. It was found that the emission color greatly depended on the self-assembly nanostructures in selective solvents. In particular, MeOH, the diblock organized in a fiber-like structure that disrupted the planar conformation of the POT segment and displayed a strong blue emission. This result provides a simple method to alter the light emission properties through control their self-assembly behaviors.

Similarly, well-defined P3AT-*b*-PLA can be prepared via ROP of D,L-lactide using P3AT bearing a hydroxy end-group as demonstrated by Hillmyer et al.⁴⁸⁸ The incorporation of the flexible PLA chain with enhanced solubility allowed for the facile preparation of thin-film preparation, followed by selective etching of the ester moieties to create nanoporous material. Coil–rod–coil triblock copolymers with P3AT, as the middle block was also successfully prepared through Sn(Oct)2-catalyzed ROP of D,L-lactide Sn(Oct)2-catalyzed using telechelic hydroxy-terminated P3AT.⁴⁸⁹

4.2.2.5. CTP and ROMP. The efficient preparation of crystalline–crystalline P3HT–PE diblock copolymer via a combination of CTP and ROMP was described by Radano et al. (Scheme 32).⁴⁹⁰ Specifically, GRIM polymerization of 3-

Scheme 32. P3HT–PE Diblock Copolymer via Tandem ROMP/Hydrogenation from Vinyl-Terminated P3HT



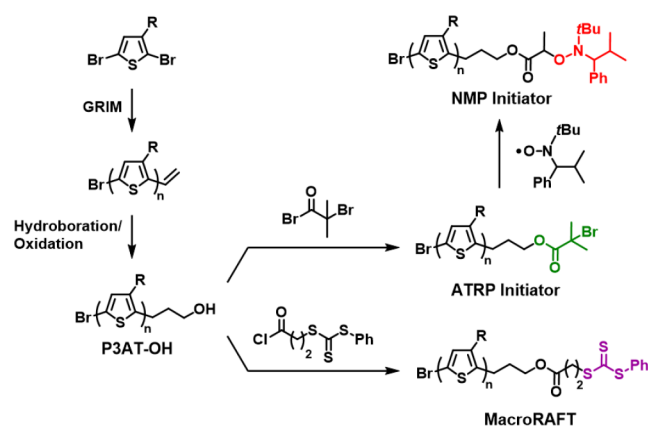
hexylthiophene followed by quenching with allylmagnesium bromide, afforded vinyl-terminated P3HT as the first block. This precursor was then used as a chain transfer agent in ROMP of cyclooctene to generate P3HT-*b*-PCO. Hydrogenation of PCO block led to the formation of P3HT-*b*-PE as semiconductor–insulator hybrid material.

4.2.2.6. CTP and Reversible Deactivation Radical Polymerizations (RDRP). As the aforementioned, GRIM polymerization developed by McCullough's group provides an efficient tool to

install a vinyl moiety at P3AT chain end,⁴⁸⁶ which can be easily converted to a hydroxy end group via hydroboration/oxidation.

As a result, numerous reports relied on the transformation of hydroxy-terminated P3AT precursor to a wide range of macroinitiators for controlled radical polymerizations (Scheme 33).^{491–493} Through this approach, McCullough and co-workers were able to synthesize P3HT-*b*-PI (NMP) and P3HT-*b*-PS (ATRP, RAFT) in a controlled fashion.

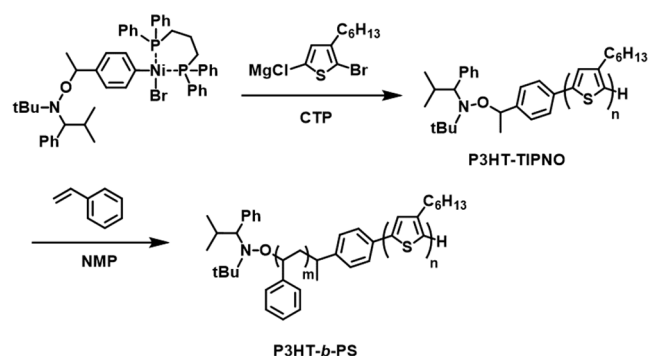
Scheme 33. End-Functionalization of P3AT to Controlled Radical Polymerization Macroinitiators^{491–493}



Brochon and Hadziioannou et al. reported the synthesis of P3HT-based diblock copolymers via tandem Ni(dppp)Cl₂-catalyzed CTP and NMP.⁴⁹⁴ P3HT macroinitiators were prepared via the GRIM method and end-capped by TIPNO-based Grignard reagent. P3HT–TIPNO was used to initiate copolymerization of nBA and CMS via NMP. Postpolymerization with fullerene afforded donor/acceptor P3HT-*b*-(P(nBA-*stat*-C₆₀MS) diblock copolymers. In the subsequent report, the authors employed the MAMA-SG1 (BlocBuilder) end-group as a more versatile and efficient NMP mediator. The combination of the two well-controlled polymerization techniques allowed for the preparation of a diverse library of well-defined P3HT-based diblock copolymers.⁴⁹⁵ Russell and Emrick et al. described a protocol to convert bromo-terminated-P3HT to NMP macroinitiator via tandem Stille coupling to first generated a vinyl group that further underwent Heck coupling with bromo-functionalized TIPNO ($M_n = 5500$ g/mol, $\bar{D} = 1.2$). Chain extension with perylene diimide acrylate yielded donor/acceptor P3HT-*b*-poly(peryene diimide acrylate) ($M_n = 11400$ – 15500 g/mol, $\bar{D} = 1.4$) that exhibited a better power conversion efficiency than their homopolymer blends.⁴⁹⁶ Lohwasser synthesized alkyne-terminated P3HT that later was “clicked” onto an azide-functionalized TIPNO ($M_n = 19.9$ kg/mol, $\bar{D} = 1.14$).⁴⁹⁷ NMP of 4-vinylpyridine (4VP) led to the formation of P3HT-*b*-P4VP diblock copolymers ($M_n = 55.3$ – 57.1 kg/mol, $\bar{D} < 1.5$).

Although being widely used, the drawbacks of the P3AT end-capping procedure via Ni-catalyzed CTP/Grignard quenching sequence include multiple-step synthesis and incomplete functionalization due to chain termination that leads to homopolymer contamination after chain extension. Diverging from this chain capping strategies, Senkovskyy and Kiriy et al. developed a method to introduce the alkoxyamine group at the beginning of polymerization through the utilization of a TIPNO-functionalized Ni-initiator (Scheme 34).⁴⁹⁸ As the TIPNO moiety was transferred directly from the Ni-initiator,

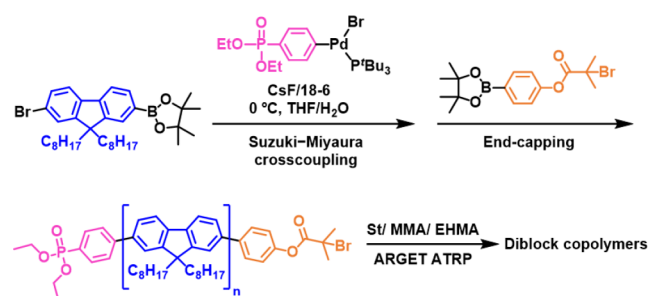
Scheme 34. P3HT-*b*-PS Synthesis by Employing TIPNO-Functionalized Ni Catalyst⁴⁹⁸



the resultant P3HT ($M_n = 15$ kg/mol, $\bar{D} = 1.20$) can be used directly as a macroinitiator in chain extension with PS via NMP to afford P3HT-*b*-PS with reasonable dispersity ($M_n = 36$ kg/mol, $\bar{D} = 1.33$).

Multiple synthetic routes of P3AT-based rod-coil block copolymers via a combination of CPT and ATRP widely employed the multistep transformation of the vinyl end-group resulting from GRIM polymerization to bromoester functionalities that serve as ATRP macroinitiators based on McCullough method.^{492,493,499,500} Various coil segments from different building block such as PS,^{492,499} P(M)MA,^{493,499} P(nBA),⁴⁹³ poly(fluorooctyl methacrylate) (PFOMA),⁵⁰¹ and poly(hydroxyethylmethacrylate) (PHEMA)⁵⁰⁰ were prepared through this procedure. In an alternative protocol, H/H-terminated P3HT obtained from the McCullough method can undergo Vilsmeier transformation to generate dialdehyde-terminated P3HT. This can be converted to ATRP telechelic macroinitiator for subsequent polymerization of styrene/MA to afford coil-rod-coil triblock copolymers.⁴⁹⁹ More recently, Mecking et al. reported a straightforward synthesis of PF8-containing rod-coil diblock copolymers. Controlled Suzuki-Miyaura cross-coupling polymerization, followed by end-capping with bromoester-functionalized arylboronic acid pinacol ester to afford difunctional PF (Phos-PF8-AlkylBr) (Scheme 35).⁵⁰² MALDI-ToF analysis of the resultant PF

Scheme 35. Tandem Suzuki-Miyaura Cross-coupling Polymerization and ARGET-ATRP for PF8-Based Diblock Copolymer Synthesis⁵⁰²



showed only one series of signals, indicating quantitatively initiation and end-capping. ARGET-ATRP of styrenic or methacrylate monomers was employed for the preparation of coil blocks.

Because of its versatility in monomer scopes and great control, RAFT was extensively utilized in addition to CTP to create block copolymers containing CPs. McCullough et al. reported

the postpolymerization of vinyl-terminated P3HT ($M_n = 11.0$ kg/mol, $\bar{D} = 1.2$) to RAFT macroinitiator by transesterification of the hydroxy-P3HT intermediate. Chain extension with styrene accomplished P3HT-*b*-PS diblock with composition by varying polymerization time ($M_n = 13.2$ – 18.4 kg/mol, $\bar{D} < 1.5$). Similarly, the incorporation of fullerene- C_{60} for donor-acceptor cBCP was also feasible.⁵⁰³ Heo et al. described the synthesis of low bandgap-wide bandgap P3HT-*b*-PVK diblock copolymer via chain extension of *N*-vinylcarbazole from the same P3HT macroRAFT agent.⁵⁰⁴ As a result, the integration of blue (PVK) and orange/red (P3HT) dual emissions produced direct white light and represents as the first example of white organic light-emitting diode (WOLEDs).

4.2.3. cBCP via Graft-onto Approach. A coupling reaction might be the most straightforward route to join two molecules and therefore has been used widely in cBCP synthesis (Figure 41). Aldehyde-terminated PPVs obtained from Siegrist

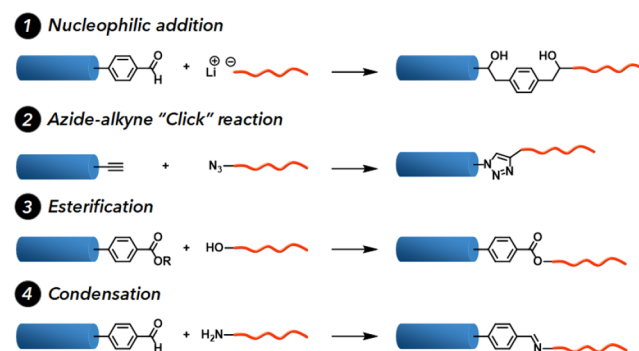


Figure 41. Common coupling reactions used in graft-onto method.

polycondensation were usually used as a “quencher” for living anionic polymers to obtain PS, P4VP, or PI as the flexible coil blocks.^{1,505,506} Ueda and co-workers reported the synthesis of PS-*b*-P3HT-*b*-PS triblock copolymers through a coupling reaction between 1,1-diphenylethylene (DPE) difunctional P3HT and PS-Li obtained from living anionic polymerization.⁵⁰⁷ Ho et al. modified the anionically grown PMMA to an azido functionality that later underwent Cu-catalyzed Huisgen cycloaddition with alkylene-terminated PPV to produce PPV-*b*-PMMA.⁵⁰⁸ ATRP technique produces a polymer bearing the bromo end-group that can be easily converted to azide functionality. In addition, the GRIM method provides a convenient pathway to end-cap P3AT with an alkyne group. This facilitated the development of multiple P3AT-based diblock copolymers via Cu-catalyzed azide-alkyne “click” reaction including P3HT-*b*-PS, PS-*b*-P3HT-*b*-PS,⁵⁰⁹ and P3HT-*b*-PtBA.⁵¹⁰

Esterification of the carboxyl and hydroxy end-groups was one of the oldest methods for linking two polymer chains together. On the basis of this method, Mullen and co-workers successfully prepared several rod-coil block copolymers including poly(*p*-phenyleneethynylene)-*b*-PEO, PF-*b*-PEO.^{511,512} Yu et al. prepared a heterodifunctional oligophenylenevinylene (CO₂Me-OPV-Br), which underwent an esterification reaction with PEG to obtain OPV-*b*-PEG diblock copolymers. Heck coupling between the resultant Br-terminated OPV-*b*-PEG and divinyl-functionalized OPV generated coil-rod-coil diblock copolymers.⁵¹³ Even though not as widely used, azomethine can serve as a linking unit in a condensation reaction as reported by Tanaka and co-workers.⁵¹⁴

