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Current status and outlook for ATRP

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ABSTRACT

Atom transfer radical polymerization (ATRP) is one of the most often used controlled radical polymerization techniques. It employs very small amounts (ppm) of Cu complexes in the presence of various chemical reducing agents but also external stimuli such as light, electrical current or mechanical forces. It can be carried out in bulk, in solution, and in dispersed media. ATRP has been successfully used to prepare various polymers with controlled architecture and well-defined topology, composition, and functionality, as well as bioconjugates and organic–inorganic hybrids. This article summarizes the current status and also an outlook for ATRP.

1. Introduction

Atom transfer radical polymerization (ATRP) is one of the most intensely investigated reversible deactivation radical polymerization (RDRP) techniques.[1] Since its discovery in 1995, over 22,000 publications have appeared on ATRP, over 2,000 US patents have been issued, and Google patents show over 100,000 patents and patent applications worldwide on "atom transfer radical polymerization". This indicates that many academic and industrial labs have used ATRP extensively. Due to its robustness and simplicity, ATRP has been employed not only by synthetic polymer chemists, by various materials scientists, biologists and also by organic chemists who use atom transfer radical addition procedures, which served as an original inspiration for ATRP. [2] However, since the activity of currently used catalysts in ATRP is billions of times more active[3] than those originally used in organic synthesis, organic chemists now employ much smaller amounts of catalysts, also in water and other benign media, making ATRP an environmentally green procedure. [4] ATRP opened avenues to facile synthesis of polymers with precisely controlled and designed molecular architecture, including block and gradient copolymers, stars, grafts, highly branched copolymers, bottlebrushes as well as various copolymers with functional groups precisely positioned at desired locations in polymer chains. Such polymers are now used to produce a range of advanced materials, with selected properties. ATRP has introduced new efficient techniques for covalently linking synthetic polymers prepared by ATRP with inorganic substrates[5] and with biomolecules such as carbohydrates, proteins and nucleic acids. [6] This perspective will cover the current status and future trends in ATRP related to the development of new synthetic procedures based on a deep mechanistic understanding of ATRP, preparation of (co)polymers with controlled architecture and advanced materials including bioconjugates and nanocomposites for applications ranging from biomedicine to environment and energy-related areas. [7].

2. Mechanistic understanding of ATRP and development of new catalytic systems

ATRP is a catalytic process in which growing radicals (R*) are intermittently activated from dormant alkyl halides (R-X) by a transition metal catalytic system.

The mechanism of ATRP involves the halogen atom abstraction from an alkyl halide substrate by an activator, Cu^{I}/L^{+} complex (L = ligand, typically multidentate N-based compounds). During this activation step, the Cu^{I} species undergoes an inner sphere electron transfer (ISET), resulting in the generation of a halogenated deactivator, $X\text{-}Cu^{II}/L^{+}$ complex and a radical, R*.[2,8] The radical adds one or a few monomer molecules and is then deactivated by $X\text{-}Cu^{II}L^{+}$, forming X-capped dormant species and regenerating $Cu^{I}L^{+}$ (Scheme 1a). [8–10] The rate constant of activation of dormant species is typically much smaller than the rate constant of radical deactivation, i.e., $k_{act} \ll k_{deact}$. Thus, the ATRP equilibrium is shifted toward dormant species. Radicals also terminate. However, the relatively low concentration of propagating radicals (10^{-7}-10^{-9} M) limits the occurrence of termination reactions, which typically involve ≪10 % of the total amount of growing chains (dormant species).

According to the persistent radical effect (PRE), [11] unavoidable radical terminations cause the accumulation of the "persistent radical" $X\text{-}Cu^{II}L^{+}$, which leads to a progressive slowdown and ultimately halts

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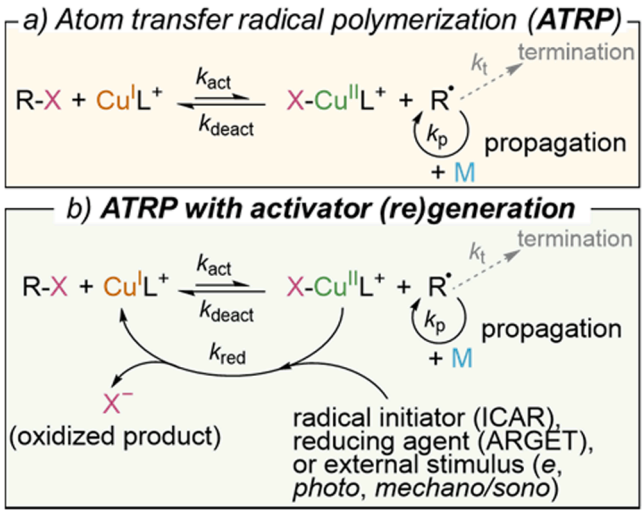


