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Polymerization of Cumulated Bonds: Isocyanates, Allenes, and Ketenes as Monomers

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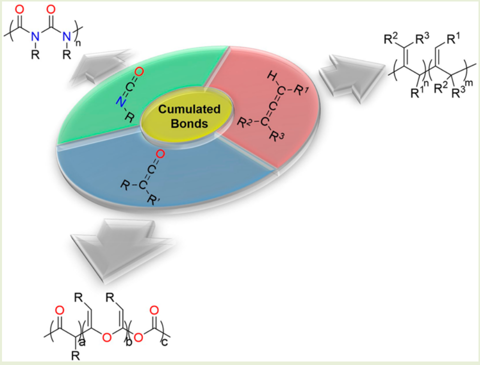

ABSTRACT: Polymer chemistry offers exciting opportunities to tailor the properties of soft materials through control of the composition of the polymers and their interaction with each other, additives, and surfaces. Ongoing advances in the synthesis of polymeric materials demonstrate the drive for materials with tailored properties for enhanced performance in the next generation of materials and devices. One class of small molecules that can serve as monomers in chain growth polymerization are cumulated double bonds of the general form $X{=}Y{=}Z$. The three most common classes of these molecules are isocyanates ($N{=}C{=}O$), allenes ($C{=}C{=}C$), and ketenes ($C{=}C{=}O$), each of which has been explored as monomers under a variety of conditions. The orthogonality of the two pi bonds of the cumulated double bonds (i.e., lack of conjugation) enables the formation of different polymer backbones from a single monomer, provided the regioreactivity is controlled. This Viewpoint outlines the use of these three cumulated double bonds as monomers, illustrating success and current limitations to established polymerization methods. We then provide an outlook to the future of cumulated double bonds as monomers for the generation of tailored polymer compositions.

Polymers impact nearly every facet of modern life, keeping food fresh, enabling life-saving technologies, providing safer transportation, and so on. The field of polymer science continues to evolve with advances in synthetic protocols and methods,[1−5] polymer architectures and molecular weights,[6−11] and polymer processing techniques.[12−18] The chemistry of polymers dictates intra- and interchain interactions that give rise to bulk properties, ultimately defining toughness, thermal stability, degradability, and so on, and thus applications. The chemistry of a polymer also determines opportunities for postpolymerization modification and compatibilization of a polymer with additives such as other polymers, particles, and surfaces.[19−23] Recent and ongoing areas of research in the field center on recyclability and self-healing,[24−27] upcycling of commodity polymers,[28−30] production of polymers from sustainable sources,[31−35] and realizing extreme molecular weights and architectures, among others.

Polymers are synthesized by step growth or chain growth polymerization methods;[36,37] the former makes use of difunctional small molecules, and the latter makes use of monomers with a unit of unsaturation (e.g., a double bond or ring). Provided appropriate relative rates of initiation and propagation and the absence of irreversible termination reactions, chain growth polymerizations can be used to control end group identity and polymer molecular weight while maintaining low molecular weight distributions. Many advances have been made in controlled chain growth polymerization techniques of radical polymerization (RP),[38] ring opening polymerization (ROP),[39] and ring opening metathesis polymerization (ROMP).[40] Less common controlled polymerization techniques include group transfer polymerization (GTP) and Grignard metathesis polymerization (GRIM).[41−43] In RP, common monomers are terminal carbon−carbon double bonds that produce hydrocarbon backbone with substituents on every other carbon atom. Alternatively, in ROP, common monomers are cyclic molecules containing one or more polar bonds, such as an ester or ether, that produce a linear polymer backbone that has the same functionality (i.e., cyclic ester produces a linear polyester). For most common monomers that undergo chain growth polymerizations, only one mode of reactivity is possible, that is, only one polymer backbone can be produced. However, much recent and ongoing work addresses advances in catalyst performance, tolerance to additives and impurities, and monomer scope.[44−58]

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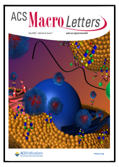

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One class of functional groups suitable for chain growth polymerization are cumulated double bonds of the general form $X{=}Y{=}Z$, in which the central atom is carbon. Figure 1A shows the three most common cumulated double bonds, which are isoelectronic with each other: isocyanate ($O{=}C{=}N$), allene ($C{=}C{=}C$), and ketene ($O{=}C{=}C$). The double bonds share a central sp-hybridized carbon atom, and thus, the neighboring pi bonds are not conjugated and are orthogonal to each other (Figure 1B). Many isocyanate containing compounds are commercially available; the most common methods for their synthesis are reaction of amines/amides with oxalyl chloride, reaction of olefins/halides/acid anhydrides with isocyanic acid, Curtius rearrangements, and phosgenation of amines, the latter of which is used commercially.[55] A handful of allenes are also commercially available, yet they are commonly synthesized as needed due to cost effectiveness. Methods to synthesize allenes include various isomerization reactions and metal mediated/catalyzed reactions of alkynes.[56−58] Alternatively, ketenes are almost always prepared and used immediately; preparation methods include pyrolysis of acids,[59,60] esters,[61] ketones,[62,63] acetic anhydrides,[64,65] and malonic anhydrides,[66] as well as photochemical methods.[67,68] The orthogonality of the double bonds in cumulated systems provides an exciting opportunity to access different polymer backbones from a single monomer, provided the regioreactivity is controlled (Figure 1C).

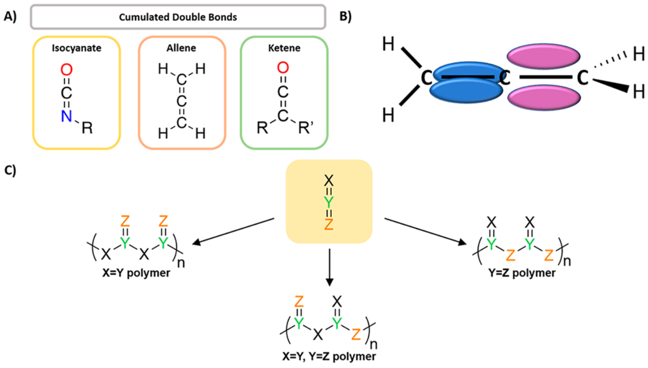

Figure 1. (A) Cumulated double bonds: isocyanate, allene, and ketene; (B) Illustration of the orthogonality of pi bonds in cumulated systems, using allene as the representative molecule; and (C) Illustration of the different regioreactivity of cumulated double bonds as monomers and polymers produced.

The purpose of this Viewpoint is to present an overview of cumulated double bonds as monomers in chain growth polymerizations and to provide a perspective and outlook on the opportunities of these systems. We note that Hawker and co-workers provided a thorough review of the use of ketenes in polymer chemistry in 2013,[69] focusing on the use of ketenes for cross-linking and postpolymerization modification. Of cumulated double bonds as monomers, isocyanates are the most developed, with both anionic and transition metal catalyzed coordination polymerizations successfully producing 1-nylons. The properties of polyisocyanates have also been vetted; they can be optically active, degradable (or depolymerizable), and have relatively stiff polymer chain conformation. Alternatively, allene monomers of varying substitution have been polymerized using transition metal and rare earth metal catalysts, though the application and properties of these polymers have not been established. Despite the role they played in the development of the concept of macromonomers (see below),[70] ketenes are relatively underdeveloped as monomers; this likely has to do with the difficulty in handling the monomers and their propensity to self-dimerize. We conclude this Viewpoint with a highlight of the limitations of the current systems and an outlook for the use of cumulated double bonds as monomers in chain growth polymerizations.

Isocyanates: Isocyanates are a highly reactive class of organic compounds containing cumulative double bonds, with the formula $R{-}N{=}C{=}O$. The reactivity of isocyanates is governed by the electron deficient nature of the central carbon atom which is susceptible to attack by various nucleophiles, whereas the oxygen, and less commonly the nitrogen, react with electrophiles. Isocyanates undergo reaction at the carbon atom with compounds, such as alcohols, amines, water, mercaptans, and carboxylic acids.[55] These reactions result in various carbonyl-containing functional groups, used in the synthesis of both small molecules and polymers. Aromatic isocyanates self-react to form dimers (uretidenediones) at low temperatures and trimers (isocyanurates) at high temperatures in the presence of acidic or basic catalysts (Figure 2).[71,72]

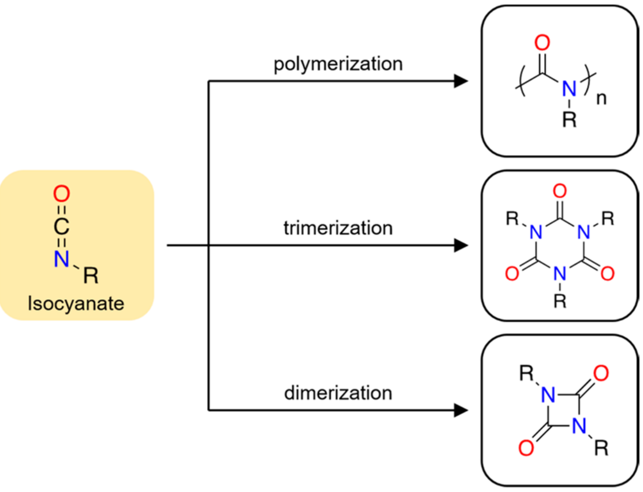

Figure 2. Products that result from polymerization, trimerization, and dimerization of isocyanates.

In the discussion of isocyanates as monomers, polyurea and polyurethanes come to mind, including many that are prepared on an industrial scale. These well-known polymers are produced by step growth polymerization of diisocyanates and diamines or diols, and the products find use as coatings, adhesives, foams, and sealants.[71,73] Bayer et al. first discovered polyurea in 1937 by reacting an aliphatic diisocyanate and diamine, and later, polyurethane was obtained by reaction of an aliphatic diisocyanate and glycol. Many difunctional isocyanates such as toluene diisocyanate (TDI) and hexamethylene diisocyanate (HDI), as well as polyfunctional isocyanates such as TDI-trimethylolpropane and the isocyanurate trimer of TDI are widely used in the polymer industry.[74] In addition to bulk and foamed polymers, polyurea capsules can be prepared by interfacial polymerization in emulsions.[75−77] Alternative to the step growth polymerization of multifunctional isocyanates and multifunctional amines or alcohols, the isocyanate functional group can be used as a monomer in chain growth polymerizations, yielding poly-

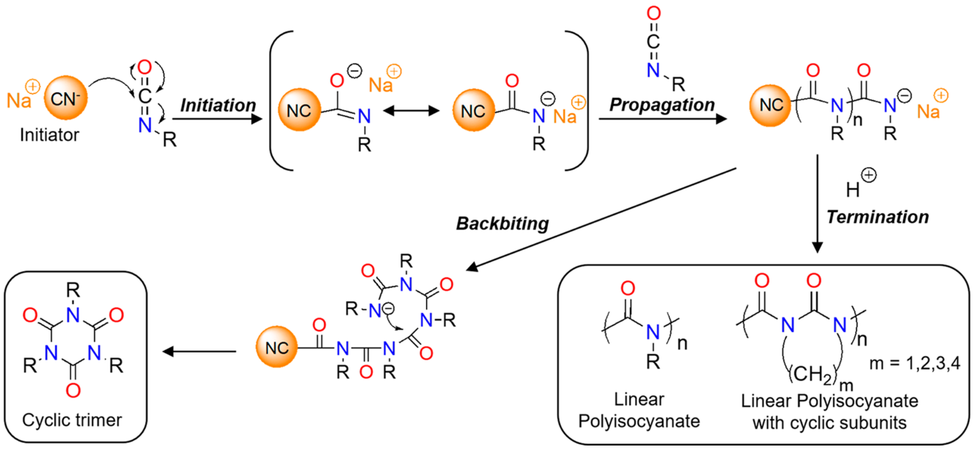

Figure 3. Proposed mechanism for anionic polymerization of isocyanate, including backbiting to give cyclic trimer. Inset on bottom right shows difference between linear polyisocyanates and those containing cyclic units in the polymer backbone.