4.3. Outlook

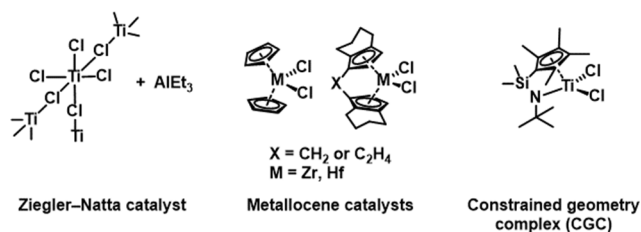
Step-growth polycondensation is a widely used method to prepare polymers containing heteroatoms. Because the dispersity is rather broad, but telechelic polymers are easily accessible, this method is mostly applied for the synthesis of ABA triblocks in which the telechelic forms the middle blocks chain extensions are made possible with RDRPs. For more control, chain-growth polycondensation is conducted using AB-type monomers which are activated and is mainly applied to prepare specialized polymers such as Kevlar-type polyamides (aramides). Block copolymers containing conducting sequences are mostly prepared by CTP. Although CTP provides many advantages in molecular weight and chain-end control over SGP, the monomer scopes of CTP remain very limited despite more than a decade since initial reports. As the mechanistic understandings have unfolded, the focus in the field perhaps lies in catalyst design to achieve more desirable materials. Another direction that has opened up recently is transition metal-free synthesis of conjugated polymers, which offer a “greener” alternative to current polymerization methods.^{515–519}

5. BLOCK COPOLYMERS FROM POLYOLEFINS

5.1. Metallocene Polymerization

5.1.1. Development of Metallocene Catalysts. The development of metal catalysts for polyolefin polymerization by Ziegler and Natta can be marked as the starting point for entering the era of metal-catalyzed olefin polymerization. Metallocene complexes are the fourth generation in which a metal is located between two aromatic rings with π -bonding interaction. The first metallocene was discovered by Fischer and Wilkinson in 1952. Later, Kaminsky discovered that zirconocene in combination with methylaluminoxane (MAO) is able to polymerize olefins with very high activity.⁵²⁰ The catalysts allowed ethylene polymerizations of up to 100 ton of polyethylene per gram of zirconium, and the yield is significantly higher than the Ziegler–Natta system due to the higher activity of the catalyst. After Brintzinger in 1982 and Ewen in 1984 demonstrated that titanocene allowed production of partially isotactic polypropylene, Kaminsky reported a chiral zirconocene catalyst which was able to synthesize highly isotactic polypropylene (>90%).⁵²¹ Soon after, the first constrained geometry catalysts (CGCs) were published by Bercaw in 1990.⁵²² Subsequently, the Dow and Exxon company also reported a series of Ti CGC catalysts which exhibited very high activity and were able to copolymerize α -olefins. The robust CGCs are not only able to operate above 120 °C but also present a lower tendency for chain transfer reactions (Chart 3). Therefore, metallocenes and CGCs are both better alternatives in comparison to the traditional Ziegler–Natta catalysts to produce high molecular weight and high tacticity polyolefins.

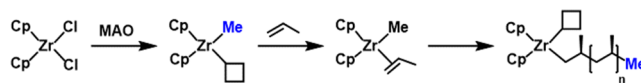
Chart 3. Structures of Ziegler–Natta Catalyst, Metallocene Catalysts, and Complexes with Constrained Geometry



5.1.2. Mechanism of Coordination Polymerization.

Metallocene catalysts must be activated with MAO or other aluminum cocatalysts. MAO plays a crucial role in the polymerization process. First, MAO abstracts the halide from the metal center to result into a free coordination site for monomers. Second, MAO can alkylate the metal to form a metal–carbon bond and is key to allow coordination insertion polymerization to progress to produce polyolefins. After polymerization, the termination step would be the cleavage of the metal–carbon bond to yield polyolefins. In general, group 4 metallocene catalysts have the following advantages. They are robust, cheap, easily synthesized, show a very high activity and productivity, and have a high control in tacticity. However, because the metallocene systems are easily deactivated by polar functional groups, the copolymerization of functional monomers is still a challenge. Therefore, metallocenes are mainly used to copolymerize olefins (Scheme 36).

Scheme 36. Mechanism of Coordination Polymerization



5.1.3. Block Copolymer Synthesis via Metallocene Catalysis.

Copolymerization of olefins with other monomers is crucial for the modification of properties of polyolefins. With the incorporation of different monomers, the property of the material can be drastically changed such as the melting point, glass transition temperature, thermal stability, toughness, density, ductility, and dyeability. Moreover, block copolymers are not only able to change the material properties but combine the advantages of the individual blocks' properties into one polymer. Since Yasuda reported the block copolymer synthesis via a metallocene type lanthanide catalyst in 1992⁵²³ and 2000,⁵²⁴ both academia and industry developed great interest in block copolymer synthesis by metallocene catalysts. In 2008, Shiono reported that [*t*-BuNSiMe₂(3,6-*t*-Bu₂ Flu)]TiMe₂ with dMMAO could polymerize norbornene in toluene at 20 °C.⁵²⁵ In addition, the block copolymer of norbornene and propylene could also be prepared by this Ti metallocene with dMMAO catalyst system with low Đ = 1.13 and 128 kDa. In this work, metallocene catalyst showed that block copolymer synthesis is not limited to α -olefin but also cyclic olefins. Later, Shiono reported in 2013 that a fluorenylamido titanium complex with MMAO produced AB and ABA block copolymers of norbornene with propylene or 1-octene at 0 °C.⁵²⁶ The 1-octene block into the block copolymer indicated that the long carbon chain did not affect the incorporation into the metallocene system. Also, Shiono et al. reported that it was possible to incorporate MMA into a block sequence with norbornene, propylene, and 1-octene.⁵²⁷ In 2015, Shiono, Grubbs, and Cai et al., reported another block sequence conducted with the same catalytic system and using ethylene, 1-hexene, and MMA to result into block copolymer structures with moderate dispersity of 1.56 and a molecular mass of around 179 kDa.⁵²⁸ Ethylene, propylene, 1-hexene, and 1-octene were all able to copolymerize with each other and showed that the α -olefins were all compatible with the Ti metallocene system. Shiono and Cai et al. reported a new fluorenylamido titanium catalyst with an adamantyl group in 2017.⁵²⁹ This titanocene with MMAO as cocatalyst not only had a high activity (over 31 000 kg of polypropylene/(mol of Ti h)) but was also able to

synthesize PE-*b*-PP block copolymers. The titanocenes have already proven that α -olefins and cyclic olefins are both able to perform homopolymerizations and copolymerizations. Shiono successfully demonstrated that titanocenes can be feasible systems to produce olefin block copolymers. Although the fluorenylamido titanium catalyst and titanocenes were able to synthesize block copolymer with olefins and MMA, the characterization of MMA block was kept to a minimum, but it can be concluded that this metallocene system has great potential for block copolymer synthesis.

5.1.3.1. Block Copolymer Synthesis using Metallocene with CTA. To further control the block synthesis, another method was developed using chain transfer reactions to produce block copolymers. For example, in 2008, Chung reported using *rac*-Me₂Si(2-Me-4-Ph)₂ZrCl₂ and MAO as catalysts using 9-BBN to polymerize propylene.⁵³⁰ The 9-BBN functions as a chain transfer agent to enable a polymer chain transfer from zirconium to borane. This resulting borane terminated PP could be further oxidized by O₂ with MMA to produce PP-*b*-MMA. In this reaction, the block copolymer was successfully prepared with 24 mol % of MMA incorporation, $\bar{D} = 3.1$. Also, the PP block of PP-*b*-MMA copolymer was about 170 kDa and without detectable homopolymers in GPC analysis. Mortazavi reported in 2017 that diethyl zinc was used as a chain transfer agent to synthesize linear/branched ethylene block copolymers.⁵³¹ The zirconocene catalyst and diimine Ni catalyst with MAO and diethyl zinc could prepare the block copolymer chain by using the two catalytic systems. The linear PE block could be made by the zirconocene, and the branched PE block could be prepared by the diimine Ni catalyst. Once the PE block is polymerized, the diethyl zinc is also responsible for the polymer chain transport to another system for another block chain propagation.

5.1.3.2. Block Copolymer Synthesis by Combined Approaches: Polyolefins and Polar Monomers. Metallocene catalyst and ATRP. The nature of olefin monomers which favor coordination polymerization does imply that an end-group functionality is needed to prepare the block copolymer from monomers which are not capable of performing coordination polymerization. The combination of olefins and polar monomers can be realized with living free radical polymerization techniques such as ATRP, which not only give a narrow $\bar{D}$ but also can control the molecular weight of polymer. In 2006, Dix reported using zirconocene/MAO and titanocene/MAO to synthesize atactic PP. After a series of modifications of the PP end-group, the ATRP macro-PP initiator was obtained. In a subsequent step, the macro-PP initiator was polymerized with MMA under ATRP conditions, and a PP-*b*-PMMA block copolymer was obtained (Scheme 37).⁵³²

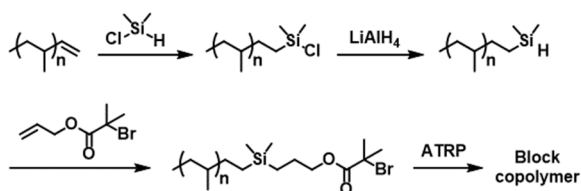
A year later, Matyjaszewski reported the preparation of [1,2-bis(η 5-9-fluorenyl)-1-(*R*)-phenylethane] zirconocene/MAO to synthesize a vinyl terminated PP, which can be directly functionalized to a 2-bromoisobutyrate terminated PP. The 2-

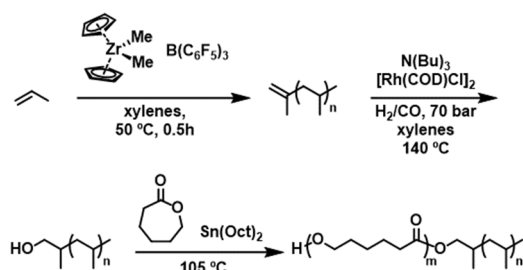
bromoisobutyrate group as part of the PP macroinitiator is ideal to conduct ATRP reactions with methyl methacrylate or *n*-butyl acrylate and yielded the PP and acrylate block copolymers.⁵³³ In 2009, PP-*b*-PS and PP-*b*-PMMA block copolymers were synthesized via zirconocene/MAO and ATRP. Dong et al. showed that the PP could be oxidized by a hydroalumination reaction and further brominated to bromo-terminated PP. This bromo-terminated PP macroinitiator was then polymerized with styrene or MMA to yield the block copolymers.⁵³⁴ In the following work, Dong reported a new synthetic strategy for block copolymer preparation. A PP via zirconocene coordination polymerization was capped with a styryl functional group. The styryl-capped PP was modified by hydrochlorination and produced 1-chloroethylbenzene terminated PP. The subsequent ATRP reaction that form the PP yielded the PP/PMMA block copolymer.⁵³⁵ In 2011, Pitsikalis and Hadjichristidis et al. reported that a block copolymer of 1-hexene or 1-octene with 1-tetradecene or MMA could be prepared by using a hafnium metallocene catalyst and ATRP.⁵³⁶

5.1.3.3. Metallocene Catalyst Initiated Polymerization Combined with ROP. In 2000, Jiang published work about Et(Ind)₂ZrCl₂ with MAO to synthesize polypropylene block polymers, in which PP were transformed into isocyanate-terminated PP through a series of chemical functionalizations. This functional PP could directly be reacted with caprolactam to form the PP and nylon-6 block copolymer.⁵³⁷ In 2002, Chung reported that [Cp*₂ZrMe]⁺[MeB(C₆F₅)₃]⁻ and [Cp*TiMe₂]⁺[MeB(C₆F₅)₃]⁻ could give borane-terminated PE and PS. The borane end group could be further transformed to a hydroxyl group via an oxidation reaction. The hydroxyl-terminated PE was able to chain extend through a ROP reaction with ethylene oxide and yielded a PE and poly(ethylene oxide) block copolymer.⁵³⁸ Later, Hu et al. designed a new strategy for the synthesis of hydroxyl-terminated PE and PP. When *rac*-Me₂Si(2-Me-4-Ph)(Ind)₂ZrCl₂/MAO polymerized ethylene or propylene with 4-(*tert*-butyldimethylsilyloxy) styrene as chain transfer agent, it yielded a 4-(*tert*-butyldimethylsilyloxy) styrene terminated polyolefins. The silyloxy group was also able to be transformed into a hydroxyl group via acidification. Similarly, the hydroxyl end group was used to form a block copolymer of polyolefin and polycaprolactone by ROP.⁵³⁹ In 2007, Dubois et al. reported a similar strategy to prepare the hydroxyl-terminated PE via a bis(2-methyl-benz[e]indenyl)-zirconium-dichloride/MAO system. Later, the group applied the functional PE with *L,L*-lactide to perform a ROP reaction and obtained poly[ethylene-*block*-(*L,L*-lactide)].⁵⁴⁰ Recently, Guironnet et al. reported a new method to synthesize iPP and lactide block copolymers. The research group used dichloro[*rac*-ethylenebis(indenyl)] zirconium/MAO to synthesize a PP block, the end-group was then functionalized with 2-hydroxyethyl acrylate by the Hoveyda-Grubbs catalyst. The hydroxyl end-group of PP could polymerize lactide via a ROP and the corresponding block copolymer was generated.⁵⁴¹ Later, Guironnet et al. reported another end-group functionalization method which included a hydroformylation/hydrogenation reaction. By using a Rh catalyst, hydrogen and carbon monoxide, the polyolefin was able to form a hydroxyl group at the chain end. The hydroxyl terminated olefin functions as macroinitiator for ROP of cyclic esters.⁵⁴² Generally, in the combined technique of metallocene polymerization and ROP, an end-group functionalization is necessary to generate a block copolymer (Scheme 38).