Scheme 1. General mechanisms of Cu-catalyzed a) normal ATRP, and b) ATRP with (re)generation of the $Cu^{I}L^{+}$ activator. The parameters k_{act}, k_{deact}, k_t, k_p and k_{red} represent rate constants of activation, deactivation, radical termination, propagation, and reduction. Reprinted with permission from *J. Am. Chem. Soc.* ***2022****, 144, 15413–15430*. Copyright American Chemical Society.

the polymerization. Therefore, to reach high monomer conversion, ATRP was originally conducted using a stoichiometric amount of catalyst and RX initiator. The relatively low activity of seminal Cu complexes with 2,2'-bipyridine (bpy) ligands toward C-X bonds required high catalyst loadings (1 mol% or 10,000 parts per million, ppm, relative to monomer concentration) and relatively harsh polymerization conditions, which could preclude the widespread utilization of ATRP.

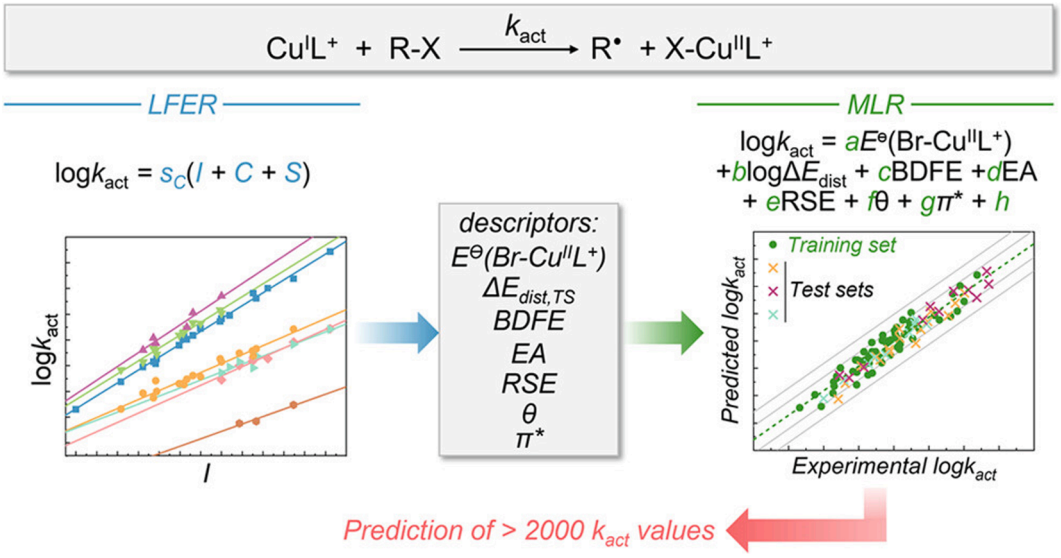
The development of methods for continuous (re)generation of the $Cu^{I}L^{+}$ activators in ATRP represented a major breakthrough, enabling a drastic reduction in catalyst concentrations. [2,3,12] In ATRP with activator (re)generation (Scheme 1b), air-stable Cu^{II} salts are employed and reduced *in situ* to Cu^{I} species, simplifying the reaction handling. [3,13,14] The accumulation of the "persistent radical" X-$Cu^{II}L^{+}$ is balanced by its continuous reduction to Cu^{I} species, thus avoiding rate retardation. Therefore, the loading of Cu catalysts can be reduced to < 10 ppm. This was facilitated by the identification and design of new ligands for more active Cu catalysts, guided by mechanistic analysis and computational approaches. [15–18].

Historically, the first ATRP with an activator (re)generation was obtained by introducing metallic Cu^{0} into the system and exploiting the comproportionation reaction between Cu^{0} and Cu^{II}/L species to form $Cu^{I}L^{+}$.[19] This method was later termed supplemental activator and reducing agent (SARA) ATRP, upon recognizing that Cu^{0} was also capable of activating dormant species, although to a much lower extent in comparison to $Cu^{I}L^{+}$.[20,21] Other compounds, including ascorbic acid and tin(II) octoate, were explored as reducing agents to continuously reduce the X-$Cu^{II}L^{+}$ deactivator via activator regenerated by electron transfer (ARGET) ATRP. [14,22] Similarly, thermal radical initiators, e.g., azobisisobutyronitrile, were employed to generate radicals during the polymerization to induce the continuous (re)generation of $Cu^{I}L^{+}$, in the so-called initiators for continuous activator regeneration (ICAR) ATRP. [22].