isocyanates with a backbone of −N(R)C(O)− repeat units in which the nitrogen atom bears a pendant R group (referred to as *N*-substituted 1-nylons). In the early development of the chain growth polymerization of isocyanates, intramolecular backbiting limited product molecular weight and led to the production of cyclic trimers.[72,78,79]

Uncontrolled anionic polymerization of isocyanates: The anionic polymerization of a monofunctional isocyanate was first reported by Shashoua et al. in 1959.[72,78] Polymerization of both aliphatic (ethyl, propyl, *n*-heptyl) and aromatic (phenyl, naphthyl) isocyanates was realized using sodium cyanide as the initiator in polar solvents such as *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) at low temperatures (−20 to −100 °C). In addition to sodium salt initiators, alkyl lithium initiators such as ethyl lithium have been used in nonpolar solvents such as toluene and benzene.[80] The proposed mechanism for initiation is attack of an anion (e.g., cyanide) at the electrophilic carbon of the isocyanate, resulting in the formation of an amidate anion with negative charge delocalized across the nitrogen and oxygen atoms. Propagation through the nitrogen atom is nearly always observed, attributed to the difference in bond strengths (C═O is 358 kJ/mol, C═N is 305 kJ/mol). A linear polymer chain is formed by adding additional monomers onto the growing chain end until termination, commonly by protonation (Figure 3). Shashoua et al. used light scattering to determine the product molecular weight; 1-nylons derived from *n*-heptyl isocyanate had degree of polymerization of up to 450, yielding polymers with M_w = 69 kDa.[78] In general, polymer yield was limited at low temperatures (<−50 °C) because of poor solubility, but higher temperatures (>−20 °C) led to intrachain backbiting. As such, the products of these reactions had high dispersity and cyclic trimer byproducts were observed.

Other studies evaluated the limitations and possibilities of isocyanate functionalization on polymerizations. Monomer scope is limited by the steric demands of the substituent on the nitrogen: isocyanates with a methylene unit attached to nitrogen were readily polymerizable, however isocyanates with a methine or ortho-substituted aromatic moiety could not be polymerized. These differences in reactivity allowed for the selective polymerization of unhindered isocyanates in the presence of hindered isocyanates,[78] the latter of which could be used for postpolymerization modification. Further, linear polymers with recurring cyclic units in the main chain were accessed by the anionic polymerization of diisocyanates containing 1, 2, 3, and 4 methylene units between the functionalities. Alternating intermolecular and intramolecular propagation was observed,[81−83] illustrating the conversion of acyclic monomers into polymers containing mono/polycycles in the backbone. This difference in structure led to distinct melting temperatures compared to the linear counterparts:[83] polymers with rings in the backbone had higher melting temperatures than those that were linear (>300 °C vs <250 °C).[78,81]

Controlled anionic polymerization of isocyanates: Controlled anionic polymerization of isocyanates was realized by leveraging bulky additives which sterically protect the propagating anion and prevent backbiting and cyclotrimerization, thereby enabling polymers with controlled molecular weights and low dispersity (Figure 4A). The first living anionic polymerization of isocyanates was reported by Lee et al. in 1999.[84] In their work, 3-(triethoxysilyl)propyl isocyanate was polymerized using sodium naphthalenide as the initiator in the presence of a crown ether (15-crown-5). The resulting cation-ligand complex increased the rate of polymerization and led to 96% yield of polymer at −98 °C after only 1 min. The sodium ion trapped in the crown ether allowed rapid dissociation of the ion pair (anion of polymer chain end and sodium cation) and led to fast propagation as well as suppression of backbiting due to the extended chain conformation caused by the bulky cation complex associating with the amidate. The living character of the polymerization was confirmed by preparing block copolymers with octyl isocyanate.[84,85] An alternative approach to the controlled anionic polymerization of isocyanates by steric hindrance is addition of sodium tetraphenylborate ($NaBPh_4$), which contains a non-nucleophilic anion.[86−88] This additive interacts with the amidate ion (as initiated by sodium naphthalenide), thereby limiting dissociation of the ion pair in polar solvents. Although the polymerization rate and polymer yield were slightly lower (89% in 10 min), the stability of the ion pair formed between $NaBPh_4$ and the propagating amidate ions prevented irreversible termination.[86] Lastly, dual-functional initiators have been used to achieve controlled anionic polymerization of isocyanates; specifically, sodium benzanilide, sodium deoxybenzoin, and sodium dipheylmethanolate have been used, serving as both initiators and chain-end protectors (Figure 4B). In these systems, only a portion of the anion

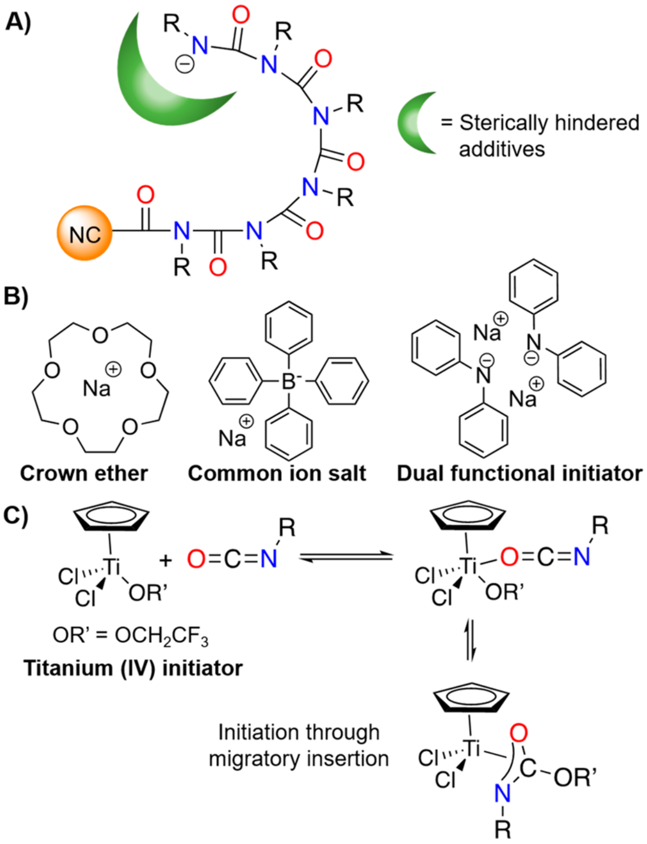

Figure 4. (A) Prevention of backbiting by different sterically hindered additives in controlled anion polymerization of isocyanates; (B) Examples of additives: crown ether, common ion salt, and dual functional initiator; and (C) Titanium(IV) initiators used in coordination polymerization.

initiates, with the remainder clustering around the growing chain end and preventing backbiting reactions.[89−91] Recently, Jang et al. utilized sodium diphenylamide (NaDPA), a robust chain-end protector as initiator in the polymerization of *n*-hexyl isocyanate. Initiator-transfer anionic polymerization with NaDPA in the presence of $NaBPh_4$ resulted in polyisocyanates with an expanded range of molecular weights (M_n = 6.09−47.8 kDa) and low dispersity ($Đ$ = 1.07−1.16).[92]

Transition metal catalyzed coordination polymerization of isocyanates: Transition metal catalyzed coordination polymerizations have been used to exhibit excellent control over isocyanate polymerizations and copolymerizations at room temperature. In 1991, Patten et al. first demonstrated that titanium(IV) catalysts can quantitatively polymerize alkyl isocyanates (*n*-hexyl) at room temperature without the formation of cyclic trimer. $TiCl_3(OCH_2CF_3)$ and $TiCl_3(OCH_2CF_3)(THF)_2$ were initially used as the initiators and the living nature of the polymerization was confirmed by controlled molecular weights (M_n = 42−47 kDa) and formation of block copolymers with the same or different aliphatic isocyanates (total M_n = 119−193 kDa, $Đ$ = 1.1−1.3).[93] However, the polymerization of isocyanates using $TiCl_3(OCH_2CF_3)$ was unsuccessful in the presence of donor solvents or monomers bearing donor groups such as 2-isocyanatoethyl methacrylate.[94] Thereafter, many Ti complexes of general form $CpTiCl_2X$ were developed, where Cp = η^5-cyclopentadiene and X = OCH_2CF_3, $N(CH_3)_2$, and CH_3 groups, and their living behavior was studied by kinetic and mechanistic investigations.[94,95] These Ti complexes showed similar initiation profiles and enabled polymerization in the presence of donor solvents and donor groups, attributed to the lower Lewis acidity of the Ti metal centers compared to $TiCl_3(OCH_2CF_3)$ and $TiCl_3(OCH_2CF_3)(THF)_2$ based on more electron donating and sterically bulkier Cp ligand.[95] Most isocyanates can be polymerized with these catalysts with the exception of sterically bulky substituents (secondary or tertiary alkyl chains) or aromatic isocyanates.[95] According to the proposed mechanism, initiation occurred through the migratory insertion of alkoxide from Ti to the carbon of the isocyanate to form a titanium-amidate species that propagates (Figure 4C), ultimately terminating by protonation.[96] Thus, the alkoxide group of the catalyst becomes the chain end functionality. Hoff and co-workers further developed bimetallic and trimetallic Ti complexes as initiators to synthesize flexible polymer segments between the rigid polyisocyanates.[96] Diblock and triblock copolymers, “once-broken worms” polymers, well-defined three-armed star polymers and cyclopolymers were prepared.[96−99]

Properties of polyisocyanates: Polyisocyanates are rod-like polymers showing distinct, stable helical conformation in solution and in the solid state due to the rigidity of the amide unit.[80,100] Therefore, these polymers can serve as simple models to mimic the secondary structure of proteins and have also been studied as optical switches, chiral recognition structures, and liquid crystal materials.[101−105] Certain polyisocyanates display liquid crystal behavior in concentrated solutions at ambient temperatures or in bulk at elevated temperatures.[106] These mesogenic polymers can be categorized in two groups: aliphatic polyisocyanates having short alkyl chains that are soluble enough to make concentrated polymer solutions, but do not have strong interchain interactions, and aryl polyisocyanates in which the aromatic group is directly attached to the nitrogen or separated by two methylene units.[106]