5.1.3.4. Metallocene Catalyst Initiated Polymerization with Anionic Polymerization. The Lee group reported that

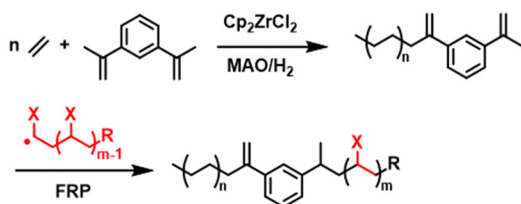
Scheme 37. Chain-End Modification of Unsaturated Polyolefin to Afford ATRP Macroinitiator⁵³²



Scheme 38. Cascade Reactions for the One-Pot Synthesis of aPP-*b*-PCL⁵⁴²

polyolefin and polystyrene block copolymers could be synthesized by combining coordination and anionic polymerization. They utilized (benzyl)₂Zn as chain transfer agent in coordination polymerization reactions for generating the polyolefin block. After the first block is made, styrene is introduced adding *n*BuLi and TMEDA to the reaction to initiate the anionic polymerization pathway. With zinc as CTA, the Li(TMEDA) end-capped polystyrene could be further transformed to the polyolefin to generate the desired block copolymer.⁵⁴³

5.1.3.5. Metallocene Catalyst Initiated Polymerization with FRP. In 2018, Scott et al. presented a new strategy for polyolefin and polar block copolymer synthesis. In this work, metallocene-based polymerization was combined with free radical polymerization. The polyolefin block was polymerized via a zirconocene catalyst containing a methylstyrene group at the chain end. The chain-end functionalization of the polyolefin styryl enables the initiation of a free radical polymerization with styrene or other monomers. A series of block copolymers from *n*BA, MMA, St, and VAc polar monomers could be prepared from these end-functionalized polyethylenes (Scheme 39).⁵⁴⁴

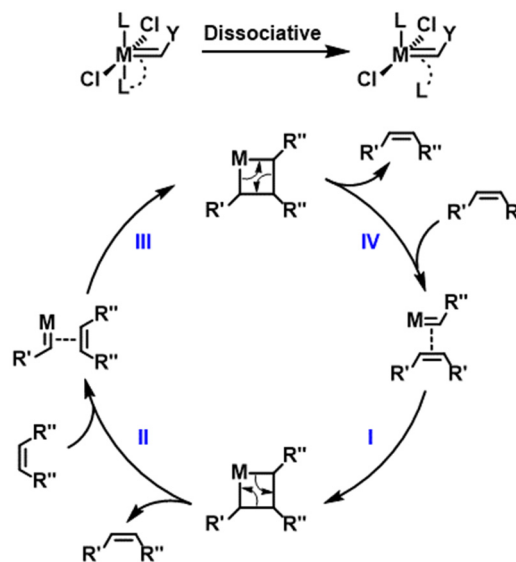
Scheme 39. Polyolefin Macromonomers Produced by Copolymerization of Ethylene and α -Methylstyrenes in the Presence of H₂⁵⁴⁴

5.1.4. Outlook. Using metallocene catalysts has led to the synthesis of block copolymers using CTA chain transfer reagents to approaches in which the anionic, cationic, ROP, and FRP can be initiated. Powerful methods will include the chain end functionalization of metallocene initiated polymerization to further advance the ease of block copolymer formation.

5.2. Ring-Opening Metathesis Polymerization (ROMP)

Olefin metathesis is a metal catalyzed carbon–carbon double bond exchange, and the process was first discovered in the 1950s. The name was coined by Calderon during his work at Goodyear in 1967. Early research used “ill-defined” tungsten catalysts that were short-lived, easily deactivated by Lewis basic functional groups, and often produced side products. The number of active metal centers at a single point was less than one percent and the activation of these catalysts were highly inefficient.⁵⁴⁵ This resulted in polymers with broad molar

mass dispersity with the need for high catalyst loading. Complex “well-defined” catalysts developed by Schrock and Grubbs allowed for advancements in mechanistic analysis and control over the catalytic activity through ligand choice.⁵⁴⁶ The accepted mechanism of olefin metathesis was elucidated by Chauvin and Herisson in 1970 and proceeds through a metallocyclobutane intermediate, generated by the coordination of the olefin to a metal alkylidene through alternating [2 + 2] cycloadditions (Figure 42).⁵⁴⁷

**Figure 42.** Olefin metathesis polymerization cycle. Adapted from ref 547. Copyright 1972 American Chemical Society.

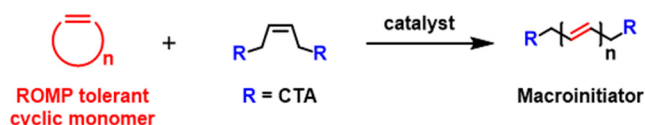
In the catalytic cycle, the precatalyst is activated by the dissociation of a labile ligand, resulting in a metal alkylidene. This metal carbene will react with an olefin to generate a metallocyclobutane intermediate via [2 + 2] cycloaddition, I, to produce the catalytic metal alkylidene II. This generated metal alkylidene will coordinate with a second equivalent olefin through a [2 + 2] cycloaddition, III, to give a metallocyclobutane intermediate. The intermediate cleaves apart via reductive elimination, IV, to yield an olefin and regenerates a metal alkylidene. This reaction will continue to synthesize olefins through successive [2 + 2] cycloadditions and reductive eliminations until the reaction has been quenched via a reagent that deactivates the metal center or when the monomer is completely consumed. Ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis polymerization (ADMET) are the two main forms of polymerization that utilize the olefin metathesis pathway. Although the structures of the polymers synthesized by both techniques are similar, their polymerization kinetics distinguishes them from one another.⁵⁴⁸ ADMET polymerization is a step-growth polymerization that requires a high extent of individual reactions to obtain high molecular weight polymers. It is often used to synthesize polymers via olefin metathesis where the ring strain would be too low to undergo ROMP or the synthesis of macrocycles to cumbersome. ROMP is the polymerization analogue of ring-opening metathesis. It is a living, chain growth polymerization that yields high molar mass polymers with narrow dispersity. The driving force of ROMP is the release of ring strain, with a decrease in entropy of the system. The most common cyclic monomers used are *cis*-cyclooctene, norbornene, cyclopentene,

and cyclobutene.⁸⁵ Close to 3000 ROMP related papers and reviews have been published since the discovery, and the field continues to grow each day. While exploring the synthesis of block copolymers utilizing just ROMP would be advantageous to those unfamiliar with polymer chemistry, the scope of this chapter would be too broad and expansive. Thus, this chapter will focus on highlighting key polymerization methods that can be used in conjunction with ROMP to afford block copolymers. Current techniques will either functionalize the chain end of ROMP polymers with an appropriate polymerization initiator or incorporate functional groups on an olefin metathesis comonomer to yield a telechelic ROMP polymer. These methods require the use of a chain transfer agent to bridge the polymerization techniques together.

5.2.1. Block Copolymers via Chain Transfer Agents.

Since the early 1980s, acyclic functionalized olefins have been used as macroinitiators in ROMP (Scheme 40).⁵⁴⁹

Scheme 40. Synthesis of Macroinitiator with Symmetric Chain Transfer Agents (CTAs)⁵⁴⁹



This allows for the incorporation of functional groups at the chain ends of the polyalkenes to synthesis a variety of telechelic polymers. Early strategies used tungsten or molybdenum-based metathesis catalysts but required the functional group of the olefin to be at least two methylene units away to avoid the “negative neighbor” effect.⁵⁵⁰ With the advancements made with more “well-defined” ruthenium catalysts, monomers can be designed with a variety of chain transfer agents (CTA) one methylene unit away from the double bond. The CTAs previously required strict protecting groups upon CTA to prevent deactivation of the metathesis pathway or unproductive side reactions.

5.2.1.1. Chain Transfer with Ring Opening Polymerization (ROP). Hillmyer and co-workers were one of the first to employ the use of Grubbs’ ruthenium catalyst with cyclobutadiene and a simple allylic CTA to synthesize hydroxytelechelic polybutadiene (HTBD), a valuable block copolymer precursor.^{551,552} ROMP derived HTBD has been used in conjunction with ring-opening polymerization (ROP) to synthesize linear ABA triblock copolymers containing polycyclooctadiene (PCOD) midblocks and polylactide (PLA) end blocks. This biodegradable polymer is viable as a renewable feedstock and biodegradability with high tensile measurements comparative to PLA. The molecular characteristics of the triblocks copolymers synthesized revealed a high end of 195 000 M_n with 19% incorporation of PCOD. Reducing the ratio of PLA to PCOD affords higher overall incorporation of ROMP monomer but at the sacrifice of molecular weight (M_n = 22 500 g/mol with 68% incorporation for 3.4–16–3.4). Hillmyer et al. further showed that olefins with multifunctionalized CTAs allows for control over chain architecture of the block copolymers synthesized. Using di-, tetra-, and octa- modified poly(*cis*-cyclooctene) with *cis*-2-butene-1,4-diol, subsequent PLA ROP afforded well-defined block copolymers with linear, H-shaped, and Arachne-arm architectures.⁵⁵³

5.2.1.2. Chain Transfer with Nitroxide-Mediated Polymerizations (NMP). Mahanthappa probed the concept of designing

a terminal alkoxyamine to act as a CTA with *trans,trans,cis*-1,5,9-cyclododecatriene (CDT).⁵⁵⁴ Reacting a symmetrical α -bromo diester bearing an internal olefin with TIPNO synthesized the desired chain transfer agent. TIPNO has long been used as the standard for NMP. Using ROMP with Grubbs’ second-generation catalyst with this CTA and CDT yields α,ω -telechelic 1,4-PB_{lin} still bearing the terminal alkoxyamine. The ratio of CDT/CTA to Grubbs’ second, 100:1, was found to minimize nonfunctional chain ends. GPC shows M_n values ranging from 6.1 to 11.4 kDa with ~ 2.0 dispersity. This macroinitiator can have NMP initiated at both ends to 11.4 kg/mol. NMP can then be initiated on both sides of this macroinitiator to afford a bidirectional triblock copolymer with styrene. These blocks have an increased molecular weight ranging from 16.1 to 30.8 kg/mol, with GPC data confirming the formation of higher molecular weight polymer by decreased elution volume compared to the macroinitiator. Isoprene was used in place of styrene and the macroinitiator afforded isoprene derived triblock copolymer. This triblock can further be extended by introducing styrene and synthesizing a unique pentablock copolymer arranged as poly(styrene-*b*-isoprene-*b*-butadiene-*b*-isoprene-*b*-styrene) (SIBIS) (Figure 43). This pentablock can be further hydrogenated to afford a poly(ethylene) block that can microphase separate despite the broad polydispersity of the internal segments.

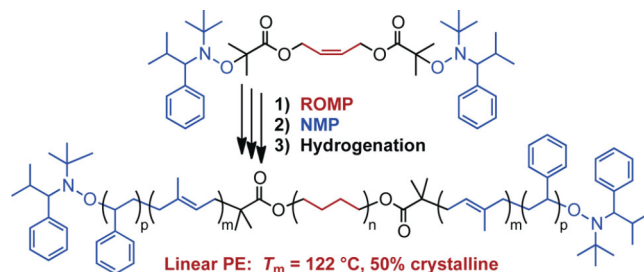
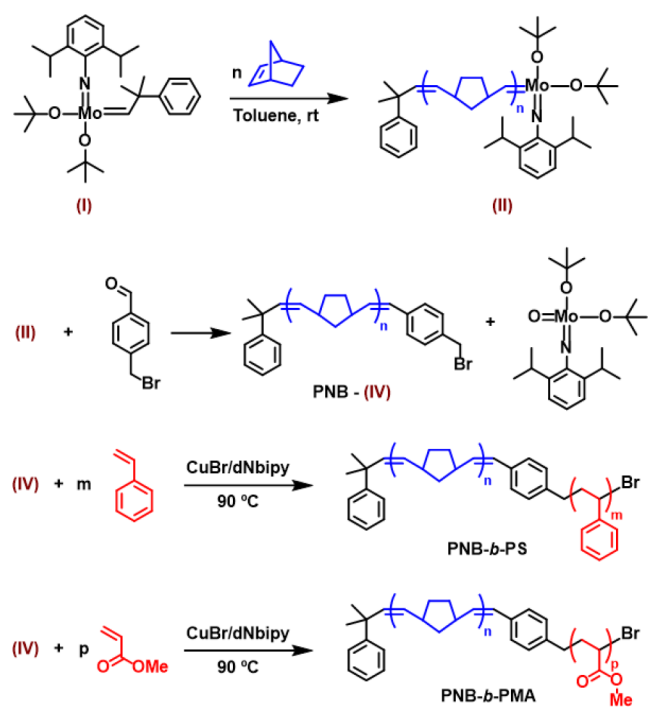


Figure 43. Synthesis of telechelic 1,4-PB macromolecular initiators for multiblock copolymers via ROMP–NMP. Adapted from ref 554. Copyright 2011 American Chemical Society.