The (re)generation of the ATRP activator can also be achieved through external stimuli such as light, electrical current/potential, and ultrasound in the presence or absence of piezoelectric materials, as in *photo*ATRP, [23,24] *e*ATRP, [25] and *mechano/sono*ATRP, [26,27] and recent tribochemically controlled ATRP by contact electrification, [28] or by ball milling. [29] These systems use mild conditions and offer the possibility to temporally and spatially control polymerizations by regulating the applied stimuli. [30] Temporal control was also achieved in ARGET[31] and SARA ATRP. [32] The design and use of more active ATRP catalysts provided more effective temporal control while potentially enabling the expansion of the scope of monomers and functional groups. [33] ATRP systems with activator (re)generation can tolerate the presence of small amounts of oxygen. By adjusting the reaction volume and diminishing the head-space, as well as by judiciously selecting the ratios between the various ATRP components, it was possible to obtain well-controlled polymerizations without deoxygenation. [34–38] More robust oxygen-tolerant ATRP was recently developed by means of enzymatic degassing, [39] via light irradiation combined with sodium pyruvate in photoinduced ICAR (PICAR) ATRP, [40,41] use of various photocatalysts which absorb low energy light (including red and NIR) and then regenerate Cu^{I}/L^{+} activators by redox processes or by modulating electrical currents in the presence of sodium pyruvate in *e*ATRP. [42] It is also possible to use oxygen as fuel using dual enzymatic catalysis (glucose oxidase and horseradish peroxidase) [43] or organoboron chemistry. [44] It will be interesting to expand these systems and catalyze ATRP not only using proteins but also nucleic acids that can form more active ATRP complexes or boost some other catalysts with nucleic acids, enabling their detection by amplification with produced polymers. [45].

The development of a billion times more active catalysts than those originally used in the first ATRP systems enabled a very significant reduction of the amount of Cu-based catalysts from ca 1 mol% to 1 ppm, vs monomers. [3] This has been accomplished by using tripodal tetradentate ligand such as tris(2-pyridylmethyl)amine (TPMA) with electron donating p-substituents. [46] Although ATRP catalysis is fairly well understood phenomenologically, a more thorough structure–reactivity and structure-selectivity is needed. Linear free energy relationship (LFER) has been used to identify reaction descriptors that enable the prediction of outcomes and the design o f more effective catalysts. [47].

The values of the activation rate constant, k_{act}, for 107 Cu complex/RX couples in 5 different solvents spanning over 13 orders of magnitude were successfully interpolated using the equation: log kact = sC(I + C + S), where I, C, and S are the initiator, catalyst, and solvent parameters, respectively, and sC is the catalyst-specific sensitivity parameter. Each of these parameters was correlated to relevant descriptors, which included the bond dissociation free energy of RX and its Tolman cone angle θ, the electron affinity of X, the radical stabilization energy, the standard reduction potential of the Cu complex, the polarizability parameter π* of the solvent, and the distortion energy of the complex in its transition state. This set of descriptors establishes the fundamental properties of Cu complexes and RX that determine their reactivity. They need to be considered when designing new systems for atom transfer radical reactions. Then, a multivariate linear regression (MLR) was employed to predict kact values for > 2000 Cu complex/RX pairs, as shown in Scheme 2. [47] Computational chemistry will help to correlate structures of Cu/L complexes, radical or dormant species with their reactivities but also should provide a deeper insight into unique Cu-X bonds and their selectivity. [16] An interesting approach was based on combining N and P-based ligands. [17,48] This could potentially expand the range of transition metal complexes, especially to inexpensive and more benign iron, [49–51] and could also develop efficient organic photocatalysts that would replace transition metals. A deeper understanding of the structure and photophysical and photochemical properties of organic photocatalysts in the ground and excited states, their redox properties, stability, as well as structure of the deactivating species is needed. [52–60] Generally, the organocatalysts, after excitation by UV light, form extremely reducing species with redox potential values $E_{1/2}$ < -2V. Therefore, they can directly reduce dormant species in ATRP. [61] On the other hand, there are many dyes that can be excited by lower energy light: green, red, or even near IR light. However, their redox potentials in the excited state are in the range of −1V, which is not sufficient to reduce alkyl halides but only reduce Cu^{II}/L species. [62,63] Thus, they could be used as ATRP co-catalysts, even at very low (ppm) concentrations, even lower than [Cu/L]. It is interesting to harness lower energy light, which can penetrate through dense media,



Scheme 2. Application of LFER to identify most relevant descriptors affecting activation rate coefficients, covering over 13 orders of magnitude for various alkyl halides, copper complexes and solvents. Reprinted with permission from *J. Am. Chem. Soc.* **2023**, *145*, 21587–21599. Copyright American Chemical Society.

including skin, but also extend the photoexcitation from homogenous to dispersed media such as emulsion. [64,65].

ATRP becomes a green chemical process by significantly reducing the amount of catalysts that could be regenerated, recycled, or efficiently removed but also carried out in water and other benign media with tolerance to air and driven by various external stimuli. [30,66–69].