Poly(*d*-β-phenylpropyl isocyanate) was the first optically active polyisocyanate reported;[100] this polymer has a negative optical rotation, opposite the sign of its monomer, demonstrating the distinct opportunities to alter properties in going from the molecular to the macromolecular scale. This optically active polymer was insoluble in most organic solvents, except chloroform, and showed sharp peaks in ^1H NMR spectrum, unlike optically inactive polymers. Circular dichroism (CD) studies of optically active polymer compared to the model compound (*d*-*N*,*N*-diacetyl-β-phenylpropylamine) indicated the importance of the dissymmetry of polymer backbone and the aromatic side chain. Based on these data, the authors confirmed that the optically active polymer possesses a preferred confirmation (helical) in chloroform.[100]

With the discovery of anionic polymerization of isocyanates, Shashoua et al. also found that polyisocyanates are depolymerizable. When dissolved in DMF, *p*-methoxyphenyl 1-nylon depolymerizes overnight at room temperature in the presence of a catalytic amount of sodium cyanide. In addition, ethyl 1-nylon and *n*-butyl 1-nylon degrade to form trimers when films are heated to their melting temperatures.[78] Iwakura et al. further investigated the degradation of aliphatic and aromatic polyisocyanates and found that these polymers readily depolymerize in the presence of di-*n*-butylamine. The proposed mechanism involved abstraction of the proton from the polymer chain end, followed by depolymerization, with the rate being higher for polymers with aromatic versus aliphatic substituents. Depending on the electronic properties of the substituent in aromatic polyisocyanates, different products form: an electron-withdrawing substituent (*p*-chlorophenyl) favors formation of isocyanates (i.e., monomers), whereas an electron-donating substituent (*p*-methoxyphenyl) favors formation of trimers through intrachain backbiting. These products further confirmed that the polymer chain is exclusively composed of uniform repeating units.[107]

Allenes: Allenes are a class of molecules with the form $R_2C{=}C{=}CR_2$, in which the R groups can be hydrogen, alkyl, aryl, or alkoxy groups (Figure 5). They exhibit a wide range of reactivity due to the high degree of unsaturation, polarizability of π-bond, and geometry; they readily undergo electrophilic additions, cyclization reactions, and rearrangements.[58] Allenes have also been utilized as building blocks in the synthesis of macromolecules (allenophane macrocycles)[108] and their oligomerization can yield 4−9 membered rings.[109−111] Allenes can be polymerized through both carbon−carbon double bonds: the less substituted C═C (1,2), the more substituted C═C (2,3), or a combination of both (Figure 5). Regardless, these polymer backbones contain alternating sp^2 and sp^3 hybridized carbon atoms, with pendant C═C bonds directly attached to the backbone, providing the opportunity to use these as handles for further functionalization. The polymerization of allenes has been studied since the 1950s, with initial reports indicating that radical and cationic techniques gave uncontrolled oligomerization and polymerization.[112−114] More successfully, the controlled polymerization of allenes has been realized by coordination polymerization, in which coordination to a transition metal complex is followed by migratory insertion to initiate the polymerization. Mono-, di-, and trisubstituted allenes with various substituents (e.g., alkoxy, phenyl, alkyl, and alkoxycarbonyl groups) have been used as monomers, with the electronic properties and steric demands used to control rate of polymerization and tailor regioreactivity.[115] A handful of examples also illustrate polymerization of allenes with more exotic substituents. For example, Suzuki et al. utilized Si-functionalized allenes to produce polymers with a higher degree of 2,3-polymerization.[115] Allenes have also been used as comonomers with 1,3-butadienes and isonitriles to obtain block and alternating copolymers, respectively.[116,117]

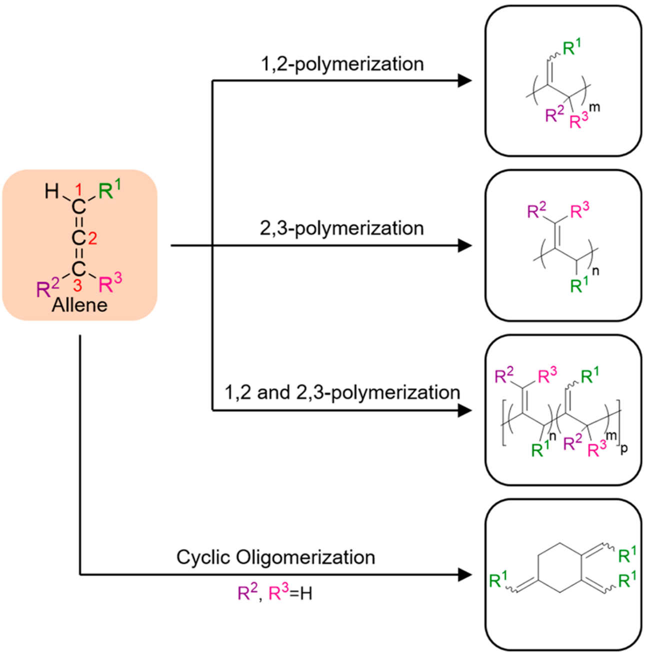

Figure 5. Possible backbones achievable through allene polymerization highlighting difference of 1,2- and 2,3-polymerization. A common side reaction of allene polymerization is production of cyclic oligomers (small molecules).

Aryl- and alkyl-substituted allenes: Aryl and alkyl groups are common substituents on allene moieties that are used as monomers. In 1997, Endo et al. investigated the effects of allene functionality on polymerization using $[(\pi\text{-allyl})\text{NiOCOCF}_3]_2$ as the initiator in toluene at 0 °C (Figure 6A).[118] The R^1, R^2, and R^3 substituents were varied, utilizing various alkyl chain lengths and aryl rings. Generally, for monosubstituted allenes the monomer identity had little effect on polymerization and good control of molecular weight was observed; for example, cyclohexyl allene gave polymers with M_n = 11.3 kDa with $Đ$ = 1.05. Monosubstituted allenes bearing a bulkier substituent, such as *tert*-butyl allene, had a lower ratio of 1,2:2,3 propagation (0:100 compared to 8:92 for cyclohexyl allene). A similar trend was observed with disubstituted alkylallenes, although these polymerizations were slower.[118]

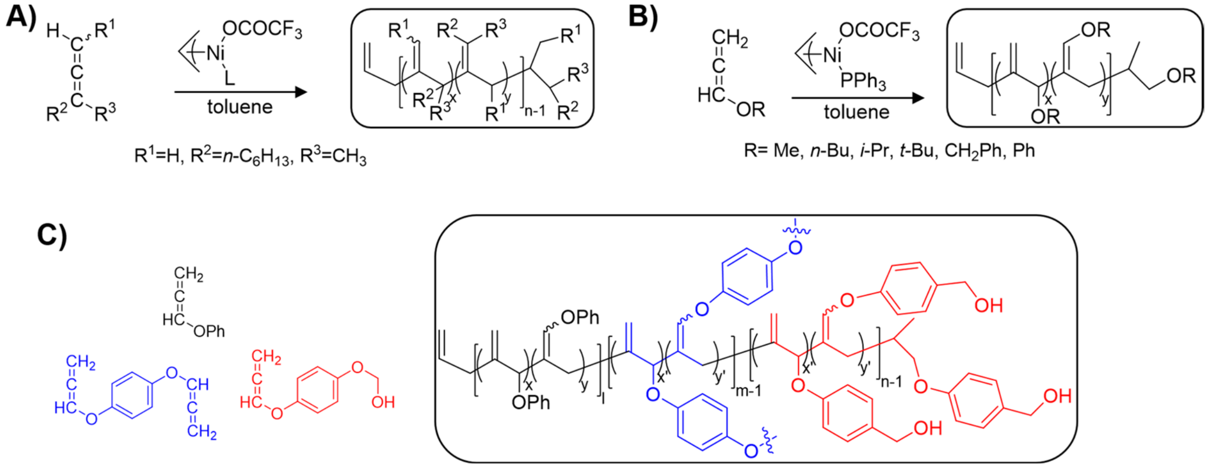

Figure 6. Examples of polymerization of allenes. Polymerization of different (A) alkylallene derivatives; (B) alkoxyallene derivatives; and (C) allene comonomers used to prepare polymer microspheres.

Takagi and co-workers further examined cyclic dialkylallenes in which the cumulated double bond is within the ring, using ring strain to increase the reaction rate.[119]

Choi et al. polymerized phenyl-substituted allene derivatives using organorhodium (i.e., $RhH(PPh_3)_4$) and organocobalt (i.e., $CoH(N_2)(PPh_3)_3$) complexes.[120] When electron-withdrawing groups were incorporated into the aryl rings (4-fluorophenylallene and 4-(trifluoromethyl)-phenylallene), the monomers did not polymerize but only produced ill-defined oligomers. Takagi et al. used a Ni complex ($[(\pi\text{-allyl})\text{-}NiOCOCF_3]_2$) to initiate polymerization of aryl substituted allenes in toluene;[121] compared to the parent phenylallene, aryl substituents bearing an electron-donating group (−OMe) had increased rates of polymerization, whereas electron-withdrawing groups (−Cl and $-CCl_3$) slowed the rate of polymerization. Takagi et al. also examined the role of sterics at the 1 and 3 positions of allene and found that the 1,3-disubstituted allene took a significantly longer time to polymerize than the 3,3-substituted allene and monosubstituted allenes (~4.6× slower).[121]

More recently, Lin et al. used rare-earth metal complexes (Sc, Lu, Tm, Y, and Gd) to polymerize phenyl-substituted allene.[122] The metal complex was activated using a Lewis acid and selectivity toward 2,3-polymerization was identified. Activity and regioselectivity increased with the metal atom radius, and thus, the Gd complex had the best performance. The authors also examined the effect of electron-withdrawing and electron-donating groups on the aryl rings; only one electron-donating group promoted polymerization, specifically complete conversion of *p*-methylphenylallene was observed after 1 h. Alternatively, *p*-chloride or *p*-bromide substituents on the aryl ring did not promote polymerization, yet *p*-fluoride substitution resulted in 77% monomer conversion and relatively high molecular weight (M_n = 28 kDa; $Đ$ = 1.58).[122] This was the first demonstration of polymerization of aryl allene bearing an electron-withdrawing group.