5.2.1.3. Chain Transfer with Atom Transfer Radical Polymerization (ATRP). From the ROMP metathesis cycle, one of the key products after the [2 + 2] cycloaddition is a metal–carbene polymer **II** that can theoretically be reacted with a CTA. Matyjaszewski used norbornene to afford polymers with a Mo–carbene terminal end that could be reacted with *p*-(bromomethyl)benzaldehyde in a Wittig-like reaction to afford a polynorbornene (PBN) containing a terminal benzyl bromide **IV**.⁵⁵⁵ This terminal bromine can then be used to initiate ATRP with either styrene or methyl acrylate to afford PBN-*b*-PMA/PS block copolymers (Scheme 41).

Using GPC to compare the homopolymer with the two block copolymers shows distinct peaks with no shoulders, increasing in weight from 30.6 to 85.1 and 110.4 kg/mol, respectively, with very narrow dispersity ($\mathcal{D}$ = 1.06–1.07). Other ROMP monomers have found success in being able to be incorporated as the midblock of the copolymer. Grubbs devised a method to incorporate cyclooctadiene with commercially available CTA 1,4-dichloro-*cis*-2-butene to afford a telechelic poly(butadiene), which can be used as a macroinitiator for ATRP of styrene and methyl methacrylate.⁵⁵⁶ Furthermore, they showed that novel monotelechelic poly(oxa)norbornene derivatives be end-functionalized to undergo ATRP.⁵⁵⁷ Liquid crystalline block

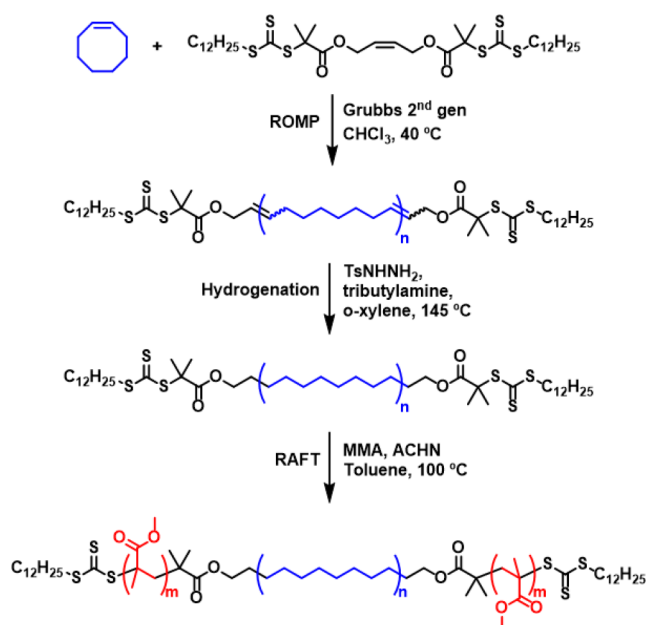
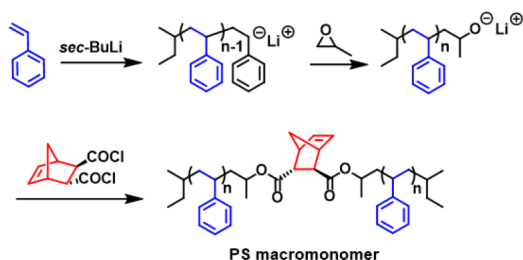
Scheme 41. PBN-*b*-PMA/PS Block Copolymer Synthesis via ROMP–ATRP via Functionalized PBN⁵⁵⁵

copolymers that generate lamellar-type microphase separation have also been achieved using *exo*-norbornene monomers that are postsynthetically modified to incorporate an ATRP initiator.⁵⁵⁸ Using an ionic liquid as a reaction medium and the compatible norbornene derivative/CTA afforded an amphiphilic ABA triblock copolymer which can self-assemble spontaneously in water to form polymeric micelles.⁵⁵⁹

5.2.1.4. Chain Transfer with Reversible Addition–Fragmentation Polymerizations (RAFT). Thiocarbonylthio compounds are the most used CTAs for RAFT and is directly responsible in controlling the molecular weight and polydispersity of the polymer.⁵⁶⁰ Hillmyer was able to synthesize a CTA for ROMP that possesses terminal trithiocarbonate groups.⁵⁶¹ The symmetric CTA is then utilized in a similar manner to that of ATRP by reacting it with 1,5-COD and Grubbs' first-generation catalyst. The molecular weight for these block copolymers ranges from 8.3 to 16.8 kg/mol and a narrow dispersity of $\bar{D} = 1.90$ –2.10. The group further expanded their work by synthesizing PMMA–PE–PMMA triblock copolymers that could be treated as compatibilizers to afford polymer blends with unique tensile and hardness values (Scheme 42).⁵⁶²

5.2.1.5. ROMP Combined with Anionic Polymerization. One of the most common techniques used in conjunction with ROMP is anionic polymerization. Mohsin first explored the concept by synthesizing a macromonomer by having styrene undergo an anionic polymerization using *sec*-butyllithium as the initiator (Scheme 43).⁵⁶³

Numerous research groups over the years have been able to utilize mono- and bis-functionalized norbornene derivatives to afford graft copolymers in conjunction with styrene and other diblock comonomers.^{564,565} The methods mentioned above can introduce undesired functionality into the polymer backbone, but Register and co-workers developed a method by preparing ω -aldehyde-functionalized polymers as macroinitiators for ROMP.⁵⁶⁶ The reaction is derived from a Wittig-like reaction

Scheme 42. Synthetic Route to PMMA–PE–PMMA via the Symmetrical RAFT Agent⁵⁶²Scheme 43. Synthesis of Polystyrene Macromonomer via Anionic Polymerization for Subsequent Mo-Mediated ROMP⁵⁶³

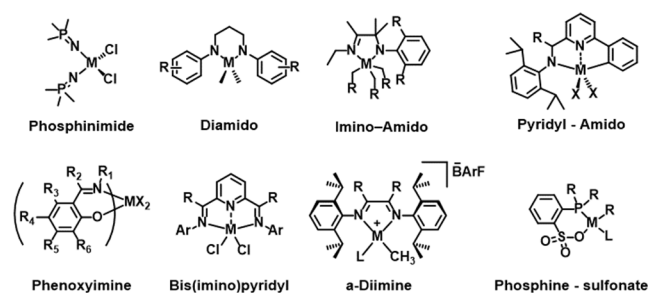
of a living ROMP polymer and a carbonyl-bearing polymeric aldehyde. Norbornene derivatives and cyclopentene were successfully used, with norbornene achieving molecular weights as high as 16.9 kg/mol and $\bar{D} = 1.03$. Most notably, Register et al. have been able to show that living ROMP can be converted to LAP via a two-step method to react with unsaturated monomers.⁵⁶⁷ The technique requires adding a terminal styrene group at the end of the ROMP chain, which can be metalated as an active site for anionic polymerization. Khosravi et al. have shown the inverse reaction can be achieved by using ethylene oxide for LAP, which can be terminated with vinylbenzyl chloride to produce a CTA macromonomer with a terminal vinyl group.^{382,568} Reacting it with a norbornene derivative afforded a PNB block achieved via living ROMP.

5.3. Postmetallocene Polymerization

Because of a wide range of physical properties and low cost, polyolefins are considered as commodity plastic with the presence in over 300 grades of commercial products globally.^{569–572} The discovery of Ziegler–Natta catalysts in the 1950s not only opened the access to high-density PEs and isotactic PPs but also opened up a new era of research toward high-performance catalysts for olefin polymerization.⁵⁷³ In the 1980s, Kaminsky reported the first example of a single site, highly active catalytic system that combines group 4 metal-

locenes bearing half-sandwich cyclopentadienyl-amide and methyl aluminoxane (MAO) as the activator.^{574,575} This system allows the control over molecular weight, polydispersities, tacticity, and uniform α -olefin comonomer incorporation, which lead to the development of a new platform of polyolefin synthesis with enhanced and tailor-made properties.^{576,577} However, the market presence of metallocenes is not as dominant as originally forecasted. Major drawbacks of the metallocene system are the high cost associated with a substantial amount of expensive activators (Al/metal = 100–10 000) and the oxophilicity of group 4 metals, which limits them from the copolymerization of functionalized olefins.⁵⁷³ This has stimulated the interest of developing a new generation of high-active, single-site, cost-effective “post-metallocene” (or nonmetallocene) catalysts with different ligand motifs for both industry and academia (Chart 4).⁵⁷⁸ These postmetallocene

Chart 4. Post-Metallocene Catalysts with Various Ligand Motifs



catalysts can be combined with different types of activators and possess a comparable or even higher activity toward olefin polymerization than what was observed with the metallocene system. Postmetallocene catalysts have also enabled the synthesis of novel polyolefins, namely, hyperbranched polyethylene, polyolefin/polar monomer copolymers, and olefinic block copolymers, which are considered to be inaccessible with metallocene catalyst.⁵⁷⁷ Reported postmetallocenes can be practically categorized based on their ligand motifs as shown in Chart 4.

The development of postmetallocene catalysts has been well documented by excellent reviews from Fujita, Gibson, and other researchers.^{575,578,579} Therefore, in this section, postmetallocenes that have been employed extensively for (1) olefinic block copolymer synthesis and (2) nonpolar and polar block copolymer synthesis will be discussed with the respect to the polymerization methods as well as ligand frameworks.

5.3.1. Postmetallocene Block Copolymerization—Olefin Block Copolymers (OBC). Polyolefins are represented in a variety of commercial grades with LDPE, HDPE, and LLDPE occupy the largest volume produced because their properties vary dramatically depending on the polymer's microstructure. Historically, LDPE is the first synthetic polyolefin via high-pressure radical polymerization at ICI in 1933.^{579,580} LDPE is significantly branched and amorphous, which results in greater flexibility and toughness and lower melting point. As a result of the low degree of crystallinity, LDPE displays an enhanced flow property, which is advantageous in the industrial processing step.⁵⁷³ A few decades later, the HDPE production commenced by the discovery of transitional metal-catalyzed polymerization. HDPE is almost without branching and is valued for its high melting point, rigidity, and stiffness due to highly crystalline

structure. LLDPE, which was first introduced to the market by DuPont in 1978 and further developed by Union Carbide, its linear structure bears a significant number of short branches.⁵⁸¹ This microstructure gives LLDPE the toughness while maintaining great flexibility. The density of the crystallinity of physical blends LDPE inevitably depends on the amount of the incorporated comonomers.⁵⁸² One major limitation of this correlation is increasing the comonomer would give rise in flexibility, however, unfortunately, lowering the melting temperature. This considerably impedes the use of these materials in thermoplastic elastomer applications. To confront this restriction, several efforts have been made to combine the advantageous properties of the “hard” and “soft” polymers in one single material, olefin block copolymer (OBC).⁵⁸³ Specifically, short α -olefin branches are introduced to a certain region (soft) while leaving the linear region (hard) untouched. The microphase separation that allows the hard region to crystallize while soft regions remain amorphous.⁵⁸⁴ Consequently, OBCs' mechanical properties embrace the best characteristics from HDPE and LLDPE such as high melting point and substantial elasticity. OBCs have found their application in various fields, but the most outstanding potential is to be served as cheap and versatile thermoplastic elastomers.^{582,585} Because of its tremendous potential as well as synthetic challenge, OBCs have drawn the attention of researchers in both industry and academia. OBCs are typically prepared to employ different strategies such as (1) living polymerization,^{577,586} (2) coordinative chain transfer polymerization (CCTP),^{577,587,588} and (3) chain shuttling polymerization (CCTP).^{589,590}

5.3.1.1. Olefin Block Copolymers by Living Polymerization.

One of the first approaches to achieve olefin block copolymers was employing living polymerization techniques. Analogous to living anionic and cationic living polymerization, living coordination catalysts enable polymer chains to grow with negligible termination or chain transfer, which means the catalyst “lives” on one end of the polymer chain under suitable conditions until they are intentionally destroyed. Hence, the block copolymers can be acquired by sequential addition of monomers or varying the reaction condition.^{586,591–593} This method can produce very well-defined OCBs with a versatile composition of monomers (Figure 44).

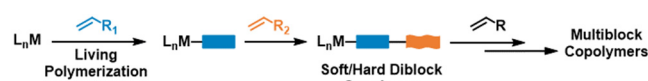
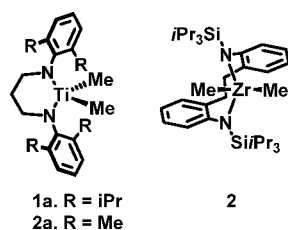


Figure 44. OCBs synthetic scheme by living polymerization.

5.3.1.1.1. Diamido Complexes. Diamino ligands were first introduced by McConville in the exploration of other non-cyclopentadienyl ligands for group 4 metals.⁵⁹⁴ After being activated by $B(C_6F_5)_3$, the dimethyl titanium complexes bearing propylene-bridged aryl-substituted diamido **1a,b** were able to polymerize 1-hexene under room temperature in a living manner. Inspired by this finding, Kim and colleagues developed a bidentate zirconium diimide ligands with ethylene as the bridging unit (Chart 5).