Other green aspects of ATRP include using monomers and initiators from renewable bio-based resources. [70–72] Polymerization in water has been efficiently carried out under homogeneous conditions (important for the synthesis of bioconjugates and hydrogels) but also in dispersed media such as emulsion, miniemulsion, microemulsion, and even in inverse miniemulsion. [73–78] Special design of surfactants, catalysts, and additives is needed for such systems. Further progress is needed to work under a several liter scale[42] for real commercialization but also on a microscale, on a scale of a few microliters, relevant for chimeras of synthetic polymers with proteins and both DNA or RNA. [79] Here oxygen tolerance is very important as it will allow working in 96-well plates. [62] Concerning other preparative procedures, flow chemistry, [80–82] continuous reactions, including photochemical processes, reactions using large inorganic substrates, and working with gaseous monomers should be developed. In general, processes at solid–liquid, and liquid–liquid interphases will be important. [83–86].

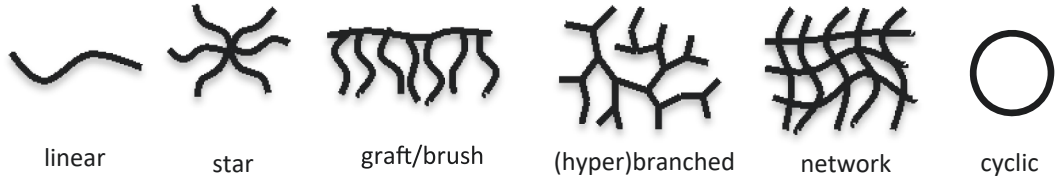
With ever-larger polymer production, exceeding 400 million tons in 2023, it is very important to recycle, reuse or degrade polymers. [87] This is relatively easy for polymers containing heteroatoms in the main chains but very challenging for polymers prepared from vinyl monomers by using radical polymerization such as ATRP. There are some approaches to incorporate degradable segments by using multifunctional initiators for stars or bottlebrushes or combining step-growth processes with ATRP. However, this could lead to sacrificed control over uniformity of polymer chains and loss of some properties. Alternatively, radical ring-opening polymerization provides access to polymers with precisely controlled dimensions and low dispersity and incorporated esters or thioesters in the main chain. [88,89] Another, even more promising approach is to employ depolymerization of polymers back to monomers and repolymerize them again. [90–92] This would offer the highest quality of polymerized materials but has several chemical and energetic limitations. For example, polymethacrylates can be depolymerized back to monomers at rather high temperatures in the range of 450 °C to 500 °C. [87] This significantly exceeds the thermodynamic ceiling temperature, which is around 300 °C for bulk poly(methyl methacrylate), i.e., PMMA or Plexiglas. Recently, depolymerization of PMMA prepared by ATRP has been accomplished at temperatures below 200 °C, offering significant energy savings. [93–95] Moreover, polymeric networks have also been depolymerized back to monomers. [96] Polymer chains are typically unzipped back to monomers in an uncontrolled way, but under appropriate conditions, controlled concurrent depolymerization of all chains is also possible. [97,98] This area should further expand to other types of monomers.

3. Polymers with controlled composition, topology, and functionality

ATRP can precisely control many aspects of macromolecular architecture. [99] It has been successfully applied to the synthesis of uniform polymers with dispersities as low as $D < 1.1$ [100] but also for polymers with designed molecular weight distributions (MWD), with symmetrical or skewed distributions, with multimodal distributions with a designed low MW plasticizing fraction and with reinforcing high MW chains. [101–103] The full potential of the effect of MWD on properties of materials based on linear chains has not yet been fully explored but even more attractive will be an investigation of hybrid materials with grafted chains with designed MWD. [104] Atom transfer radical addition was the inspiration and the origin of ATRP. It was based on adding one or a few precisely controlled vinyl compounds in a cascade fashion, optionally followed by cyclization. [2,105] The other extreme case is a synthesis of polymers with very high molecular weight in the range of millions. [106–110] They have unique properties and very high viscosities even at very low concentrations, with potentially interesting applications in biological systems but also in lubrication and drag-reducing systems. Thus, the synthesis and characterization of polymers with molar masses exceeding 10 million are very interesting. This will require the development of new and selective catalytic systems with the suppression of chain-breaking reactions (transfer and termination).

ATRP provides easy access to controlling three elements of molecular architecture: chain topology, composition, and functionality. In addition to traditional linear chains, ATRP has been successfully employed to introduce branching, as shown in Scheme 3.

For example, multifunctional initiators at the localized core give access to multiarm stars with interesting functionalities at the arm terminal units. [111] Alternatively, growing ends of linear macroinitiators can be fused together with a crosslinker to form a similar set of stars. [112] Crosslinker can be diluted to make the core less dense and can also be loaded with a dye or other functionality. The core can be built with a



Scheme 3. Examples of polymers with controlled topologies prepared by ATRP.

cleavable crosslinker and degrade upon the addition of a specific chemical, including acid/base or a reducing agent for e. g., disulfide linkers. [113–115] Cores can also be charged. Such cationic cores can form complexes with polyanions, including nucleic acid, and can be used for their delivery. [116,117] This has been applied to siRNA but also DNA and RNA delivery systems. Branching can be extended to grafting-from and grafting-onto linear chains. It is possible to control graft density and switch from loose combs to dense bottlebrush structures. They present a unique class of materials with supersoft properties with bulk moduli in the range of less than 1 kPa value, similar to hydrogels, but they will never dry and lose their properties because they are diluted by 99 % of soft short side chains covalently linked to the backbone rather than 99 % of water like hydrogels. [118] Such materials can be designed to mimic the mechanical properties of human tissue, veins, brain, lungs, and even fat tissue. [119–123] These giant bottlebrushes can reach molar masses exceeding 10 million Da.