Alkoxy allene derivatives: Another class of allene derivatives used as monomers are alkoxyallenes, in which one of the terminal carbons bears an electron-donating −OR group. Tomita et al. used $[(\eta^3\text{-allyl})NiOCOCF_3]_2/PPh_3$ to initiate the controlled polymerization of methoxyallene, obtaining 1,2 and 2,3 propagation to give a molecular weight of M_n = 18 kDa, $Đ$ = 1.08.[123] Examination of other alkoxyallene derivatives revealed that the proportion of 2,3 propagation increased with bulkiness of the substituents. Inspired by this work, Tomita and co-workers performed block copolymerizations of alkoxyallenes and confirmed that the copolymers had low dispersities, regardless of the order of monomer addition.[124] By varying the ligands of $[(\pi\text{-allyl})NiX_2]_2/PPh_3$ (X = carboxylate and halides), the impact of initiator electronics on polymerization of *n*-octyloxyallene was studied (Figure 6B).[125] For monosubstituted allene, the percentage of 2,3 propagation decreased for ligands that were more electron-withdrawing carboxylate ligands and larger radii halides. In 2006, Kino et al. examined the polymerization of various allene derivatives including alkoxyallenes and aryl/alkyl allenes in different solvents.[126] Regardless of the solvent, all allene derivatives underwent polymerization in a controlled manner using $[(allyl)NiOCOF_3]_2/PPh_3$ as the initiator. Protic solvents, however, increased the rate of polymerization and gave a higher selectivity for 1,2 propagation.[126]

Applications of allene-derived polymers: The applications of allene-derived polymers have been understudied and only a few reports demonstrating tailored morphologies. In 2016, Yamauchi et al. used coordination dispersion copolymerization of allenes to synthesize polymer microspheres, using phenoxy-substituted allene as monomer and a diallene as cross-linker.[127] The size of the microspheres was dictated by the identity and concentration of monomer, solvents, and stabilizer (polyvinylpyrrolidone). The authors further demonstrated incorporation of a hydroxyl bearing allene comonomer that was subsequently used for postpolymerization modification, altering the hydrophilicity of the microspheres (Figure 6C). Sakai et al. also used monosubstituted allene derivatives to make block copolymers consisting of polyethylene glycol and polyallene blocks[128] and used these to prepare a thin film consisting of perpendicular nanocylindrical structures. One of the few properties of polyallenes that have been reported is the crystallinity of the polymers;[129] a recent study from Lin et al. illustrated high crystallinity of polyallenes which have high regularity of the backbones (strictly 2,3-polymerization).[122]

Ketenes: Ketenes are a class of molecules of the general form $O{=}C{=}CR_2$ in which the R groups can be hydrogen, alkyl, or aryl and can be different (Figure 7). The tendency of ketenes to self-dimerize through thermally induced [2 + 2] cycloaddition has limited the broad examination of these cumulated double bonds as monomers.[130−132] Ketene dimerization was reported by Huisgen et al. in 1968, revealing that substituted ketenes predominantly yield cyclobutene-1,3-diones, while nonsubstituted ketene (R=H) dimerizes to produce γ-methylene-β-propiolactone (Figure 7).[130] Substituted ketenes are classified in two categories: ketoketenes ($O{=}C{=}CR_2$)

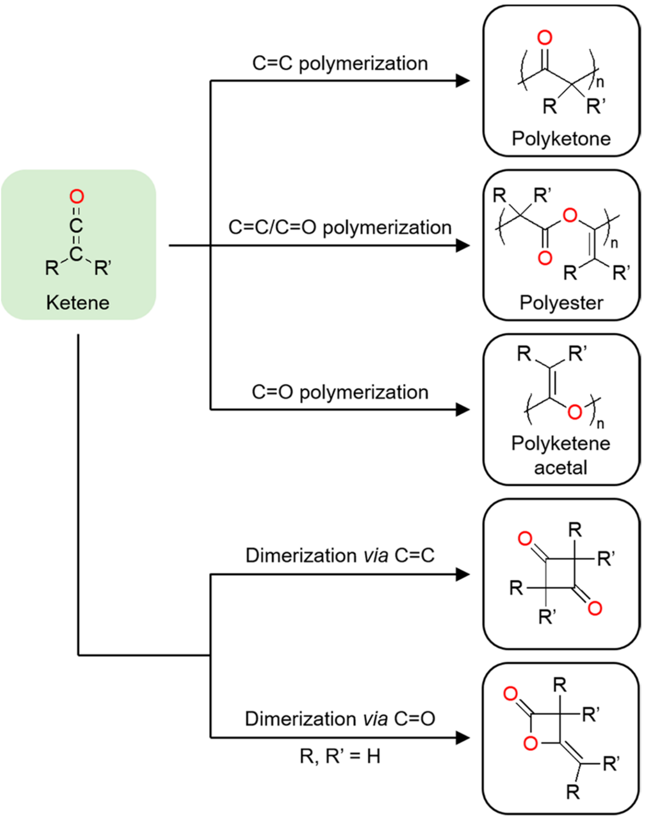

Figure 7. Three possible polymer backbones that can be prepared by the polymerization of ketenes and the products of self-dimerization.

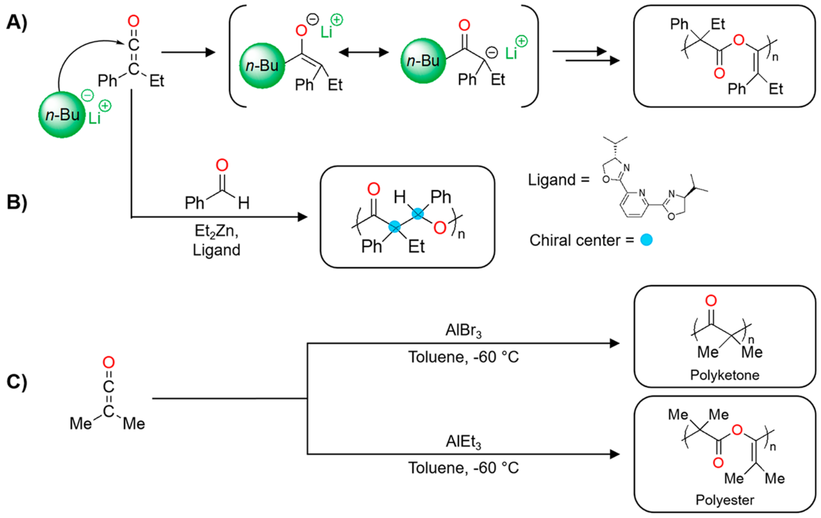

Figure 8. (A) Anionic homopolymerization of ethylphenylketene using *n*-BuLi as the initiator; (B) Stereoregular ketene polymer synthesis; (C) Cationic polymerization of dimethylketene, illustrating the impact of initiator identity on product identity.

and aldoketenes (O═C═CRH), with the former having a lower tendency to self-dimerize.

For ketenes, depending on the mode of polymerization, three different polymer backbones could possibly be obtained: polymerization of C═O produces a polyketene acetal, polymerization of C═C produces a polyketone, and alternating polymerization of C═O and C═C yields polyester (Figure 7). In 1925, Staudinger discovered ketene polymerization, which had been previously misinterpreted as spontaneous decomposition of ketenes.[133] He reported the polymerization of dimethylketene in the presence of triethylamine as the initiator, although a definitive polymer structure was not obtained at the time. Decades later, Natta et al. and Pregaglia et al. demonstrated that different polymeric backbone functionalities (polyketones, polyesters, and polyketene acetals) can be obtained by altering reaction conditions, as supported by infrared (IR) spectroscopy studies.[134,135] A majority of reports on the use of ketenes as monomers focus on anionic and cationic polymerization techniques.

Anionic polymerization of ketenes: Anionic polymerization proceeds by attack of an initiator anion on the electropositive central carbon atom of ketene, forming an enolate anion with electron density delocalized over the carbon and oxygen atom. C-acylation of the enolate anion yields polyketones, while O-acylation affords polyketene acetals, and alternating C- and O-acylation leads to the formation of polyester structures. As is evident from literature, polyesters have been the predominant product of anionic polymerization of ketenes, with the most successful conditions utilizing low-polarity solvent.[136] Early studies on anionic polymerization of ketenes were limited to copolymerization with ketones, aldehydes, and isocyanates. In 1960, Natta et al. demonstrated the alternating copolymerization of dimethyl ketene and acetone using *n*-butyl lithium as the initiator, obtaining highly crystalline polyesters.[137] The presence of ester linkages was confirmed by reduction of the polymer with lithium aluminum hydride ($LiAlH_4$) to obtain the corresponding glycol. IR spectroscopy provided further confirmation, revealing the characteristic stretching frequencies of ester linkages. Subsequent work demonstrated the synthesis of a stereospecific polyester by the alternating copolymerization of dimethyl ketene and benzaldehyde derivatives initiated by alkyl lithium reagents (product molecular weight not reported).[138] These copolymers contained an asymmetric carbon atom in the repeat unit, and the formation of the corresponding glycol upon reduction by $LiAlH_4$ confirmed the stereoregularity of the chemical structure of the polyesters. The authors showed that the crystallinity of the polymers depended on the benzaldehyde derivative. Phenylmethyl ketene could also be copolymerized with aldehydes using *n*-butyl lithium and sodium *tert*-butoxide initiators;[139] the resulting polyesters had poor crystallinity compared to the dimethylketene/benzaldehyde copolymers, as confirmed by X-ray diffraction measurements. Among the comonomers investigated, isocyanates attracted substantial interest due to their isoelectronic structure.[140,141] Yamashita et al. observed the alternating copolymerization of diphenylketene and phenyl isocyanate initiated by sodium cyanide in DMF at −45 °C.[140] These polymers were formed by polymerization of the C═O bond of diphenylketene and the C═N bond of phenyl isocyanate. Likewise, Sincich and co-workers used sodium naphthalenide as initiator to copolymerize phenylethylketene and various alkyl and aryl isocyanates;[141] under the same conditions (DMF at −45 °C), product molecular weight ranged from 1.7−4.0 kDa, but in THF at −78 °C, higher molecular weights were observed (2.8−10.5 kDa).

To this point, achieving control over the molecular weight of polymer derived from ketene monomers remained a challenge. In 1999, Sudo et al. developed the first controlled anionic homopolymerization of ethylphenylketene in THF at −20 °C using *n*-butyl lithium as the initiator to obtain a polyester (Figure 8A).[142] To confirm the living character of the system, after complete consumption of monomer, a second infusion of monomer was introduced; this resulted in an increase in molecular weight consistent with added monomer. Further, block copolymers were obtained under these conditions by chain extending the ethylphenylketene block with *tert*-butyl methacrylate. In subsequent work, the authors applied this protocol to the monomer ethyl(4-methoxyphenyl)ketene to produce a novel polyester with alkoxyphenyl side chains.[143] A range of polymer molecular weights were accessed (M_n = 4.2−16.5 kDa), all with low dispersities ($Đ$ = 1.10−1.12). The polymerization of aldoketenes posed a greater challenge owing to their propensity to self-dimerize, even at room temperature. The first successful polymerization of an aldoketene was reported by Burel and co-workers in 2011 when the uncontrolled polymerization of ethylketene gave a polyester.[144] The polymerization was carried out in THF at −78 °C using a lithium diisopropylamide/butyl lithium aggregate as initiator. The resulting polyesters displayed high molecular weights (up to 24.0 kDa) and dispersities close to 1.5.

An intriguing opportunity presented by ketene monomers is the ability to access stereoregular polymers, provided adequate substitution of the ketene and suitable reaction conditions. Nagai and co-workers demonstrated enantioselective control of a ketene-aldehyde alternating copolymerization via a transition metal-mediated pathway.[145,146] Ethylphenylketene was copolymerized with benzaldehyde using diethylzinc ($ZnEt_2$) as initiator and the optically active tridentate 2,6-bis(4-isopropyl-2-oxazolin-2-yl)pyridine (Pybox) as ligand, forming the active initiator in situ (Figure 8B).[146] Of the conditions studied, the highest molecular weight was observed in toluene at −40 °C (26 kDa), but with a relatively low specific optical rotation ($[\alpha_D{}^{25}] = -58°$). Conversely, the maximum optical rotation ($[\alpha_D{}^{25}] = -158°$) was achieved from polymer prepared at −78 °C in dichloromethane (DCM), though it had a slightly lower molecular weight of 22.7 kDa. This marked the first successful synthesis of optically active polyesters by the anionic alternating copolymerization of a ketene and aldehyde.