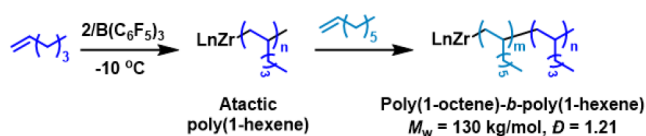
This precursor can be activated by either MAO or $B(C_6F_5)_3$ to yield a highly active catalyst for the polymerization of α -olefins including ethylene, propylene, and higher α -olefins. Noticeably, polymerization of 1-hexene in toluene by $2/B(C_6F_5)_3$ at $-10^\circ C$ exhibited a linear increase of M_n with monomer loading and the obtained polymers. Furthermore, the complete consumption of

Chart 5. Diamido Complexes Developed by McConville (1a,b) and Kim (2) for Living α -Olefin Polymerization



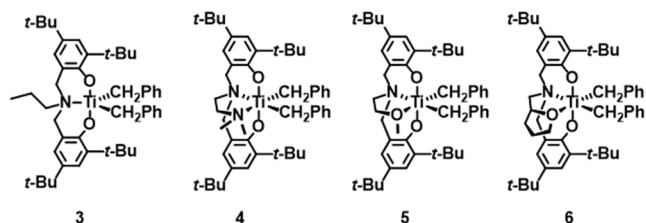
the monomers, as well as narrow polydispersities of obtained polymers, highly suggested the “livingness” of the system under these conditions. An atactic diblock copolymer of 1-hexene and 1-octene was synthesized with a relatively high molecular weight and low PDI via monomer sequential addition ($M_w = 130$ kg/mol, $\bar{D} = 1.21$) (Scheme 44).

Scheme 44. Synthesis of Block Copolymers from the Sequential Addition of 1-Hexene and 1-Octene by Diamido Zirconium Catalytic System



5.3.1.1.2. Amine–Phenolate Complexes. In 1999, Kol and Goldsmith introduced titanium complexes bearing amine (bis)phenolate ligand (3) via a simple synthetic route as a new family of Cp-free group 4 complexes (Chart 6).⁵⁹⁵ An early

Chart 6. Diamido Complexes Developed by McConville (1a,b) and Kim (2) for Living α -Olefin Polymerization



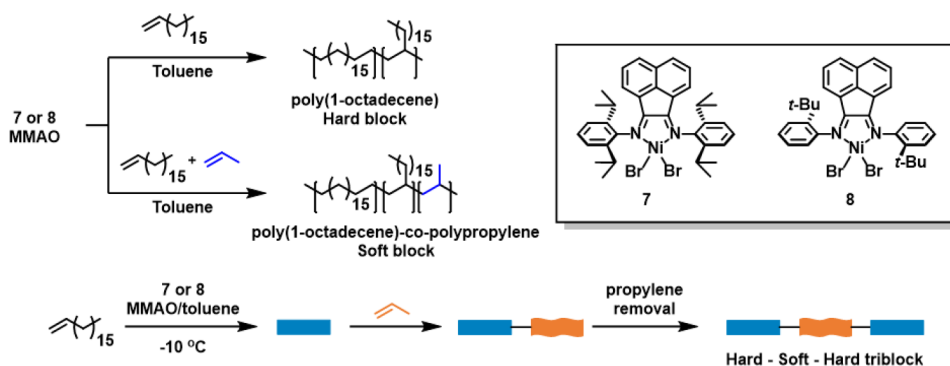
investigation revealed the dramatic difference in catalytic activity toward 1-hexene polymerization when an extra donor is present in the ligand.⁵⁹⁶ In particular, when activated with $B(C_6F_5)_3$ at

room temperature, 3 exhibits a low activity and only produced 1-hexene oligomers ($M_n = 1500$ g/mol) with broad polydispersity ($\bar{D} \approx 2.0$). However, with an additional amino extra donor arm, complex 4 after being activated with $B(C_6F_5)_3$ was capable of polymerizing 1-hexene in neat at room temperature, generating atactic poly(1-hexene) with narrow molecular weight distribution.

Additionally, the livingness of the system was evidenced by the linear increase in M_n over time. The presence of the side arm donor was believed to suppress the chain transfer reaction, yielding in saturated polymers. This successful discovery motivated the incorporation of a different donor into the ligand to evaluate the effect as well as the limits on the living nature of the polymerization. When the amine side arm is substituted with a strongly binding-to-metal oxygen donor, the catalytic activity surprisingly changed. After activation, catalyst 5 was found to be capable of prolonging the livingness of 1-hexene polymerization dramatically up to 31 h and produced high molecular weight polymers (M_n up to 445 000/mol) while maintaining an extremely low dispersity (1.07–1.122). Remarkably, the living nature was also displayed at elevated temperatures, furnishing poly(1-hexene) of $M_n = 22000$ /mol and $\bar{D} = 1.30$. This living behavior was exploited to synthesize block copolymers from 1-hexene and 1-octene via sequential monomer addition. 1-Hexene was polymerized by $5/B(C_6F_5)_3$ in chlorobenzene to produce poly(1-hexene) of $M_n = 9000$ g/mol with narrow molecular weight distribution ($\bar{D} = 1.2$) after 3.5 h. The polymers were then extended by the subsequently addition of 1-octene after a 1.5 h interval and allowed the polymerization to proceed for 3 h. The diblock formation was evidenced by the increase in molecular weight to $M_n = 11600$ g/mol and ^{13}C analysis. This was the first example of olefin block copolymer synthesis at room temperature by the time published.⁵⁹⁵ In a similar manner, the poly(1-hexene)-*b*-poly(1-octene) was prepared by the catalyst obtained by activating 6 with $B(C_6F_5)_3$ (Chart 6). Changing the methoxy donor to a THF group increased the living limits of 1-hexene polymerization from 31 to 48 h, which facilitates the synthesis of block copolymers with high molecular weight and narrow dispersity ($M_n = 34000$ g/mol and $\bar{D} = 1/16$).⁵⁹⁷

5.3.1.1.3. Palladium and Nickel Catalyst with α -Diimine Ligand. The potential of late transition metals in ethylene polymerization has been revealed through Keim and co-workers' studies in 1978.⁵⁹⁸ Since then, seminal works have been done to leverage their use in olefin polymerization.^{599,600} However, a breakthrough took place in 1995 when Brookhart and co-

Scheme 45. Synthesis of Elastomeric Triblock Polyolefin by Ni-Diimine Complex/MMAO from Octadecene and Propylene^{585,604}



workers introduced the α -diimine palladium and nickel catalysts which are capable of living olefin polymerization.⁶⁰¹ This discovery has laid the foundation for several studies to expand the scope of late transition metals for olefin polymerization. The mechanistic peculiarity of this class of catalysts is “chain-walking” that involves β -H elimination, followed by reinsertion with the opposite regiochemistry.^{602,603} Interestingly, these catalysts can produce polyolefins with different morphologies from highly branched to linear, depending on the ligand structure and reaction conditions. Together with the livingness, this furnishes a new strategy for the synthesis of OBCs that was demonstrated in the latter work from the same group.⁶⁰⁴

Employing the nickel(II)- α -diimine catalysts and MAO as an activator, the authors were able to prepare diblock copolymers with low dispersity from propylene and 1-hexene by sequential addition of monomers. This catalytic system also allows the preparation of triblock polyolefins with elastomeric characteristics (Scheme 45). The elastomeric behavior relied on differences in branching densities due to the difference in the insertion rate of propylene compared to higher α -olefins. That the rate of chain walking is much faster than the rate of olefin insertion leads to the “chain straightening” effect, which results in the lower number of branches. As a result, while propylene produced by these nickel catalysts was amorphous, the polymerization of octadecene yields a semicrystalline material given by the crystalline domains from unbranched segments.⁶⁰⁴ When tested the catalytic activity to ethylene, an industrial relevant monomer, **7**, did not provide a living polymerization due to the chain transfer occurring even at very low temperatures (<0 °C). However, this limitation can be tolerated in the synthesis of 1-hexene/ethylene multiblock copolymer by an elegant strategy from Killian and Brookhart.⁶⁰⁵ When activated by MMAO at low temperature, the living polymerization of 1-hexene was attained. Therefore, by adding ethylene repeatedly in short sequences, multiblock polymers with high molecular weight (23 8000 g/mol) were collected as the main product despite the side reaction. Interestingly, diversified microstructures were accessible by varying the time intervals of each monomer. The block copolymers show the properties of elastomers with impressive profiles (1090% of elongation, 860 psi of tensile strength).

Although living polymerization of ethylene could not be pursued with nickel diimine complex **7**, the palladium **9** diimine catalyst was shown to polymerize ethylene to yield highly branched, amorphous polymers with narrow polydispersity ($M_w = 250\,000$ g/mol, $\bar{D} = 1.1$). Employing this catalyst, Brookhart et al. have demonstrated a method to synthesize diblock copolymers of ethylene and 1-octadecene.⁵⁹² Two monomers were sequentially added in reversed order to ensure the achievement of distinct and “clean” block segment, not random copolymers. When the first synthesized block is polyethylene, the monomers could be easily removed from the reactor, then 1-octadecene was subsequently added to achieve an exclusive poly(1-octadecene) as the second block. Meanwhile, if poly(1-octadecene) was introduced as the first block, the removal of the monomer is more challenging due to the low volatility of 1-octadecene. Therefore, when 1-octadecene was almost fully consumed, the reaction was diluted, then high-pressure ethylene (400 psi) was applied. Because there is a significant difference in the insertion rate and binding activity of ethylene, this practically eradicated the incorporation of 1-octadecene into the second block. In both cases, the diblock copolymers were obtained with low molecular weight distribution ($\bar{D} = 1.06$ – 1.22). In 2015,

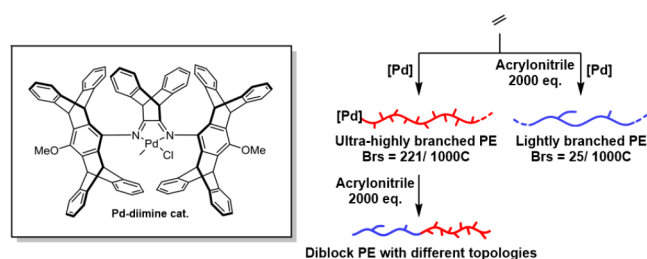
Ricci et al. reported a protocol to prepare di- and triblock copolymers comprising poly(1-dodecene) and polyethylene through the use of an α -diimine Ni(II) complex.⁶⁰⁶ As the Ni(II)-catalyzed polymerization of olefin is living, sequential addition of 1-dodecene monomers followed by ethylene leads to the formation of crystalline–amorphous AB type diblock copolymers. Recognizing the loss of livingness as the ethylene polymerization is progressing, and the authors performed the ethylene polymerization only in a short time frame (2 min) then recharged with 1-dodecene to achieve an ABA triblock copolymers. The triblock copolymer with the amorphous block as the middle block exhibits an impressive tensile strength (18 MPa) and strain at break (ca. 1000%) compared to the homopoly(1-dodecene).

Recently, an exciting approach in olefin block copolymer synthesis was discovered by Harth et al. with the utilization of additives to regulate the branching degrees of each polyolefin segments. In 2019, the authors observed the change in branching of obtained poly(1-hexene) when adding 4 equiv of AlCl_3 to Brookhart's Pd(II) α -diimine catalysts.⁶⁰⁷ Specifically, the number of branching increases from 105 to 152 branches (per 1000C), with the earlier being attained with standard Brookhart's catalyst. This was explained by the capability of triggering isomerization of 1-hexene to internal hexenes prior to polymerization by the addition of AlCl_3 . As a result, a different enchainment via the insertion of 2- and 3-hexene was observed with the increase of ethyl, propyl, and butyl branches. A similar phenomenon also occurred with higher α -olefins such as 1-octene and 1-decene. This unique mechanism allows the preparation of poly(1-hexene) block copolymers with different branching structure per segment by adding AlCl_3 midway through the polymerization. A complete shift toward higher molecular weight was seen in the GPC trace from the first segment ($M_n = 24.0$ kDa, $\bar{D} = 1.03$, 95B/1000C) to the final diblock copolymer ($M_n = 32.5$ kDa, $\bar{D} = 1.05$, 116B/1000C), which indicates the livingness of the system.

More recently, Jian and co-workers reported another method for branching regulation by the addition of polar additive, thus, allowing the preparation of polyethylene block copolymers comprising ultrahigh branched and light-branched topology. This was feasible with the discovery of a Pd(II)-diimine bearing a bulky dibenzobarrelene (DBB) ligand that can produce ultrahigh branched polyethylene (220B/1000C) from earlier work.⁶⁰⁹ The group later found that adding a polar additive such as acrylonitrile, acetonitrile or benzonitrile would lead to the significant drop in branching degrees of resultant polyethylene.⁶⁰⁸ Taking advantage of this finding, a diblock polyethylene synthesis was carried out with the addition of 2000 equiv of acrylonitrile in the middle of the polymerization. A wide range of polyethylene block copolymers with amorphous–semicrystalline structures and different molecular weights were achievable via this method (Scheme 46).