Dendrimers show beautiful regular branching structures but are very difficult to make, requiring complicated protection-deprotection strategies. Recent advances in ATRP provide access to controlled branching using inimers and inibramers. The former consists of ATRP *init*iator linker with a polymerizable mono*mer*. [121] Their homopolymerization provides hyperbranched polymers but with high dispersity due to a unique combination of step-growth and chain-growth processes. [124] A clever way to suppress the step growth process and promote a chain growth process is to either employ compartmentalization or prevent reaction between monomers[124,125]. Another approach to prevent the spontaneous generation of new chains from inimer and allow the new chains generation only after their incorporation to a growing chain is to use inibramers, compounds that contain ATRP inactive halogen atoms bound strongly to polymerizable double bonds which become activated only after incorporation to polymer chains providing enhanced control of molecular architecture. [126–128].

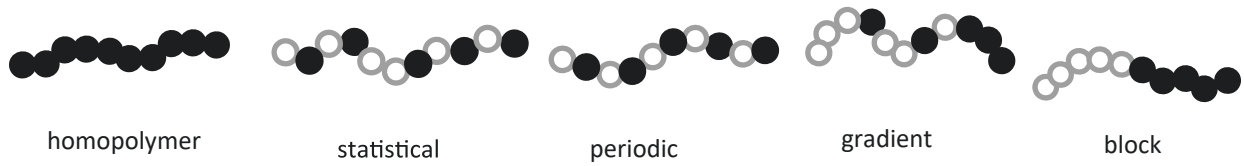
The addition of crosslinker after a sufficiently long macroinitiator is formed results in star polymers. However, the same amount of crosslinker added at the beginning will lead to insoluble networks. The structure of networks prepared by controlled radical polymerization differs significantly from those made by conventional free radical polymerization. The latter is very heterogeneous, while the former is much more uniform due to the delayed gelation point. [129,130] In ATRP, primary chains start growing, then form progressively the branched structure, and reach the gel point when approximately one crosslinker is incorporated into every primary chain. It is possible to design even more uniform networks by linking star polymers. In ATRP, the gel point is defined by the stoichiometry between the converted crosslinker and the introduced initiator if initiation is fast. [131,132] It is also affected by the relative exchange rate between active and dormant species to the propagation rate. It can be finely tuned by the amount of deactivator and by the relative reactivities of monomers and crosslinkers. [132] It is possible to incorporate functional groups into networks that can initiate the growth of additional chains in structurally tailored engineered macromolecular (STEM) gels, offering the possibility of additive but also subtractive manufacturing. [133] These systems can encompass two or more interpenetrating networks of different properties and miscibility. These gels can grow, expand, and also transform into other shapes. [134] They can self-heal and self-repair. Finally, controlled polymerization provides access to cyclic polymers. [135–137] The most efficient route is based on end-to-end coupling, using "click" reactions or radical cross-termination but also ring expansion. It will be interesting to prepare functional organic nanoparticles by miniemulsion or microemulsion polymerization of not only crosslinker but also crosslinker with inimers and prepare nanoparticles with large number of ATRP active Br-initiators on the surface, mimicking materials based on functionalized silica nanoparticles. This will open avenues to organic nanoparticles with dense polymeric brushes. [125,138].

The second element of macromolecular architecture involves control of the composition of copolymers along the backbone as shown in Scheme 4.

One of the most attractive structures are block copolymers which phase-separate on the scale of ca. 10–30 nm. Very incompatible blocks can lead to sub-10 nm domains, attractive for microelectronics. [139,140] However, block copolymers based on bottlebrushes form regular domains of $>$ 100 nm size and provide interesting refraction patterns as a function of block size and their refractive indices. [141,142] Amphiphilic block copolymers can self-organize in dilute solution into micelles, worms, or vesicles. Using polymerization-induced self-assembly (PISA) such morphologies can also be produced at much more concentrated solutions. [143–145] It is interesting to extend binary diblock copolymers to tri, tetra an even longer multiblock copolymers. [146,147] It is, however, difficult to predict and control phase separation in such multicomponent systems and mesoscale modeling is necessary to aid synthetic design for such systems.