Cationic polymerization of ketenes: In comparison to anionic polymerization, cationic polymerization of ketenes has been sparsely reported. Cationic polymerization utilizes electrophilic initiators that coordinate to the oxygen of ketene, activating the central carbon for electrophilic attack; the subsequent propagation pathway is dependent on the initiator identity and solvent polarity. Cationic polymerization of ketene was first reported by Natta et al. in 1960, using dimethylketene;[134] crystalline polyketone was prepared using aluminum tribromide ($AlBr_3$) as initiator in toluene at −60 °C (Figure 8C), as supported by IR spectroscopy. Intriguingly, by simply changing initiator to triethyl aluminum ($AlEt_3$), polyester was obtained (Figure 8C), again characterized by IR spectroscopy (no molecular weight was reported). Using the same monomer system, Egret et al. evaluated the effect of solvents, examining toluene, DCM, nitrobenzene ($PhNO_2$), carbon tetrachloride (CCl_4), and so on.[147] The authors reported that a 50:50 $PhNO_2/CCl_4$ solvent mixture gave polyketones with molecular weights 20−40 kDa and that these polymers displayed thermal stability up to 205 °C. Alternatively, the use of other Lewis acid initiators such as $BF_3{\cdot}OEt_2$ and $TiCl_4$ led to the observation of both dimerization and polymerization of the ketene. The authors also observed the formation of a cyclic trimer of dimethylketene as a result of backbiting when $AlBr_3$/toluene initiator system was used. Yet another side reaction was observed when dimethyl ketene was polymerized in acetone: a cyclic lactone resulted from an addition reaction between dimethylketene and acetone.

Silyl ketenes: As previously mentioned, one difficulty in developing ketenes as monomers is that they are susceptible to irreversible self-dimerization, with the rate dependent on substitution.[130−132] In contrast to aryl and alkyl ketenes, silyl ketenes in which the terminal carbon bears a trialkyl(aryl)silyl group are significantly more stable and easier to handle. The increased stability toward self-dimerization is attributed to hyperconjugation provided by the β-silicon effect, in which electrons from C−Si σ-orbital delocalize into the antibonding π^* orbital of the C═O bond (Figure 9).[148] In addition to providing increased stability based on these electronic effects, the trialkyl(aryl)silyl group also imparts steric stabilization and can provide solubility to growing polymer chains.

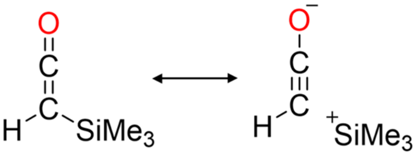

Figure 9. β-Silicon effect for silyl ketenes provides enhanced stability over alkyl/aryl ketenes.

Our group is interested in establishing the utility and reactivity of silyl ketenes as monomers for chain-growth polymerizations. We initially attempted the radical polymerization of silyl ketenes using standard radical initiators (those derived from AIBN, $^tBuOO^tBu$, etc.), but found no reaction; further studies revealed *tert*-butoxide radicals decomposed to give alcohols, which then reacted with the silyl ketene. As such, we turned our focus to the polymerization of silyl ketenes using alkoxide initiators. Using sodium and potassium *tert*-butoxide in THF, polymers of modest MW were obtained, and these products had broad dispersities and a complex mixture of polymer backbone functionalities (Figure 10A).[149] In addition to ester, ketene acetal, and ketone functionalities, silyl enol ether units were obtained upon the Brook rearrangement of α-silyl ketone and α-silyl ester units. By simply changing the counterion to lithium, no oligomer or polymer was observed and instead >70% of a highly functionalized 2-pyranone small molecule was isolated (Figure 10B).[150] The composition of this compound is that of a trimer of the silyl ketene monomer. Its formation is attributed to deprotonation of the terminal carbon of silyl ketene to form an alkynoate anion which then undergoes nucleophilic addition to another equivalent of silyl ketene, followed by subsequent thermal rearrangement. As

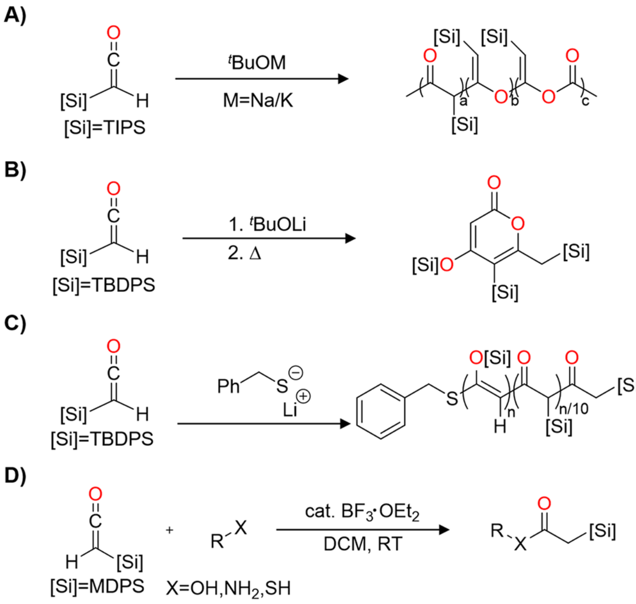

Figure 10. (A) Anionic polymerization of silyl ketene with sodium and potassium alkoxide initiators; (B) Formation of functionalized 2-pyranone initiated by lithium alkoxide initiator; (C) Formation of ketene oligomers initiated by thiolate initiators; (D) Lewis acid activation of silyl ketenes to form α-silyl carbonyls.

such, the expected nucleophilic addition of the initiator to the central carbon did not occur. The varied outcomes of these reactions indicate the high sensitivity of reaction pathway to conditions, providing ample opportunities to tailor product formation.

Evaluation of a number of reagents indicated that selectivity between nucleophilic addition and deprotonation is dependent on the initiator composition. We identified lithium thiolates as reagents that selectively undergo nucleophilic addition to *tert*-butyl diphenyl silyl ketene and demonstrated that under solvent-free conditions, well-defined oligomers were observed (Figure 10C). The chemical composition of the oligomers was characterized using IR and NMR spectroscopies, including Heteronuclear Multi-Bond Correlation (HMBC) NMR spectroscopy. Polymerization of the C═C was dominant; however, polymerization of the C═O was observed as well as Brook rearrangement of the α-silyl ketene unit. This experimental work was complimented by computational studies that indicate the functional groups present in the backbone dictate rigidity of the oligomers and that highly polarizable materials can be obtained. In contrast to the oligomers obtained under neat conditions, if THF or cyclohexane was used as solvent, two different six-membered ring byproducts were obtained.[151] Their formation was attributed to oligomerization, followed by intrachain backbiting and thermally induced rearrangements; as such, their formation did not result from deprotonation of the ketene, as noted above, and instead is attributed to backbiting after the expected initiation and oligomerization.

We have also explored initiators for the cationic polymerization of silyl ketenes. The ketene moiety is activated by coordination to a Lewis acid (LA), yet no subsequent polymerization occurred (i.e., coordination to LA did not activate the silyl ketene for addition of another equivalent of monomer). However, we did demonstrate that such activation enables the synthesis of α-silyl carbonyl compounds (esters, amides, thioesters) in high yield (Figure 10D).[152] In the absence of a LA, full consumption of silyl ketene was only observed in 4 days (phenol and triisopropyl silyl (TIPS) ketene in DCM). In contrast, in the presence of a LA full consumption of silyl ketene occurred in under 60 s. The LAs examined include $BF_3 \cdot OEt_2$, $Al(O^iPr)_3$, $B(C_6F_5)_3$, $La(OTf)_3$, and $Mg(OTf)_2$. We identified $BF_3 \cdot OEt_2$ as the best LA to active the ketene, as substoichiometric amounts (<0.2 equiv) facilitated complete consumption of silyl ketene. Alcohol and amine nucleophiles produced higher isolated yields of the expected products compared to thiol-based nucleophiles, but no trend in reaction time was observed. Five silyl ketenes with silyl substituents of varied size and electronic properties were studied, but no trend in reaction time or yield was observed. As such, silyl ketenes can be activated by coordination to LA, but the conditions explored were not suitable for cationic polymerization.

Summary and perspective/outlook: Cumulated double bonds are relatively underexplored as monomers for chain growth polymerizations, yet offer the potential to access polymers and materials not possible with other monomer systems. Of the three classes discussed above, isocyanates have been the most widely studied (anionic and transition metal catalyzed polymerizations), in comparison to allenes (transition metal polymerization) or ketenes (anionic and cationic polymerization). In all reports, exclusively the C═N of isocyanate monomers undergo polymerization to give poly(1-nylons); in contrast, allenes and ketenes have demonstrated opportunity to polymerize through different double bonds, with allenes undergoing polymerization of the 1,2 C═C versus 2,3 C═C bonds and ketenes offering polymerization of C═C versus C═O. The ability to selectively polymerize each double bond within a single monomer could enable a single feedstock for polymers with distinctly different properties or even the possibility to prepare block copolymers from a single monomer feed.

Polymerization of isocyanates has been developed throughout the past 60 years and controlled techniques include anionic and coordination polymerization with copolymerizations being demonstrated. Controlled anionic polymerization of isocyanates requires the presence of additives to sterically hinder the growing polymer chain end and low temperatures (−78 to −98 °C). In contrast, coordination polymerization allows for the controlled polymerizations at room temperature. Various titanium(IV) catalysts have been developed to obtain rigid polymers with complex architectures, including triblock copolymers, three-arm star polymers, and once-broken worm polymers.[96−98] One limitation of the current techniques to polymerize isocyanates is limitation of monomer scope, and thus, expansion to isocyanates with sterically demanding substituents proves a point for further success. In addition to polymerization techniques, the observation that polyisocyanates are depolymerizable is intriguing, especially given the pressing concern of sustainability of polymers and plastic waste. Depending on substitution pattern, polyisocyanates degrade into monomers or trimers in the presence of simple bases and thus design of tailored end groups could be used to control depolymerization conditions.

A majority of the reports on the polymerization of allenes have made use of metal catalyzed coordination polymerizations and allene substituents have included alkyl, aryl, alkoxy, and aryloxy units. There has been success in controlling the ratio of 1,2 versus 2,3-polymerization favoring one or the other. A general trend is that alkyl- or aryl-substituted allenes have a higher preference for 2,3-polymerization, whereas alkoxy-substituted allenes have an increased preference for 1,2-polymerization. However, the ligand on the catalyst can also affect the preference, and can decrease the extent of 1,2-polymerization for alkoxyallenes. Of note, an electron-withdrawing ligand is necessary to avoid oligomeric byproducts. Lacking from the current study of these polymers is an understanding of their thermal and mechanical properties, as well as degradation. Further, one intriguing opportunity is to switch propagation pathways (1,2 vs 2,3) as the polymerization progresses; such control would produce copolymers with the same atomic composition in each block and provide opportunities to identify the impact on properties. Substitution pattern of allenes also provides a route to tune the polymer structure. For example, polymers derived from monosubstituted allenes will have asymmetric carbon atoms in the backbone, the control of which could produce chiral polymers with extended rod-like structures valuable for catalysis or optoelectronics. Further, all polymers derived from allenes retain C═C double bonds pendant to the polymer backbone on every other carbon atom; these functional groups are suitable for cross-linking or postpolymerization modification, such as thiol−ene addition or hydrosilylation reactions.