5.3.1.1.4. Phenoxy–Imine Complexes. Early work on the salicyladimine (phenoxy-imine) ligand was first reported Cozzi and Floriani in 1995, which showed modest activity toward ethylene polymerization.⁶¹⁰ Phenoxy-imine was proven to be an excellent ligand framework for olefin polymerization with early transition metals, especially group 4, through seminal work from Fujita and co-workers (Mitsui Chemicals).^{579,611–614} The rationale behind the ligand-oriented design developed by the authors was based on the DFT calculations of metallocene complexes, which demonstrated a great electronic flexibility. Another class of phenoxy-imine catalysts are built up on late

Scheme 46. Ultrahighly Branched PE–Lightly Branched PE Block Topology Triggered by a Polar Additive⁶⁰⁸



transition metals with the examples from Johnson (Dupont)⁶¹⁵ and Grubbs (Caltech)^{616,617} in 1977. The rationale behind the ligand-oriented design developed by the authors was based on DFT calculations of metallocene complexes, which shows a great electronic exchange between a ligand and a metal center during ethylene polymerization. Both early and late transition metals bearing phenoxy-imine ligand frameworks were developed in parallel with the later processes with a higher degree of tolerance toward polar functional groups.^{579,618}

With the ability of catalyzing living polymerization of ethylene, propylene, and higher α -olefins as well as manipulating the polymer tacticity, bis(phenoxy-imine) Ti catalysts allow the synthesis of multiblock copolymers comprising amorphous and semicrystalline segments. The first example was introduced by Minati et al. from Mitsui Chemicals with the preparation of di- and triblock copolymers including PE-*b*-sPP, PE-*b*-EPR, PE-*b*-EPR-*b*-sPP, PE-*b*-EPR-*b*-EPR (EPR: poly(ethylene-*co*-but-1-ene)), PE-*b*-EBR, sPP-*b*-EPR, sPP-*b*-EPR-*b*-PE, and EPR-*b*-EPR-*b*-PE in a controlled fashion by sequential monomer feedings (Figure 45).⁶¹⁹ The authors later showcased the

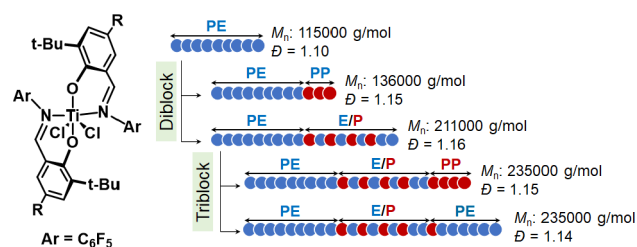


Figure 45. Preparation of multiblock copolymers using Ti complex bearing fluorine containing phenoxy-imine chelate ligand.

synthesis of di- and multiblock copolymers using Ti -FI catalyst bearing a *t*-butyl group substitution on the phenoxy ring.⁶²⁰ The first PE segments ($M_n = 115\,000$ g/mol, $D = 1.10$) were formed rapidly at 25 °C upon the addition of *x*/MAO in an ethylene-saturated toluene solvent. Introduction of an ethylene/propylene with the ratio of 25:75 resulted in the generation of the second poly(ethylene-*co*-propylene) block segment. A shift toward a higher molecular weight range with a narrow dispersity ($M_n = 211\,000$, $D = 1.16$) was indicative for the successful chain extension. Finally, ethylene or propylene was fed to the reactor to create triblock copolymers with different composition of propylene (Figure 45). Similarly, a sPP-*b*-poly(ethylene-*co*-propylene) diblock copolymer was also prepared by Coates and co-workers using similar catalytic system.⁶²¹ It is notable that many block copolymers described above were inaccessible prior to pioneering studies on the bis(phenoxy-imine) titanium(IV) complexes.

5.3.1.2. Olefin Block Copolymers by Coordinative Chain Transfer Polymerization (CCTP). As aforementioned, well-defined, monodisperse, and precise OBCs can be obtained with a metal-catalyzed living polymerization system. However, the major drawback of this system is indivisibly associated with its fundamental properties so-called “single-site” and “livingness”.^{589,622} With conventional, multisited catalysts, once the propagating chains are terminated, and leave the catalytic sites, they can start to grow another chain. Furthermore, this process can happen hundreds to thousands of times, which diminishes the catalyst loading required. However, in a living system, only one chain is attained per active metal center. As a result, multiple grams of expensive transitional metal catalysts are needed to produce a small batch of polymers. Living polymerization, additionally, also requires multistep syntheses and quick alteration of reactor composition.⁶²³ These drawbacks place practical hurdles on their commercial utilization. Acknowledging that these drawbacks are practical hurdles to their commercial utilization, many industrial researchers have been focusing on the development of alternatives for the “one-chain-per-catalyst” concept. Coordinate chain transfer polymerization (CCTP) is based on the idea for transfer of the growing chains to a chain transfer agent (CTAs) via transmetalation to form a “dormant” species, while the propagation continues to take place on the active catalyst.⁶²⁴ Because of the rapid and reversible exchange properties of CTAs, several polymers can be produced per metal center, while the living character of the polymerization

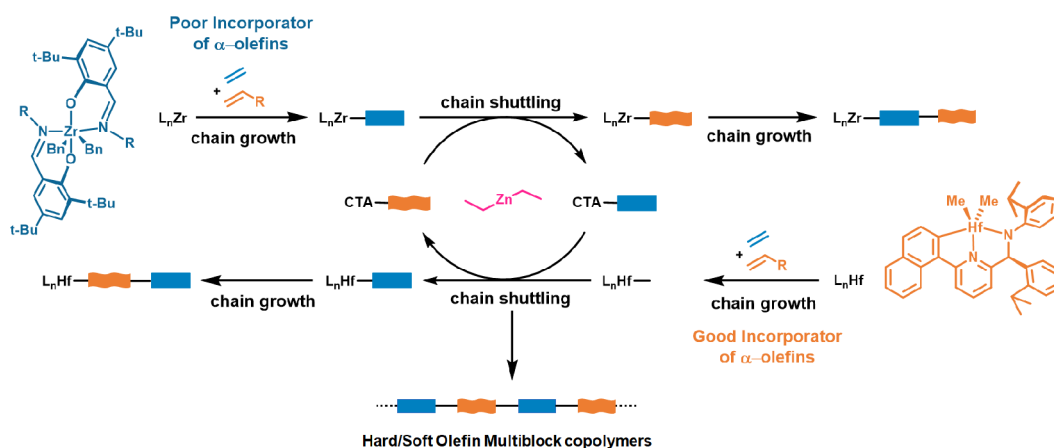


Figure 46. Chain shuttling polymerization developed by Dow Chemical. Adapted from ref 623. Copyright 2007 American Chemical Society.

is quite preserved.⁶²⁵ This mechanism makes CCTP belong to the group of degenerative group transfer polymerization, similar to, i.e., RAFT or OMRP, in which a dynamic equilibrium of propagating and dormant species is involved.⁶²⁴

Chain shuttling polymerization (CSP) is another elegant approach for the solution of “one-chain-per-catalyst” that was developed by Arriola and co-workers from Dow Chemical in 2006.⁵⁹⁰ This method is employing a dual catalytic system for chain growth, together with a main-group alkyl complex that serves as a chain transfer/shuttling agent for reversible transfer of polymer chains. The key to block copolymer formation of this system is based on the different selectivity toward comonomers between two catalysts.⁵⁸³ This permits each catalyst to grow a distinct polymer type on its own (“hard” and “soft” segments), then reversible transfers by CTA and joints these polymer chains into a single polymer chain, resulting in the formation of block copolymers (Figure 46).^{347,626} Although CCTP and CSP are both required a CTA, CSP is distinguished by that the reversible exchange of polymer chains happen between different catalysts.

5.3.2. Polyolefin–Polar Block Copolymers. Along with advantageous properties such as flexibility, chemical, and mechanical durability, and low production cost, polyolefin without any functionality is interactive and usually suffers from interactive surface problems.^{21,627} Undesirable properties associated with the inherent inertness are, namely, no compatibility, no dyeability, no printability, and poor adhesion. This significantly obstructs applications of polyolefins in coating, printing, composite manufacture, and recycling.⁶²⁸ Hence, tremendous efforts have been made in both academia and industry to overcome these limitations for valuable polyolefin-derived products. Polyolefin-polar block copolymers are considered as the most desirable materials because these materials can embody many functional groups while leaving the polyolefin segments unadulterated. As a consequence, the unique assets of polyolefins including crystallinity, melting temperature, and hydrophobicity are preserved.⁶²⁹

Besides, polyolefin-polar block copolymers are prominent regarding their compatibilizing ability. The high interfacial activity of these blocky materials allows them to permeate the immiscible parent domains, and therefore enhance the adhesion dramatically even when using a small amount.⁶³⁰ Block copolymers are traditionally prepared by sequential additions of monomers in living polymerization such as anionic and cationic polymerization. However, in the living olefin polymerization, the great challenges are associated with the low tolerance of metal catalysts toward functional groups.⁶³¹ This section will discuss the most studied methods of polyolefin-polar block copolymers that include (1) combining of postmetallocene to other polymerization techniques, (2) coupling reaction between two distinct polymers, (3) “switchable” system, and (4) other new developed methods.

5.3.2.1. Combination of Postmetallocene Initiated Polymerization and Other Techniques. Using combination techniques is, theoretically, the best method to prepare olefin-polar block copolymers considering the significant differences in reactivity of the two distinct classes of monomers.

Following this path, each block segment is synthesized via the most suitable polymerization method, and the control over copolymer structure and composition can be achieved in distinct manners. The great challenge of this route is to achieve a smooth and efficient transition/transformation between two dissimilar techniques. During the metal-catalyzed polyolefin polymerization, the active site is at the metal center; thus to start another

polymerization, this active site has to be changed to grow the other polymer chain.⁶²⁹ A common strategy is to introduce a suitable functional group to end-cap the polyolefins, which later can act as macroinitiators for the subsequent polymerization of the polar monomers.⁶³² This is usually can be accomplished through several approaches including direct copolymerization with polar monomers, copolymerization with reactive monomers bearing “latent”/ “masked” groups, which later can be easily converted to functional groups, postpolymerization modification, and employing CTA for end-group functionality introduction (Figure 47).^{627–629,632–635}

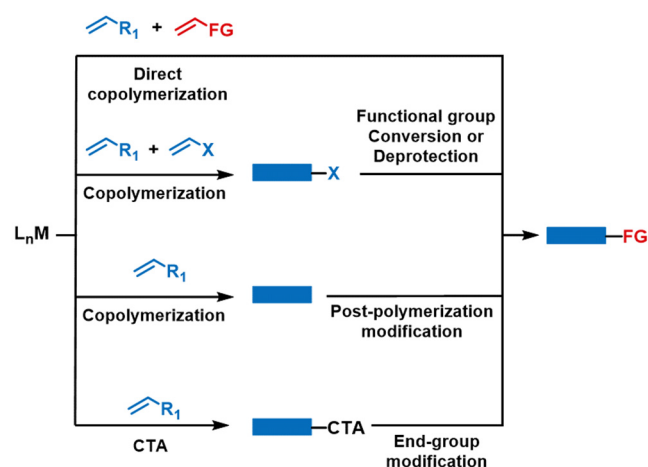


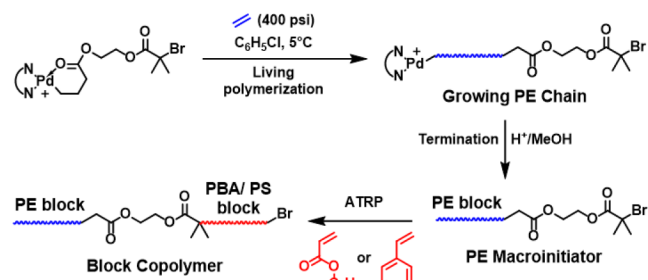
Figure 47. Major approaches to produce functionalized polyolefins as macroinitiators.

5.3.2.2. Combination of Postmetallocenes and ATRP. The earliest example of combining insertion by nonmetallocene catalysts with ATRP was reported by Matyjaszewski and Brookhart in 2002.⁶³⁶ It was made possible by utilizing the palladium diimine catalyst functionalized with a methyl methacrylate unit that can polymerize ethylene in a living manner at a low temperature. It led to the formation of methacrylate macromonomers bearing polyethylene chains that later could be copolymerized with *n*-butyl acrylate through ATRP to generate poly(*n*-butyl acrylate)-graft-polyethylene. Atomic force microscopy (AFM) was used to characterize the thin-film samples of the graft copolymers and revealed the nanoscale cylindrical morphologies due to microphase separation. One characteristic of a Pd-diimine catalyzed copolymerization of olefin and acrylate monomers is that the acrylate units are located at the chain-ends of the obtained branched polyolefins. Recognizing this, Guan et al. was able to obtain branched polyethylene with terminal α -bromoisobutyryl groups by copolymerization of ethylene and acrylate monomers functionalized with an ATRP-initiator moiety.⁶³⁷ The obtained PE was extended with oligo(ethylene glycol) methacrylate (OEGMA) and *N*-acryloyloxy succinimide (NAS) to generate NAS-activated nanoparticles as the scaffolds through Cu-mediated ATRP. Because both polymerization methods are living, the size of the nanoparticles can be precisely controlled. These scaffolds were conjugated with dyes and protein (ovalbumin) as demonstration for the high efficacy of multivalent bioconjugation. In a similar strategy, Ye and co-workers employed the Pd-diimine catalyst in the copolymerization of 2-(2-bromoisobutyryloxy) ethyl acrylate (BIEA) with ethylene, which yielded ATRP macroinitiators bearing multiple initiation sites.⁶³⁸ PE-BIEA

copolymers with molecular weights ranging from 10×10^3 to 200×10^3 g/mol and moderate dispersities (1.4–1.8) were prepared. The BIEA content was tunable depending on the concentration of BIEA monomers in the copolymerization and varied from 1.6–3.9%. Afterward, these ATRP macroinitiators were utilized to initiate MMA polymerization through ATRP using CuBr/CuBr₂/PMDETA as the catalyst system in anisole at 80 °C. A successful chain extension was evidenced through the increase in molecular weight of the copolymers over time, which eventually formed core–shell structures with a hyper-branched PE core grafted with side chains of PMMA.