ATRP of comonomers of similar reactivities, such as various acrylates or various methacrylates, provides access to truly statistical copolymers. However, copolymerization of more reactive methacrylates with less reactive acrylates generates gradient copolymers with a progressive increase of the content of polyacrylates along the chain length. Such gradient copolymers have very different properties than statistical and block copolymers. They are characterized by a very broad glass transition temperature, higher critical micellar concentration than block copolymers or excellent surfactant properties. [148] It is possible to prepare spontaneous gradient copolymers using monomers of different reactivity but also forced gradient copolymers by feeding one comonomer if they have the same reactivity. Appropriate feeding of a more active monomer to the less active one can convert the gradient to the statistical copolymer. [149–151] The changes to the composition for gradient and block copolymers typically rely on segments of $>$ 10 nm scale.

Inspired by sequence control in natural products such as proteins and nucleic acids, there have been many attempts to control sequence in synthetic polymers. [152,153] It is possible to use this approach for trimers or tetramers as in cascade-based ATRA systems, but then one can link such oligomers by a step growth process resulting in high dispersity macromolecules. [154] A more powerful approach is possible for alternating copolymers, this requires very low reactivity ratios, meaning that cross-propagation should be much faster than homopropagation. There are a few comonomer pairs such as styrene and maleic anhydride or maleimide, or the potential use of reactive monomers that cannot homopolymerize for thermodynamic reasons due to very bulky substituents preventing their homopropagation. [155,156] It is also possible to boost the reactivity of comonomer by special additives such as Lewis acids complexing methacrylates in their copolymerization with



Scheme 4. Examples of copolymers with controlled compositions prepared by ATRP.

styrenes. This provided alternating copolymers with up to 90 % alternating dyads. [157] Statistical gradient and alternating copolymers based on methyl methacrylate and butyl acrylate of the same molecular weight and the same overall composition had very different mechanical and self-healing properties. [158] Alternating copolymers have the narrowest glass transition temperature range; they are also the fastest to recover their original properties after damage and quickly self-heal but have the lowest toughness, lowest modulus, and lowest ultimate elongation. Gradient copolymers have the broadest glass transition and require several times longer recovery time than alternating copolymers but are characterized by the best mechanical properties, toughness, modulus, and elongation at break. This demonstrates how composition can affect materials' properties. [159–162].

ATRP offers several possibilities to incorporate functionality into polymer chains, as shown in Scheme 5. [163] The most obvious is the use of monomers with functional groups tolerant in ATRP, such as hydroxy groups, amino groups, or acidic groups. However, the latter may protonate ligands and can also displace halogen atoms from the chain ends. Thus, a careful selection of ligands for Cu complexes, pH, and other parameters is needed. [164] Alternatively, it is possible to use protected groups, e.g., t-butyl acrylate instead of acrylic acid, and deprotect it after polymerization. It is also possible to incorporate functional groups at a specific position of polymer chains, typically at α or ω chain ends, using either functional initiators or replacing halogen at the chain end by nucleophilic substitution, the addition of only one less reactive monomer, and other transformation chemistry. It is also possible to use functional two-directional initiators and place functionality in the center of the chain, using, e.g., disulfide di α -bromoisobutyrate initiators. [165,166] These terminal functional groups can be used to make block copolymers by linking chain ends but also by transformation to other polymerization mechanisms and switching from ATRP to anionic, cationic ring-opening polymerization, etc. [166,167] Another possibility is to transform chain ends of polymers prepared by other mechanism to ATRP initiators and prepare block copolymers consisting of polyolefins and polar polyacrylates. [168–170].

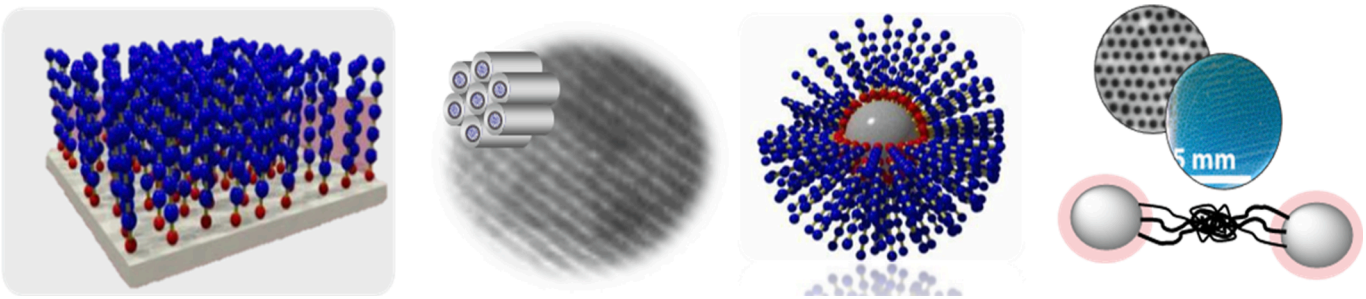
There are many new functional monomers which can be incorporated via e.g. radical ring-opening polymerization but also monomers that can be activated by light and induce photodegradation or even photodepolymerization. [89,171–176].