Ketenes were perhaps the first cumulated double bonds studied as monomers and also the unit that provides opportunity to access the widest diversity of backbone functionalities. To date, polymerization of ketenes has primarily focused on anionic and cationic polymerization pathways. Anionic polymerizations yield polyesters, whereas the less reported cationic polymerization can afford polyketones. Little to no studies have reported the formation of polyketene acetals. The tendency of ketenes to self-dimerize, even at room temperature, has likely limited their utility as monomers, as has the limited solubility of polymers derived from aryl or alkyl ketenes. Given the isoelectronic properties of isocyanates and ketenes, techniques employed for controlled polymerization of isocyanates may be suitable for ketenes, in addition to group transfer polymerization methods. Further, a fundamental understanding of the mechanical properties, thermal stability, and degradability of polymers derived from ketenes are required.

Silyl ketenes provide an exciting opportunity to overcome the limitations associated with alkyl and aryl ketenes, as they are stable under common conditions and the silyl substituents can be used to tune the solubility and electronic properties of the monomer. Our group's work indicates that silyl ketenes can be polymerized using anionic initiators, that both the C═C and C═O undergo polymerization, and that initiator and solvent are critical to enable nucleophilic addition over deprotonation, prevent backbiting, and ensure propagation. Anionic polymerization may be limited by competition between propagation and intra- and interchain reactions, specifically nucleophilic addition to ketone and ester functionalities in the backbone or deprotonation alpha to these carbonyls. Tailoring initiator, solvent, temperature, and silyl substituents are required to not only dictate the polymerization pathway, but also control the molecular weight of the polymers.

Cumulated double bonds offer enchanting opportunities to produce polymers with distinct chemical composition and polymer chain dynamics compared to polymers prepared from common monomers. The polymers derived from isocyanates, allenes, and ketenes all have alternating sp^2-hybridized carbon atoms in their polymer backbones; as such, the polymer chains are expected to be extended and more rod-like compared to random coil polymers. Establishing the experimental techniques that control propagation pathway; stereochemistry of the double bonds and asymmetric carbon atoms; and relative rates of initiation, propagation, and side reactions would benefit from complementary computational results rather than a guess-and-check approach. Advancing cumulated double bonds as monomers will enable a better understanding of the reactivity of these molecules, as well as establishment of structure−property−application relationships in the development of next-generation materials.

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■ REFERENCES

(1) Buss, B. L.; Miyake, G. M. Photoinduced Controlled Radical Polymerizations Performed in Flow: Methods, Products, and Opportunities. *Chem. Mater.* **2018**, *30* (12), 3931−3942.

(2) Reis, M. H.; Leibfarth, F. A.; Pitet, L. M. Polymerizations in Continuous Flow: Recent Advances in the Synthesis of Diverse Polymeric Materials. *ACS Macro Lett.* **2020**, *9* (1), 123−133.

(3) Holloway, J. O.; Wetzel, K. S.; Martens, S.; Du Prez, F. E.; Meier, M. A. R. Direct Comparison of Solution and Solid Phase Synthesis of Sequence-Defined Macromolecules. *Polym. Chem.* **2019**, *10* (28), 3859−3867.

(4) Vrijsen, J. H.; Osiro Medeiros, C.; Gruber, J.; Junkers, T. Continuous Flow Synthesis of Core Cross-Linked Star Polymers: Via Photo-Induced Copper Mediated Polymerization. *Polym. Chem.* **2019**, *10* (13), 1591−1598.

(5) Reis, M. H.; Davidson, C. L. G.; Leibfarth, F. A. Continuous-Flow Chemistry for the Determination of Comonomer Reactivity Ratios. *Polym. Chem.* **2018**, *9* (13), 1728−1734.

(6) Radzinski, S. C.; Foster, J. C.; Scannelli, S. J.; Weaver, J. R.; Arrington, K. J.; Matson, J. B. Tapered Bottlebrush Polymers: Cone-Shaped Nanostructures by Sequential Addition of Macromonomers. *ACS Macro Lett.* **2017**, *6* (10), 1175−1179.

(7) Lee, J.; Kalin, A. J.; Yuan, T.; Al-Hashimi, M.; Fang, L. Fully Conjugated Ladder Polymers. *Chem. Sci.* **2017**, *8* (4), 2503−2521.

(8) Haque, F. M.; Grayson, S. M. The Synthesis, Properties and Potential Applications of Cyclic Polymers. *Nat. Chem.* **2020**, *12*, 433−444.

(9) Carmean, R. N.; Becker, T. E.; Sims, M. B.; Sumerlin, B. S. Ultra-High Molecular Weights via Aqueous Reversible-Deactivation Radical Polymerization. *Chem.* **2017**, *2* (1), 93−101.

(10) Beyer, V. P.; Kim, J.; Becer, C. R. Synthetic Approaches for Multiblock Copolymers. *Polym. Chem.* **2020**, *11* (7), 1271−1291.

(11) Teo, Y. C.; Lai, H. W. H.; Xia, Y. Synthesis of Ladder Polymers: Developments, Challenges, and Opportunities. *Chem. - Eur. J.* **2017**, *23* (57), 14101−14112.

(12) Shafranek, R. T.; Millik, S. C.; Smith, P. T.; Lee, C. U.; Boydston, A. J.; Nelson, A. Stimuli-Responsive Materials in Additive Manufacturing. *Prog. Polym. Sci.* **2019**, *93*, 36−67.

(13) Wei, P.; Leng, H.; Chen, Q.; Advincula, R. C.; Pentzer, E. B. Reprocessable 3D-Printed Conductive Elastomeric Composite Foams for Strain and Gas Sensing. *ACS Appl. Polym. Mater.* **2019**, *1* (4), 885−892.

(14) Ligon, S. C.; Liska, R.; Stampfl, J.; Gurr, M.; Mülhaupt, R. Polymers for 3D Printing and Customized Additive Manufacturing. *Chem. Rev.* **2017**, *117* (15), 10212−10290.

(15) Zaquen, N.; Yeow, J.; Junkers, T.; Boyer, C.; Zetterlund, P. B. Visible Light-Mediated Polymerization-Induced Self-Assembly Using

Continuous Flow Reactors. *Macromolecules* **2018**, *51* (14), 5165−5172.

(16) Scott, P. J.; Kasprzak, C. R.; Feller, K. D.; Meenakshisundaram, V.; Williams, C. B.; Long, T. E. Light and Latex: Advances in the Photochemistry of Polymer Colloids. *Polym. Chem.* **2020**, *11*, 3498−3524.

(17) Varlas, S.; Keogh, R.; Xie, Y.; Horswell, S. L.; Foster, J. C.; O'Reilly, R. K. Polymerization-Induced Polymersome Fusion. *J. Am. Chem. Soc.* **2019**, *141* (51), 20234−20248.

(18) Canning, S. L.; Smith, G. N.; Armes, S. P. A Critical Appraisal of RAFT-Mediated Polymerization-Induced Self-Assembly. *Macromolecules* **2016**, *49* (6), 1985−2001.

(19) Arrington, K. J.; Haag, J. V.; French, E. V.; Murayama, M.; Edgar, K. J.; Matson, J. B. Toughening Cellulose: Compatibilizing Polybutadiene and Cellulose Triacetate Blends. *ACS Macro Lett.* **2019**, *8* (4), 447−453.

(20) Blasco, E.; Sims, M. B.; Goldmann, A. S.; Sumerlin, B. S.; Barner-Kowollik, C. 50th Anniversary Perspective: Polymer Functionalization. *Macromolecules* **2017**, *50* (14), 5215−5252.

(21) Xu, J.; Eagan, J. M.; Kim, S. S.; Pan, S.; Lee, B.; Klimovica, K.; Jin, K.; Lin, T. W.; Howard, M. J.; Ellison, C. J.; Lapointe, A. M.; Coates, G. W.; Bates, F. S. Compatibilization of Isotactic Polypropylene (IPP) and High-Density Polyethylene (HDPE) with IPP-PE Multiblock Copolymers. *Macromolecules* **2018**, *51* (21), 8585−8596.

(22) Xiang, T.; Wang, L. R.; Ma, L.; Han, Z. Y.; Wang, R.; Cheng, C.; Xia, Y.; Qin, H.; Zhao, C. S. From Commodity Polymers to Functional Polymers. *Sci. Rep.* **2015**, *4*, 4604.

(23) Barkley, D. A.; Jiang, N.; Sen, M.; Endoh, M. K.; Rudick, J. G.; Koga, T.; Zhang, Y.; Gang, O.; Yuan, G.; Satija, S. K.; Kawaguchi, D.; Tanaka, K.; Karim, A. Chain Conformation near the Buried Interface in Nanoparticle-Stabilized Polymer Thin Films. *Macromolecules* **2017**, *50* (19), 7657−7665.

(24) Chakma, P.; Konkolewicz, D. Dynamic Covalent Bonds in Polymeric Materials. *Angew. Chem., Int. Ed.* **2019**, *58* (29), 9682−9695.

(25) He, C.; Shi, S.; Wang, D.; Helms, B. A.; Russell, T. P. Poly(Oxime-Ester) Vitrimers with Catalyst-Free Bond Exchange. *J. Am. Chem. Soc.* **2019**, *141* (35), 13753−13757.

(26) Li, L.; Chen, X.; Jin, K.; Torkelson, J. M. Vitrimers Designed Both to Strongly Suppress Creep and to Recover Original Cross-Link Density after Reprocessing: Quantitative Theory and Experiments. *Macromolecules* **2018**, *51* (15), 5537−5546.

(27) El-Zaatari, B. M.; Ishibashi, J. S. A.; Kalow, J. A. Cross-Linker Control of Vitrimer Flow. *Polym. Chem.* **2020**, na.

(28) Lewis, S. E.; Wilhelmy, B. E.; Leibfarth, F. A. Upcycling Aromatic Polymers through C-H Fluoroalkylation. *Chem. Sci.* **2019**, *10* (25), 6270−6277.

(29) Lewis, S. E.; Wilhelmy, B. E.; Leibfarth, F. A. Organocatalytic C-H Fluoroalkylation of Commodity Polymers. *Polym. Chem.* **2020**, na.

(30) Arslan, M.; Acik, G.; Tasdelen, M. A. The Emerging Applications of Click Chemistry Reactions in the Modification of Industrial Polymers. *Polym. Chem.* **2019**, *10* (28), 3806−3821.

(31) Short, G. N.; Nguyen, H. T. H.; Scheurle, P. I.; Miller, S. A. Aromatic Polyesters from Biosuccinic Acid. *Polym. Chem.* **2018**, *9* (30), 4113−4119.

(32) Gandini, A.; Lacerda, T. M.; Carvalho, A. J. F.; Trovatti, E. Progress of Polymers from Renewable Resources: Furans, Vegetable Oils, and Polysaccharides. *Chem. Rev.* **2016**, *116* (3), 1637−1669.

(33) Hatton, F. L. Recent Advances in RAFT Polymerization of Monomers Derived from Renewable Resources. *Polym. Chem.* **2020**, *11* (2), 220−229.