The work emphasized the ability to form block copolymers with grafted polyacrylic structures based on the ability of postmetallocene catalysts to copolymerize with polar acrylic monomers and which are considered nonlinear structures in the scope of the review. In 2008, linear diblock copolymers of branched polyethylene and polystyrene or poly(*n*-butyl acrylate) were introduced by Ye et al. (Scheme 47).⁶³⁹ The

Scheme 47. Tandem Strategy of Pd-Diimine Catalyzed Ethylene Polymerization and ATRP to Afford Linear Diblock Copolymers of Polyethylene and Polystyrene/Poly(*n*-butyl acrylate)



synthesis is based on a Brookhart-type palladium diimine chelate functionalized with a single ATRP initiating unit that can polymerize ethylene in a living fashion. The Pd(II) complex was obtained through a single 2,1-insertion of BIEA monomers, following by rearrangement through chain walking to the six-membered ring functionalized chelate compound. Under

standard conditions for Pd-diimine catalyzed living ethylene polymerization (400 psi and 5 °C), the linear correlation of M_n^{PE} as a function of polymerization time was observed. The livingness of the coordination–insertion polymerization allows the preparation of macroinitiators PEMI-1 and PEMI-2 with molecular weights of 12.8 and 30.6 kg/mol, respectively, with narrow dispersities by varying the reaction time. The PE macroinitiators were then subjected to ATRP with styrene/*n*-butyl acrylate to afford diblock copolymers with good control over molecular weight and polydispersity. Thermal analysis of the diblock copolymers was carried out to evaluate the effect of length of the functional blocks. Compared to the homopolyethylene precursors, the glass transition of the PE segment of the block copolymers was significantly increased with the extension of the polystyrene/polyacrylate block.

More recently, Guironnet and co-workers reported a novel methodology for the preparation of polyolefin containing diblock copolymers, with a key feature of relying on the cross-coupling metathesis reaction by the Hoveyda–Grubbs catalyst (Figure 48).⁵⁴¹ By using different postmetallocene catalysts, the authors could produce a polyolefin library with different molecular weights and properties. Subsequently, the cross-metathesis reaction using Hoveyda–Grubbs II catalyst with an acrylate bearing desired functional groups was used to transform the alkene terminated polyolefin into functional groups suitable for controlled living polymerization techniques such as ring-opening polymerization and ATRP. To optimize the reaction condition, 1-HDPE ($M_{n,NMR} = 0.8$ kg/mol) was first used for the coupling with 2-hydroxyethyl acrylate (HEA) or 2-(2-bromoisobutyl) ethyl acrylate (BIEA) using 1 mol % of the catalyst loading. The author found that slow feeding of the olefin metathesis catalyst prevents its thermal deactivation.

After 30 min of the reaction, both terminal and internal olefins, were converted in a quantitative conversion as evidenced through the disappearance of the olefinic double bonds in the ¹H NMR. This condition was next applied to the library of polyolefins with the HEA feed correlated to the ratio of the double bond present. HEA-functionalized polyolefins were employed to initiate the cROP of lactide and aROP of *tert*-butyl glycidyl ether (*t*BuGE). Furthermore, ATRP of styrene was

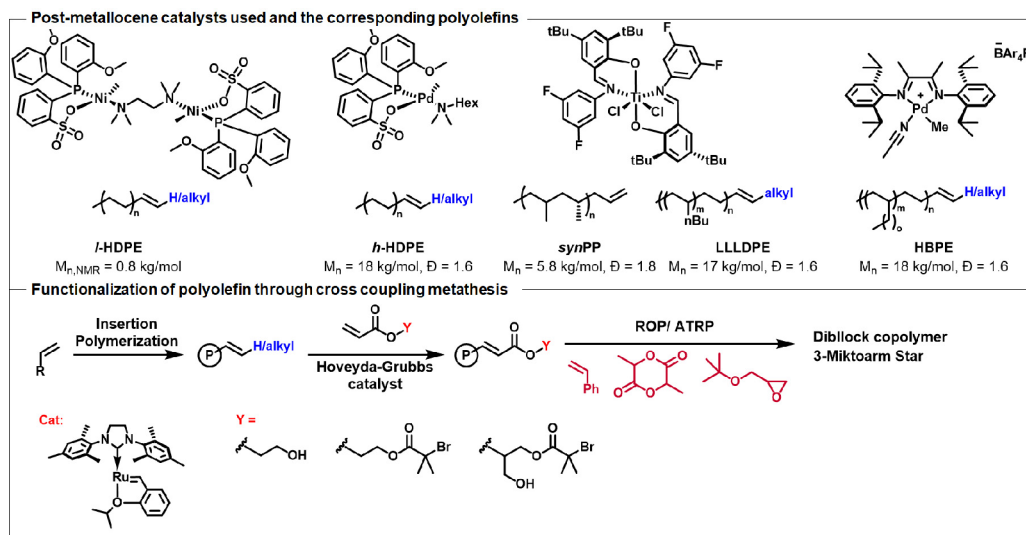


Figure 48. Cross coupling metathesis for the preparation of polyolefin macroinitiators. Chain extension using ATRP or/and ROP yield diblock copolymers or 3-miktoarm star block copolymers. Adapted with permission from ref 541. Copyright 2018 Royal Chemical Society.

performed with the BIEA functionalized *l*-HDPE to afford *l*-HDPE-PS block copolymers. The authors further showed the versatility of the method with the synthesis of dual-functionalized polyolefins containing hydroxyl and 2-bromoisobutyrate functionalities. Impressively, the utilization of highly active catalysts throughout the protocol results in the high productivity overall, which opened up access to potential industrial applications.

5.3.2.3. Combination of Postmetallocenes and RAFT. The combination of metal complexes and RAFT polymerization remains rare due to the notorious poisoning effect of sulfur compounds. Wu and co-workers overcame this problem by employing “masked” acrylate monomers, 2-hydroxyethyl acrylate with trimethylsilyl protected hydroxyl group (HEA-TMS), to be copolymerized with ethylene via Pd-catalyzed coordination–insertion mechanism.⁶⁴⁰

A postpolymerization through esterification with 3-benzylsulfanythiocarbonyl sulfanylpropionic acid (BSPA) afforded multifunctional-RAFT agents. A RAFT-mediated polymerization with *N,N*-dimethylaminoethyl methacrylate (DMAEMA) generated hyperbranched PE amphiphiles HBPE-PDMAEMA. The amphiphilic block copolymers can form nanoparticles in aqueous solution with a hydrophobic core (HBPE) and a hydrophilic shell (PDMAEMA). More interestingly, the thermo/pH double responsiveness of PDMAEMA was remained in the new materials.

5.3.2.4. Combination of Postmetallocenes and NMP. Recently, Mecking et al. reported a catalytic chain transfer polymerization (CTP) of ethylene and an alkoxyamine-functionalized silane as a chain transfer agent (CTA) with the use of α -diimine palladium catalyst. By screening different ratios of the palladium catalyst and alkoxyamine-substitute, the authors were able to optimize the polymerization conditions for a high degree of functionality in the resultant PE.⁶⁴¹ Two TIPNO-terminated PE precursors with molecular weights of 19.2×10^3 g/mol and 14.5×10^3 g/mol were then exposed to NMP with styrene or acrylate monomers.

Because NMP is a controlled radical polymerization method, the molecular weight of second block of polystyrene or polyacrylate can be easily tuned by varying the reaction time (Figure 49).

As a result, diblock copolymers were obtained with different compositions and molecular weights. Extensive characterization methods, including ^1H NMR, DOSY, and SEC/GPC with RI/

UV detectors pointed toward the successful formation of the block copolymers. Another way to prepare PE-*b*-PS block copolymers was presented by Matyjaszewski and Harth and co-workers in an approach in which the introduction of CTA reagents during the insertion polymerization is avoided, and a living insertion polymerization and a macroradical is formatted by a photodynamic process, to be captured by a TIPNO functionality which is capable for performing NMP. In this fashion, the PE chain can be extended with styrene and *n*-butyl acrylate to diblock copolymers.⁶⁴² Because radical trapping leads also to PE macroradical species that cannot undergo an N–O cleavage, PBN derivatives can be used as spin traps to give a stable nitroxide for further polymerization through NMP. To achieve linear triblock copolymer architectures, dinuclear Pd(II) diimine catalysts can be used to give BAB-type PS-*b*-PE-*b*-PS triblock copolymers.⁶⁴²

5.3.2.5. Combination of Postmetallocenes and Ring-Opening Polymerization. Successful combination of coordination insertion polymerization and ring-opening polymerization (ROP) affords novel materials that are inaccessible using other approaches. Considering the enormous difference in polymerization mechanisms, many strategies focused on installing hydroxy functional groups into polyolefin chains. The resulting polyolefins then undergo under ring-opening polymerization via metal-catalyzed, ionic, or thermal process.

In 2006, Fujita and co-workers introduced a series of phenoxy-cycloalkylamine ligated zirconium complexes that after being activated with MAO can produce vinyl-terminated low molecular weight polyethylene.⁶⁴³ The terminated vinyl could be converted into an epoxide group through postpolymerization modification via epoxidation with hydrogen peroxide in the presence of Na_2WO_4 as a catalyst. Further hydrolysis or amination of the epoxide end-group generated a diol- or triol-terminated PEs that served as macroinitiator in ROP with ethylene glycol.^{643,644} As a consequence, AB_2 - and AB_3 -type hybrid materials of polyethylene and poly(ethylene glycol) were obtained.⁶⁴⁴ These materials can be dispersed in water to create micrometer- or nanosized particles. The authors explained that the particle size was more likely due to the polymer architecture rather than the copolymer compositions. Interestingly, the nanoparticles derived from AB_3 -type copolymers can be isolated as nanopowders and redispersed in organic solvents. The hydrophobic nature of the particle core was demonstrated by the ability to successfully incorporate a water-insoluble dye molecule or an environmentally sensitive fluorescent probe (Figure 50).

5.3.2.6. “Switchable” Systems. “Switchable” system methods have been an emergent strategy for block copolymer synthesis.⁶⁴⁵ It stems from the rationale that the reactivity can be toggled between two or more states by external stimuli, which allows the selectivity toward different monomer classes and, eventually, the formation of di/multiblock copolymers. Even though the switchable system has been impressively utilized for the block copolymer synthesis through ring-opening polymerization, RAFT, or ATRP, its application with postmetallocene remains scarce.^{646–649} However, there were some reports on the ability to generate radicals through metal–alkyl bond homolysis Ni and Pd complexes, which can facilitate radical polymerization of (meth)acrylate monomers.^{650–654} Noticeably, in 2011, Monteil et al. demonstrated that salicylaldiminato nickel(II) catalysts could undergo both coordination–insertion and radical polymerization of ethylene and acrylate monomers, respectively. The obtained copolymers of ethylene and (meth)-

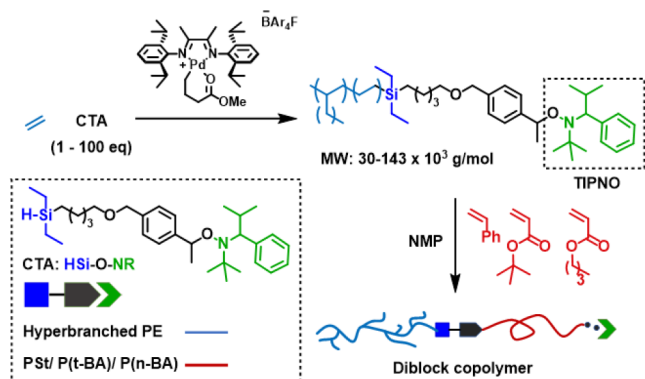


Figure 49. Functionalized silane as catalytic chain transfer in the coordination insertion polymerization with palladium diimine catalyst to afford polyethylene bearing TIPNO for subsequent nitroxide mediated polymerization.

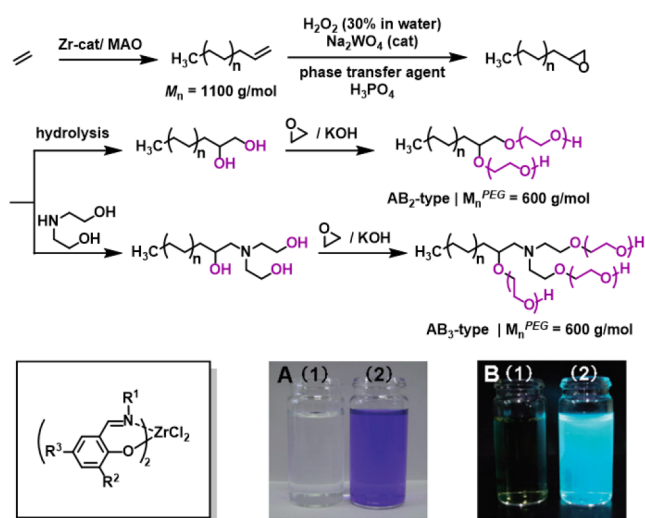


Figure 50. Synthesis of diol- and triol-terminated polyethylene using phenoxy-cycloalkylamine ligated zirconium complex and subsequent chain extension with ethylene glycol to obtain hybrid materials. Adapted from ref 643. Copyright 2006 American Chemical Society.

acrylates were proposed to be di/multiblock copolymers and exhibit a blocky microstructure. However, an in-depth mechanistic study by Mecking and co-workers showed that the radical source of this system is only accessible after a series of β -H elimination and bimolecular reductive coupling to eventually decompose to Ni(0) from Ni-alkyl species.⁶⁵⁵ Particularly, radical polymerization of MMA was initiated from the product of the ligand and Ni(0) no longer carries the growing polyethylene chains, precluding the formation of the block copolymer.