Finally, the most challenging element of macromolecular architecture is controlled tacticity. Since radicals are sp2 hybridized, they generally lead to atactic copolymers, in contrast to coordination polymerization. A few examples of controlled tacticity are based on the polymerization of acrylamides in the presence of lanthanides such as Y $(OTf)_3$ and Yb$(OTf)_3$. [177] These salts coordinate preferentially to the penultimate and the last unit and force them to the meso configuration. The incoming monomer fixes the meso dyad and generates isotactic polyacrylamide with > 90 % meso dyad with a catalytic salt amount (5 %). Interestingly, the addition of the complexing salt after 50 % acrylamide conversion in ATRP converted atactic to isotactic placement and produced atactic-isotactic stereoblock copolymers. [178] More recent studies enhanced the isotactic content by the auxiliary placement of lanthanide within the bimetallic catalysts. [179] It will be interesting to explore the effect of external fields such as pressure and high electric field as well as a confined environment on tacticity, for example during the growth of dense brushes from various substrates. [180,181].

4. Organic-inorganic hybrid materials

ATRP has been successfully used to synthesize hybris materials by linking well-defined synthetic polymers with inorganic substrates to form various nanocomposites, as shown in Scheme 6. [5,182,183] The organic–inorganic hybrids were prepared using several approaches: (i) functionalization of inorganic surfaces with ATRP initiators followed by grafting from such modified surfaces, (ii) attachment of end-functional polymers to inorganic surfaces, (iii) ligand exchange [184,185] and (iv) templating methods by generating nanosize inorganics in preorganized segmented copolymers such as stars or cylindrical bottlebrushes. [186–189] Inorganic substrates comprise flat wafers and other planar substrates, as well as various beads and nanoparticles, such as silica, titania, ZnO, $BaTiO_3$, magnetic Fe_3O_4, pigments, or Au. [184,190,191] Nanoparticles with densely grafted polymer brushes had excellent dispersibility in either organic solvents or water, forming stable dispersions and preventing their aggregation. Bulk properties showed enhanced toughness, moduli, and tunable self-healing properties. Depending on grafting density, nanoparticles can form regular bcc or fcc morphology but, at lower graft density, can self-organize into strings or controlled small aggregates. [192,193] This provides the possibility to fine-tune mechanical, thermal, and transport properties. Initially, preparation of such hybrids required anaerobic conditions and a high concentration of Cu-based catalysts, but new low ppm Cu catalytic systems with activators regeneration introduced oxygen tolerance and opened "ATRP-for everyone" conditions with easily functionalized systems with chemical reducing agents, light, and even Cu or Zn plates. [194–200] Light offers an additional possibility of spatial control and patterning. This has been successfully done on a small scale but also on 10x10 cm wafers and even much larger surfaces as well as roll-to-roll procedures. [84–86,201,202] An interesting possibility of generating gradients via eATRP with tilted electrode were reported. [203] Use of nanocomposites by grafting copolymers from silica nanoparticles provided very strong improvement of mechanical properties and strong creep reduction in self-healing materials. They were also successfully used for fabrication of shape-memory materials. [150,151,159] Grafting well defined (co)polymers from regular large silica nanoparticles (120

Scheme 5. Examples of polymers with controlled functionalities prepared by ATRP.



Scheme 6. Examples of organic -inorganic hybrids prepared by ATRP using grafting from flat wafers, from concave cylindrical structures and convex nanoparticles as well as photonic crystals with enhanced mechanical properties due to chain entanglements of polymeric brushes.

nm) provided interesting photonic materials with strong blue iridescent colors based on periodic arrangements of materials with different refractive properties. It will be interesting to employ self-healing copolymers to improve the mechanical properties of such photonic paints, inks, and other materials. [204].

Some nanostructured polymers and hybrids prepared by ATRP are successful components for membranes or batteries. [205–208] Grafting ATRP polymers from or onto liquid metals such as eutectic Ga-In alloys provides attractive materials for soft robotics with excellent thermomechanical and conductive properties. [209–213].

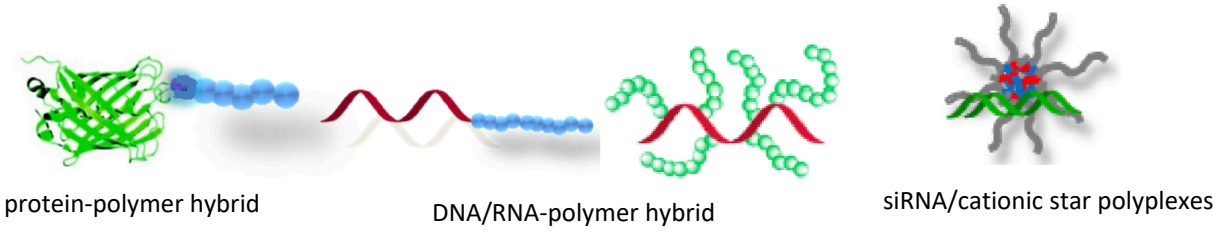
5. Hybrids with proteins and nucleic acids

Another attractive group of hybrid materials comprises bioconjugates prepared by covalent linking polymers to nucleic acids, proteins, and carbohydrates as shown in Scheme 7. [6] The latter hybrids were prepared by, e.g., esterification of hydroxy groups in (nano) cellulose with ATRP initiators and grafting various well-defined side chains in a bottle-brush function. [186,214] Other natural products, such as cyclodextranes or tannic acid, were decorated with ATRP initiators and formed stars with degradable cores. [189,215–217].