(34) De Hoe, G. X.; Zumstein, M. T.; Tiegs, B. J.; Brutman, J. P.; McNeill, K.; Sander, M.; Coates, G. W.; Hillmyer, M. A. Sustainable Polyester Elastomers from Lactones: Synthesis, Properties, and Enzymatic Hydrolyzability. *J. Am. Chem. Soc.* **2018**, *140* (3), 963−973.

(35) Lundberg, D. J.; Lundberg, D. J.; Hillmyer, M. A.; Dauenhauer, P. J. Techno-Economic Analysis of a Chemical Process to Manufacture Methyl-ε-Caprolactone from Cresols. *ACS Sustainable Chem. Eng.* **2018**, *6* (11), 15316−15324.

(36) Odian, G. *Principles of Polymerization*, 4th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2004.

(37) Rudin, A.; Choi, P. *The Elements of Polymer Science and Engineering*, 3rd ed.; Academic Press, 2012.

(38) *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P., Eds.; John Wiley & Sons, Inc., 2002.

(39) *Handbook of Ring-Opening Polymerization*; Dubois, P., Coulembier, O., Raquez, J., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA, 2009.

(40) Buchmeiser, M. R. Ring-Opening Metathesis Polymerization. In *Ring-Opening Polymerization*; Dubois, P., Coulembier, O., Raquez, J., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA, 2009; pp 197−225.

(41) Chen, Y.; Kakuchi, T. Organocatalyzed Group Transfer Polymerization. *Chem. Rec.* **2016**, *16* (4), 2161−2183.

(42) Stefan, M. C.; Javier, A. E.; Osaka, I.; McCullough, R. D. Grignard Metathesis Method (GRIM): Toward a Universal Method for the Synthesis of Conjugated Polymers. *Macromolecules* **2009**, *42* (1), 30−32.

(43) Stefan, M. C.; Bhatt, M. P.; Sista, P.; Magurudeniya, H. D. Grignard Metathesis (GRIM) Polymerization for the Synthesis of Conjugated Block Copolymers Containing Regioregular. *Polym. Chem.* **2012**, *3*, 1693.

(44) Buss, B. L.; Lim, C. H.; Miyake, G. M. Dimethyl Dihydroacridines as Photocatalysts in Organocatalyzed Atom Transfer Radical Polymerization of Acrylate Monomers. *Angew. Chem., Int. Ed.* **2020**, *59* (8), 3209−3217.

(45) Feist, J. D.; Xia, Y. Enol Ethers Are Effective Monomers for Ring-Opening Metathesis Polymerization: Synthesis of Degradable and Depolymerizable Poly(2,3-Dihydrofuran). *J. Am. Chem. Soc.* **2020**, *142* (3), 1186−1189.

(46) Lu, P.; Boydston, A. J. Integration of Metal-Free Ring-Opening Metathesis Polymerization and Organocatalyzed Ring-Opening Polymerization through a Bifunctional Initiator. *Polym. Chem.* **2019**, *10* (23), 2975−2979.

(47) Teator, A. J.; Leibfarth, F. A. Catalyst-Controlled Stereoselective Cationic Polymerization of Vinyl Ethers. *Science* **2019**, *363* (6434), 1439−1443.

(48) Folster, C. P.; Klausen, R. S. Metallocene Influence on Poly(Cyclosilane) Structure and Properties. *Polym. Chem.* **2018**, *9* (15), 1938−1941.

(49) Kensy, V. K.; Tritt, R. L.; Haque, F. M.; Murphy, L. M.; Knorr, D. B.; Grayson, S. M.; Boydston, A. J. Molecular Weight Control via Cross Metathesis in Photo-Redox Mediated Ring-Opening Metathesis Polymerization. *Angew. Chem., Int. Ed.* **2020**, *59*, 9074−8.

(50) Ji, Y.; Zhou, T.; Van De Wouw, H. L.; Klausen, R. S. Organoborane Strategy for Polymers Bearing Lactone, Ester, and Alcohol Functionality. *Macromolecules* **2020**, *53* (1), 249−255.

(51) Dadashi-Silab, S.; Lorandi, F.; Fantin, M.; Matyjaszewski, K. Redox-Switchable Atom Transfer Radical Polymerization. *Chem. Commun.* **2019**, *55* (5), 612−615.

(52) Wang, K.; Amin, K.; An, Z.; Cai, Z.; Chen, H.; Chen, H.; Dong, Y.; Feng, X.; Fu, W.; Gu, J.; Han, Y.; Hu, D.; Hu, R.; Huang, D.; Huang, F.; Huang, F.; Huang, Y.; Jin, J.; Jin, X.; Li, Q.; Li, T.; Li, Z.; Li, Z.; Liu, J.; Liu, J.; Liu, S.; Peng, H.; Qin, A.; Qing, X.; Shen, Y.; Shi, J.; Sun, X.; Tong, B.; Wang, B.; Wang, H.; Wang, L.; Wang, S.; Wei, Z.; Xie, T.; Xu, C.; Xu, H.; Xu, Z.-K.; Yang, B.; Yu, Y.; Zeng, X.; Zhan, X.; Zhang, G.; Zhang, J.; Zhang, M. Q.; Zhang, X.-Z.; Zhang, X.; Zhang, Y.; Zhang, Y.; Zhao, C.-S.; Zhao, W.; Zhou, Y.; Zhou, Z.; Zhu, J.; Zhu, X.; Tang, B. Z. Advanced Functional Polymer Materials. *Mater. Chem. Front.* **2020**, *4*, 1803.

(53) Varlas, S.; Foster, J. C.; Arkinstall, L. A.; Jones, J. R.; Keogh, R.; Mathers, R. T.; O'Reilly, R. K. Predicting Monomers for Use in Aqueous Ring-Opening Metathesis Polymerization-Induced Self-Assembly. *ACS Macro Lett.* **2019**, *8* (4), 466−472.

(54) Hufendiek, A.; Lingier, S.; Du Prez, F. E. Thermoplastic Polyacetals: Chemistry from the Past for a Sustainable Future? *Polym. Chem.* **2019**, *10* (1), 9−33.

(55) Ozaki, S. Recent Advances in Isocyanate Chemistry. *Chem. Rev.* **1972**, *72* (5), 457−496.

(56) *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA, 2004.

(57) Hoff, S.; Brandsma, L.; Arens, J. F. Preparation, Metallation and Alkylation of Allenyl Ethers. *Recl. des Trav. Chim. des Pays-Bas* **1968**, *87* (8), 916−924.

(58) Taylor, D. R. The Chemistry of Allenes. *Chem. Rev.* **1967**, *67* (3), 317−359.

(59) Mackie, J. C.; Doolan, K. R. High-Temperature Kinetics of Thermal Decomposition of Acetic Acid and Its Products. *Int. J. Chem. Kinet.* **1984**, *16* (5), 525−541.

(60) Green, I. X.; Tang, W.; Neurock, M.; Yates, J. T. Localized Partial Oxidation of Acetic Acid at the Dual Perimeter Sites of the Au/TiO2 Catalyst-Formation of Gold Ketenylidene. *J. Am. Chem. Soc.* **2012**, *134* (33), 13569−13572.

(61) Hurd, C. D.; Blunck, F. H. The Pyrolysis of Esters. *J. Am. Chem. Soc.* **1938**, *60* (10), 2419−2425.

(62) Williams, J. W.; Hurd, C. D. An Improved Apparatus For The Laboratory Preparation Of Ketene and Butadiene. *J. Org. Chem.* **1940**, *5* (2), 122−125.

(63) Hurd, C. D. The Ketenic Decomposition Of Ketones, Ketene and Methyl Ketene. *J. Am. Chem. Soc.* **1923**, *45* (12), 3095−3101.

(64) Wilsmore, N. T. M. CLXXXVIII.—Keten. *J. Chem. Soc., Trans.* **1907**, *91*, 1938−1941.

(65) Fisher, G. J.; MacLean, A. F.; Schnizer, A. W. Apparatus For The Preparation Of Ketene By The Pyrolysis Of Acetic Anhydride. *J. Org. Chem.* **1953**, *18* (8), 1055−1057.

(66) Perrin, C. L.; Arrhenius, T. Malonic Anhydride. *J. Am. Chem. Soc.* **1978**, *100* (16), 5249−5251.

(67) Haller, I.; Srinivasan, R. Primary Processes in the Photochemistry of TetramethyI-1,3-Cyclobutanedione. *J. Am. Chem. Soc.* **1965**, *87* (5), 1144−1145.

(68) Turro, N. J.; Leermakers, P. A.; Wilson, H. R.; Neckers, D. C.; Byers, G. W.; Vesley, G. F. Photochemistry of 1,3-Cyclobutanediones. Decomposition Modes and Chemical Intermediates. *J. Am. Chem. Soc.* **1965**, *87* (12), 2613−2619.

(69) Leibfarth, F. A.; Hawker, C. J. The Emerging Utility of Ketenes in Polymer Chemistry. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 3769−3782.

(70) Frey, H.; Johann, T. Celebrating 100 Years of "Polymer Science": Hermann Staudinger's 1920 Manifesto. *Polym. Chem.* **2020**, *11* (1), 8−14.

(71) Lyman, D. J. Polyurethanes. I. The Solution Polymerization of Diisocyanates with Ethylene Glycol. *J. Polym. Sci.* **1960**, *45* (145), 49−59.

(72) Shashoua, V. E. The Homopolymerization of Monoisocyanates. *J. Am. Chem. Soc.* **1959**, *81* (12), 3156−3156.

(73) Sardon, H.; Pascual, A.; Mecerreyes, D.; Taton, D.; Cramail, H.; Hedrick, J. L. Synthesis of Polyurethanes Using Organocatalysis: A Perspective. *Macromolecules* **2015**, *48* (10), 3153−3165.

(74) Sharmin, E.; Zafar, F. *Polyurethane: An Introduction*; IntechOpen, 2012.

(75) Lu, S.; Xing, J.; Zhang, Z.; Jia, G. Preparation and Characterization of Polyurea/Polyurethane Double-Shell Microcapsules Containing Butyl Stearate Through Interfacial Polymerization. *J. Appl. Polym. Sci.* **2011**, *121* (6), 3377−3383.

(76) Luo, Q.; Wang, Y.; Chen, Z.; Wei, P.; Yoo, E.; Pentzer, E. Pickering Emulsion-Templated Encapsulation of Ionic Liquids for Contaminant Removal. *ACS Appl. Mater. Interfaces* **2019**, *11* (9), 9612−9620.

(77) Li, H.; Feng, Y.; Cui, Y.; Ma, Y.; Zheng, Z.; Qian, B.; Wang, H.; Semenov, A.; Shchukin, D. Polyurea/Polyaniline Hybrid Shell Microcapsules Loaded with Isophorone Diisocyanate for Synergetic Self-Healing Coatings. *Prog. Org. Coat.* **2020**, *145*, 105684.

(78) Shashoua, V. E.; Sweeny, W.; Tietz, R. F. The Homopolymerization of Monoisocyanates. *J. Am. Chem. Soc.* **1960**, *82* (4), 866−873.

(79) Okamoto, Y.; Nagamura, Y.; Hatada, K.; Khatri, C.; Green, M. M. An Unexpected Chiral Spiro Tetramer Offers Mechanistic Insight into an Improved Sodium Cyanide Initiated Polymerization of N-Hexyl Isocyanate in Toluene. *Macromolecules* **1992**, *25* (20), 5536−5538.