An attempt to integrate the coordination–insertion mechanism and radical mechanism in a photoswitch platform was reported from Harth and co-workers.⁶⁵⁶ In 2018, the Harth group discovered that upon blue light irradiation, Brookhart's Pd(II) diimine complex can initiate radical polymerization of MA to yield PMA with molecular weights ranging from 49 000 to 402 000 g/mol in reasonable dispersities. Interestingly, the photoinitiated radical polymerization exhibits a temporal control in an “ON–OFF” light switching experiment, as no polymerization was observed in the dark. This allowed for the development of MILRad (metal–organic insertion/light-

initiated radical) polymerization technique, in which the direct copolymerization of 1-hexene and MA can take place in a one-pot reaction.

Specifically, in the dark 1-hexene was polymerized by Pd-diimine catalyzed coordination–insertion mechanism. Under blue light, the coordination–insertion no longer occurred, MA was then polymerized via radical polymerization to afford poly(1-hexene)-*b*-PMA in a wide range of molecular weights (14800–17400 g/mol) and with moderate dispersity ($\bar{D}$ = 1.47–1.56). A subsequent study was also conducted on the systematic investigation on the Pd-diimine complexes bearing different ligand frameworks and polar monomer scope.⁶⁵⁷

A wide range of monomers were tested for radical polymerization under blue light, including MA, 2-hydroxyethyl acrylate (HEA), *n*-butyl acrylate (nBA), *tert*-butyl acrylate (t-BA), methyl methacrylate (MMA), glycidyl methacrylate (GMA), *N,N*-dimethyl acrylamide (DMAm), *N*-isopropylacrylamide (NIPAm), vinyl acetate (VAc), styrene (St), and isobutyl vinyl ether (IBVE).⁶⁵⁷ The screening result revealed that (meth)acrylates and acrylamides can be selectively polymerized under blue light. Eventually, DFT calculations were performed across the Pd complexes, which shows that under photo-excitation, a shift in electron density from the metal–carbon bond to the ligand frame was seen. This metal-to-ligand-charge-transfer (MLCT) transition was suggested to be responsible for the metal–carbon bond photolysis. The ligand variation, however, shows no significant effect on the photoinitiation process.

In 2020, the group conducted an in-depth study on the mechanism of MILRad and established the integral molecular parameters for a successful transition from coordination insertion to light-initiated radical polymerization.⁶⁵⁸ Through exhaustive analytical techniques using NMR, EPR, and MS, Harth and co-workers found that the key intermediate in the MILRad's success is the Pd–polyolefin–MA chelate formed through a single insertion of MA into a growing Pd–polyolefin bond (Figure 51). This macrochelate, because of its enhanced thermal stability, is mostly unaffected by light. However, the photoswitch was feasible through a series of ancillary ligand-mediated chelate opening, chain walking, and eventually Pd–C bond photolysis. This photoinitiated “switch” gives access to polyolefin macroradicals that continue to propagate with available MA monomers through a free radical polymerization mechanism. MALDI-TOF analysis on the block copolymer shows

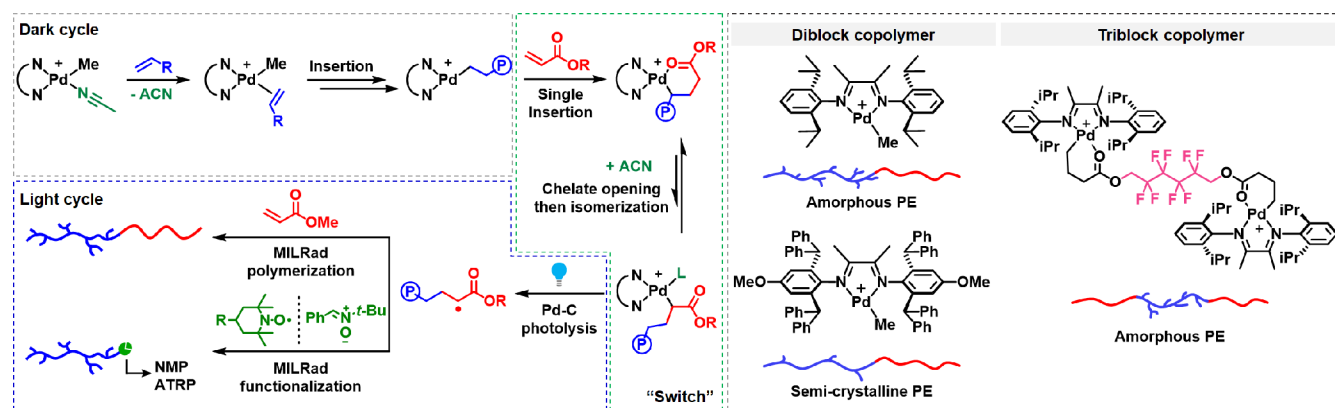


Figure 51. Mechanism of MILRad polymerization for one-pot synthesis of polyolefin–polyacrylate block copolymers with coordination–insertion polymerization in the dark and photoinitiated free radical polymerization under blue light and different properties and structures of the block copolymers can be obtained through MILRad. Adapted from ref 658. Copyright 2020 American Chemical Society.

that the MA polymerization terminates through disproportionation, which leads to the formation of saturated and unsaturated chain-ends with the same degree of polymerization. Interestingly, the crystallinity of the polyolefin segment is tunable through the use of a Pd(II) complex bearing a benzhydryl-derived diimine ligand.⁶⁵⁸

To further showcase the versatility of the MILRad technique, the authors developed a dinuclear palladium complex connected through a 1,6-bis(acryloyloxy)-2,2,3,3,4,4,5,5-octafluorohexane linkage that can polymerize ethylene in a living fashion. Upon the sequential addition of MA monomers and photoirradiation, PMA-*b*-PE-*b*-PMA triblock copolymers were obtained. The amphiphilic nature of the collected block copolymers was demonstrated through the ability to self-assemble in selective solvents to form nanostructures evidenced through DLS and TEM experiments. The scope of MILRad was further broadened in the follow-up work wherein ethylene/acrylic diblock copolymers with tailored mechanical properties ranging from hard plastics, elastomer, to semiarmorphous were prepared using a distorted sandwich α -diimine Pd complex (Figure 52).⁶⁵⁹ The same work also demonstrated one-pot synthesis of PE-*b*-P(MA-*co*-NAS) that can undergo postmodification to accomplish fluorescent polyolefin-based material.

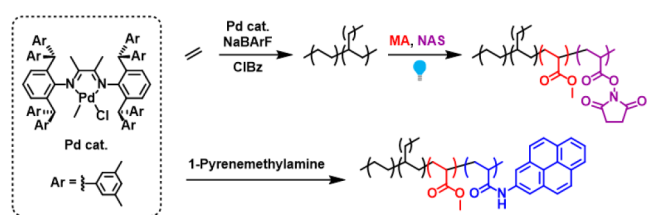


Figure 52. Synthesis of fluorescent polyolefin-based material via MILRad following by postmodification. Adapted with permission from ref 659. Copyright 2021 Wiley.

The mechanistic study also shines light on the ability to capture the polyolefin macroradical by radical/spin trapping agents such as TEMPO and *N*-tert-butyl- α -phenylnitrone (PBN). Taking advantage of this result, Matyjaszewski, Harth, and co-workers extended the initial observations into a complete approach for one-pot, light-driven synthesis of functionalized PE, namely MILRad functionalization (Figure 51).⁶⁴² A variety of nitroxide radicals and nitrones such as TIPNO, TEMPO-Br, and PBN were examined on their trapping ability, with the aim of producing PE macroinitiators capable of chain-extension through subsequent NMP or ATRP. The authors found that the trapping quality depends greatly on the steric hindrance and polar functional group presented in the nitroxides' structure. For example, ester moiety in TEMPO-Br would promote chain transfer and give a lower yield of end-functionalized PE compared to its analogues. Nevertheless, all the PE macroinitiators were able to facilitate controlled radical polymerizations to afford di- and triblock copolymers comprising PE and vinylic polymers such as PS, PI, P(*n*-BA), and PMMA.

More recently, Nozaki et al. introduced a method of "self-switching" between coordination–insertion polymerization and OMRP to prepare multiblock copolymers of PE and PMA.⁶⁶⁰ This was accomplished through the utilization of pentamethylcyclopentadienyl cobalt complex ($\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_5)\text{P}(\text{OMe})_3\text{I}_2$)/MMAO system. The mechanism was proposed by methyl or *iso*-butyl groups transfer from Al of MMAO to the Co metal center, followed by a single insertion of MA unit to

generate a $\text{Co-C}(\text{CO}_2\text{Me})$ complex. From here, coordination–insertion of ethylene or OMRP of MA may happen asynchronously to eventually form multiple segments of PE and PMA. Although the switching process is uncontrolled, this study represents a new facet for the preparation of polyolefin-polar di- or multiblock copolymers.

5.3.3. Outlook. The control/livingness observed in olefin polymerization by postmetallocene catalysts was proven as a powerful tool for the synthesis of not only OBCs but also polyolefin-polar block copolymers. Ligand design plays a direct role in manipulating polyolefin microstructures as well as enhancing functional group tolerance. CCTP was illustrated as an efficient way to reduce the high cost caused by "one metal per chain". In addition, recent advancement showed that "switchable" system triggered by external stimuli would lead to the development of more "exotic" and highly desirable materials.

6. CONCLUSION/OUTLOOK

The gaining importance of block copolymers in all aspects of fundamental and applied science has accelerated synthetic efforts to combine monomer families to access the desired structures. A few strategies have emerged; one is capitalizing on the ability of the polymerization method to afford a chain extension with another monomer family. This requires a continuous advancement of the polymerization method and, therefore, to mention one example, controlled radical polymerization pathways are still being optimized and developed. Chain transfer reagents, redox, or photocatalytic switches are the other options when either a switching of the polymerization pathway is necessary because of the incompatibility of the monomer family or through a postfunctionalization of the polymer chain end to install the initiation unit for the other polymerization pathway. Another important aspect of choosing the most suitable polymerization method for block copolymer synthesis is the order and nature of the block copolymer segment which can determine which polymerization pathway has to be chosen. Because block copolymers are such important building blocks with numerous applications in emerging areas such as energy storage, separation media, plastic upcycling, information technology, and biotechnology, this overview gives a comprehensive account of the current research status in linear block copolymer synthesis to this date.

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Notes

The authors declare no competing financial interest.

Biographies

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Glen R. Jones from Cambridgeshire, UK, graduated with a MChem degree in 2014 and Ph.D. in 2018 from the University of Warwick (PI Haddleton) on a Lubrizol-sponsored project synthesizing amphiphilic block copolymers by aqueous SET-LRP. He joined the Harth group from 2018 to 2020 as a postdoctoral fellow and is undertaking currently postdoctoral studies at the ETH Zurich in the Anastasaki group.

Enkhjargal Tsogtgerel grew up in Mongolia and graduated from the University of Dartmouth in 2016 with a B.S. degree in Chemistry (magna cum laude) and joined the Harth group in the Fall of 2017 and graduated in 2022.

Dung Nguyen grew up in Vietnam and graduated from Case Western Reserve University with a B.S. degree in 2019 and joined UH and Harth group in the same year.

Anthony Keyes received his B.S. degree from Jackson State University and went to obtain his M.S. degree at the University of Bordeaux, LCPO, France, in 2017. In the same year he received the NSF Graduate Research Fellowship and joined the Harth group in 2017 with a Center of Excellence Fellowship. During his tenure he received the SPE Scholarship and the Jay E. Kochi Graduate Research Award and graduated in 2021 from UH.

Yu-Sheng Liu grew up in Taiwan and graduated in 2014 from National Sun Yat-Sen University in Taipei. He worked for a few years as a Research Assistant at Academia Sinica. He moved to the U.S. and

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Hasaan Rauf graduated in 2019 with a B.S. and M.S. degree from San Jose State University with work on ADMET polymerization. He then joined the graduate program at UH and the Harth research group in the same year.

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Chenying Zhao grew up in China and received her B.S. degree from Beijing University of Chemical Technology. She moved to the U.S. and joined the University of Akron, College of Polymer Science, and graduated with a M.S. degree in 2019 with work on ATRP. In the same year, she joined the graduate program at UH and the Harth lab.

Eva Harth received her B.S. from the University of Bonn, Germany, and graduated with a M.S. degree from the University of Zurich, Switzerland. After her Ph.D. at the MPI for Polymer Research, Mainz, Germany, she held a NSF postdoctoral fellow position at Stanford University and the IBM Research Center, Almaden, CA. She started her academic career in 2004 at Vanderbilt University and is currently a Full Professor at the University of Houston. Her research centers on building polymer architectures such as block copolymers and polymer networks with functions in energy and biology. The work encompasses the investigation of polymer mechanisms, catalytic design, polymer functionalization, and synthesis by radical and coordination-insertion polymerization.

ACKNOWLEDGMENTS

We gratefully acknowledge funding and support by the Welch Foundation (no. H-E-0041 and no. E-2066-20210327) and National Science Foundation (NSF) for support of this work CHE-2108576 and CHE-1808664. A.K. acknowledges funding through the NSF Graduate Fellowship (no. 1324585) and the Center of Excellence in Polymer Chemistry Fellowship. H.D. thanks the Department of Chemistry UH for the Jay E. Kochi Graduate Fellowship.

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