Proteins were linked to polymer chains by the grafting-onto method using end-functional polymers and complementary functional groups on proteins (typically lysins or cysteines). [218] This could be more specifically carried out with end-functional amino or carboxylic acids. [219–221] More dense grafting was achieved by using grafting-from procedures after the conversion of surface lysine groups into Br-amido ATRP initiators. Because lysine groups have different reactivity (pKa and steric accessibility), it is possible to control the attachment of initiators using active and “dummy” initiating sites. [222] Then, the polymerization of various monomers from the protein surface provided protein-polymer hybrids with tolerance to harsh conditions (high temperature, pH) that were used as powerful catalysts also in organic solvents. [223] Even more interesting is to modify proteins and use them for therapeutic purposes. [224–230] Such bioconjugates preserve their activity but also increase circulation time and reduce immunogenic response. [226,231–233] An interesting opportunity is to conjugate antibodies with polymers carrying drugs. It is possible to use multifunctional bottlebrushes with tens or even hundreds of cleavable drugs attached to one antibody. [234–236] ATRP offers the possibility to grow not only linear but also branched chains and various responsive polymers with lower or upper critical solution temperature. [6].

Another class of bioconjugates was prepared by linking polymers to nucleic acids, both DNA and RNA. This was accomplished by using a classical solid-state synthesis of nucleic acids followed by a final addition of phosphoramidite with ATRP initiation site to prepare block copolymers. [237] Recent development is based on using serinol-based phosphoramidites with ATRP initiating sites, which were incorporated at any specific position in DNA or RNA. [238] This opened up the possibility of forming graft copolymers and multisegmented block copolymers. Another interesting opportunity for bioconjugation of RNA is by acylation of OH-groups with either ATRP initiators or polymerizable methacrylate or methacrylamide functionalities. [239,240] This approach was applied not only to the expensive synthetic RNA but also to the biomass-derived RNA for the preparation of selectively degradable hydrogels. [241] Strong interactions of DNA with some fluorescent dyes can be explored for new selective photocatalytic systems. Also, surface initiated ATRP could be used for amplified electrochemical detection of nucleic acids. [242] In a similar way, hemazoin-catalyzed precipitation ATRP was used as a successful assay for malaria detection. [243] Negatively charged nucleic acids interact with positively charged (toxic) polymers. This was used for delivering siRNA through cell membranes by the formation of complexes with stars comprising cationically charged degradable cores. The strength of the interactions and release of RNA was fine-tuned by the architecture of polymeric arms emanating from the star core. [117,244] The attachment of ATRP initiators to cholesterol-like hydrophobic units offers a possibility of placement of these initiators at a cell membrane and growing polymers from the cell surface. [245,246] A similar approach was also applied to various short-shelf lifetime vesicles, such as exosomes reaching a strongly extended shelf lifetime and stability against nucleases. [247,248].

Thus, ATRP can be applied for the modification of many natural products to enhance their performance and produce new-generation drugs or delivery systems. Modification of solid surfaces with polymers by ATRP can dramatically affect their antifouling or antibacterial properties[249–251] or lubricity relevant in joints. [252–258] On the other hand, precise design and control of molecular architecture can generate materials with mechanical properties closely resembling bone or tissue with properties matching hard cartilage, soft brain, or even



Scheme 7. Examples of bioconjugates prepared by ATRP.

softer fat tissue. [119,120].

6. Commercial aspects

Cu-based ATRP was first reported in 1995. [259] Carnegie Mellon University (CMU) has licensed ATRP technology 18 times, and commercial production of ATRP polymers started in the US, Japan, and Europe in 2004. At CMU, 61 companies have been members of ATRP and CRP Consortia aimed at dissemination of fundamentals and know-how of ATRP. Although ATRP has been used at nearly every synthetic laboratory in academia or industry, a large-scale production has not yet been accomplished at the anticipated level[260–262] in spite of the significant research progress reached by reducing Cu catalyst concentration to ppm level, carrying out ATRP in aqueous media and in open air, [62] ATRP is mostly employed in the synthesis of high-value products such as cosmetics, dispersants, sealants, etc. It can be expected that new nanocomposites and especially bioconjugates will be prepared by employing ATRP to produce the next generation of various advanced materials.

CRediT authorship contribution statement

Krzysztof Matyjaszewski: Writing – review & editing, Writing – original draft, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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