(80) Natta, G.; DiPietro, J.; Cambini, M. Crystalline Polymers of Phenyl- and n-Butylisocyanates. *Makromol. Chem.* **1962**, *56* (1), 200−207.

(81) King, C. Cyclopolymerization of Alipahatic 1,2-Diisocyanates. *J. Am. Chem. Soc.* **1964**, *86* (3), 437−440.

(82) Iwakura, Y.; Uno, K.; Ichikawa, K. Cyclopolymerization of a, w-Polymethylene Diisocyanates. *J. Polym. Sci., Part A: Gen. Pap.* **1964**, *2* (8), 3387−3404.

(83) Butler, G. B. Cyclopolymerization and Cyclocopolymerization. *Acc. Chem. Res.* **1982**, *15* (11), 370−378.

(84) Lee, J. S.; Ryu, S. W. Anionic Living Polymerization of 3-(Triethoxysilyl)Propyl Isocyanate. *Macromolecules* **1999**, *32* (6), 2085−2087.

(85) Shin, Y. D.; Ahn, J. H.; Lee, J. S. Anionic Polymerization of Isocyanates with Optical Functionalities. *Polymer* **2001**, *42* (19), 7979−7985.

(86) Shin, Y. D.; Kim, S. Y.; Ahn, J. H.; Lee, J. S. Synthesis of Poly(n-Hexyl Isocyanate) by Controlled Anionic Polymerization in the Presence of NaBPh4. *Macromolecules* **2001**, *34* (8), 2408−2410.

(87) Chae, C.-G.; Seo, H.-B.; Bak, I.-G.; Lee, J.-S. Synthesis of Amphiphilic Helix-Coil-Helix Poly(3- (Glycerylthio)Propyl Isocyanate)-Block-Polystyrene-Block-Poly(3- (Glycerylthio)Propyl Isocyanate). *Macromolecules* **2018**, *51* (3), 697−704.

(88) Zorba, G.; Vazaios, A.; Pitsikalis, M.; Hadjichristidis, N. Anionic Polymerization of N-Hexyl Isocyanate with Monofuctional Initiators. Synthesis of Well-Defined Diblock Copolymers with Styrene and Isoprene. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43* (16), 3533−3542.

(89) Ahn, J. H.; Shin, Y. D.; Nath, G. Y.; Park, S. Y.; Rahman, M. S.; Samal, S.; Lee, J. S. Unprecedented Control over Polymerization of N-Hexyl Isocyanate Using an Anionic Initiator Having Synchronized Function of Chain-End Protection. *J. Am. Chem. Soc.* **2005**, *127* (12), 4132−4133.

(90) Min, J.; Yoo, H. S.; Shah, P. N.; Chae, C. G.; Lee, J. S. Enolate Anionic Initiator, Sodium Deoxybenzoin, for Leading Living Natures by Formation of Aggregators at the Growth Chain Ends. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51* (8), 1742−1748.

(91) Min, J.; Shah, P. N.; Ahn, J. H.; Lee, J. S. Effects of Different Reactive Oxyanionic Initiators on the Anionic Polymerizaition of N-Hexyl Isocyanate. *Macromolecules* **2011**, *44* (9), 3211−3216.

(92) Jang, Y. H.; Lansac, Y.; Kim, J. K.; Yoo, H. S.; Chae, C. G.; Choi, C. H.; Samal, S.; Lee, J. S. Dual Function of a Living Polymerization Initiator through the Formation of a Chain-End-Protecting Cluster: Density Functional Theory Calculation. *Phys. Chem. Chem. Phys.* **2014**, *16* (45), 24929−24935.

(93) Patten, T. E.; Novak, B. M. Living" Titanium(IV) Catalyzed Coordination Polymerizations of Isocyanates. *J. Am. Chem. Soc.* **1991**, *113* (13), 5065−5066.

(94) Patten, T. E.; Novak, B. M. Organotitanium(IV) Compounds as Catalysts for the Polymerization of Isocyanates: The Polymerization of Isocyanates with Functionalized Side Chains. *Macromolecules* **1993**, *26* (3), 436−439.

(95) Patten, T. E.; Novak, B. M. Living Organotitanium(IV)-Catalyzed Polymerizations of Isocyanates. *J. Am. Chem. Soc.* **1996**, *118* (8), 1906−1916.

(96) Hoff, S. M.; Novak, B. M. Complex Architectures through Living Polymerizations. The Synthesis of "Once-Broken Worms" and Triblock Copolymers Using Bimetallic Initiators. *Macromolecules* **1993**, *26* (15), 4067−4069.

(97) Touris, A.; Kostakis, K.; Mourmouris, S.; Kotzabasakis, Y.; Pitsikalis, M.; Hadjichristidis, N. Complex Macromolecular Archi-

tectures Based on N-Hexyl Isocyanate and ε-Caprolactone Using Titanium-Mediated Coordination Polymerization. *Macromolecules* **2008**, *41* (7), 2426−2438.

(98) Goodson, S. H.; Novak, B. M. Synthesis and Characterization of Wormlike Three-Arm Poly(n-Hexyl Isocyanate) Star Polymers. *Macromolecules* **2001**, *34* (12), 3849−3855.

(99) Patten, T. E.; Novak, B. M. Organotitanium(IV)-Catalyzed Cyclopolymerizations of 1,2-Diisocyanates and Cyclocopolymerizations of Monoisocyanates with 1,2-Diisocyanates. *Macromolecules* **1996**, *29* (18), 5882−5892.

(100) Goodman, M.; Chen, S. Optically Active Polyisocyanates. *Macromolecules* **1970**, *3* (4), 398−402.

(101) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. A Helical Polymer with a Cooperative Response to Chiral Information. *Science (Washington, DC, U. S.)* **1995**, *268* (5219), 1860−1866.

(102) Maeda, K.; Okamoto, Y. Synthesis and Conformation of Optically Active Poly(Phenyl Isocyanate)s Bearing an ((S)-(R-Methylbenzyl)Carbamoyl) Group. *Macromolecules* **1998**, *31* (4), 1046−1052.

(103) Green, M. M.; Khatri, C. A.; Reidy, M. P.; Levon, K. Dilute-Solution Chiral Optical Changes Signal the Thermally Reversible Gelation of Poly(n-Hexyl Isocyanate) in Hydrocarbon Solvents. *Macromolecules* **1993**, *26* (17), 4723−4725.

(104) Maxein, G.; Mayer, S.; Zentel, R. Structure-Property Relations in Cholesteric Networks from Chiral Polyisocyanates. *Macromolecules* **1999**, *32* (18), 5747−5754.

(105) Itou, T.; Teramoto, A. Isotropic-Liquid Crystal Phase Equilibrium in Solutions of Semiflexible Polymers: Poly(Hexyl Isocyanate). *Macromolecules* **1988**, *21* (7), 2225−2230.

(106) Aharoni, S. M. Rigid Backbone Polymers. 2. Polyisocyanates and Their Liquid-Crystal Behavior. *Macromolecules* **1979**, *12* (1), 94−103.

(107) Iwakura, Y.; Uno, K.; Kobayashi, N. Polymerization of Isocyanates. III. Chemical Behavior and Structure of Polyisocyanates. *J. Polym. Sci., Part A-1: Polym. Chem.* **1968**, *6* (5), 1087−1096.

(108) Rivera-Fuentes, P.; Diederich, F. Allenes in Molecular Materials. *Angew. Chem., Int. Ed.* **2012**, *51* (12), 2818−2828.

(109) Weinstein, B.; Fenselau, A. Oligomers of Allene. Part II. Dimers and Trimers Formed in the Thermal Polymerisation of Liquid Allene. *J. Chem. Soc. C* **1967**, 368−372.

(110) Weinstein, B.; Fenselau, A. H. Oligomers of Allene. III. Tetramers Formed in the Thermal Polymerization of Liquid Allene. *J. Org. Chem.* **1967**, *32* (7), 2278−2283.

(111) Dai, S. H.; Dolbier, W. R. Oligomerization and Co-Oligomerizations of Allene. *J. Org. Chem.* **1972**, *37* (7), 950−955.

(112) Takahashi, T.; Yokozawa, T.; Endo, T. Cationic Polymerization of Methoxyallene with Lewis Acids. *Makromol. Chem.* **1991**, *192* (5), 1207−1212.

(113) Takahashi, T.; Yokozawa, T.; Endo, T. Cationic Polymerization of Gamma-Methyl- and Alpha-Methylphenylallene. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 583−587.

(114) Yokozawa, T.; Tanaka, M.; Endo, T. Radical Polymerization of Alkoxyallenes. *Chem. Lett.* **1987**, *16* (9), 1831−1834.

(115) Suzuki, M.; Takao, T.; Sakamoto, N.; Tomita, I.; Endo, T. Ni-Catalyzed Living Coordination Polymerization of Allenes Having Si-Based Functional Groups. *Polym. J.* **1999**, *31*, 1021−1024.

(116) Taguchi, M.; Tomita, I.; Yoshida, Y.; Endo, T. Block Copolymerization of Allene Derivatives with 1,3□Butadiene by Living Coordination Polymerization with □-Allylnickel Catalyst. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37* (21), 3916−3921.

(117) Kanbayashi, N.; Ikegami, J.; Kataoka, Y.; Okamura, T. A.; Onitsuka, K. Cyclocopolymerization Based on Alternating Insertions of Isocyanide and Allene Units into a Palladium-Carbon Bond. *Macromolecules* **2018**, *51* (15), 6092−6098.

(118) Endo, T.; Takagi, K.; Tomita, I. Design and Synthesis of Polymerizable Cumulated Double Bond System. - Living Coordination Polymerization of Alkylallenes by □-Allylnickel Catalyst-. *Tetrahedron* **1997**, *53* (45), 15187−15196.

(119) Takagi, K.; Tomita, I.; Endo, T. Living Coordination Polymerization of Alkylallenes by π-Allylnickel Catalyst: Observation of an Extremely High Polymerizability of 1,2-Cyclononadiene. *Chem. Lett.* **1997**, *26*, 1187−1188.

(120) Choi, J. C.; Osakada, K.; Yamaguchi, I.; Yamamoto, T. Polymerization of Arylallenes Catalyzed by Organo-Rhodium(I) and -Cobalt (I) Complexes to Give Structurally Regulated High-Mass Polymers. *Appl. Organomet. Chem.* **1997**, *11* (12), 957−961.

(121) Takagi, K.; Tomita, I.; Endo, T. A Novel Living Coordination Polymerization of Phenylallene Derivatives by π-Allylnickel Catalyst. *Macromolecules* **1997**, *30* (24), 7386−7390.

(122) Lin, F.; Liu, Z.; Wang, T.; Cui, D. Highly 2,3-Selective Polymerization of Phenylallene and Its Derivatives with Rare-Earth Metal Catalysts: From Amorphous to Crystalline Products. *Angew. Chem., Int. Ed.* **2017**, *56* (46), 14653−14657.

(123) Tomita, I.; Kondo, Y.; Takagi, K.; Endo, T. A Novel Living Coordination Polymerization of Alkoxyallenes by a Pi-Allylnickel Catalyst. *Acta Polym.* **1995**, *46* (6), 432−436.

(124) Tomita, I.; Abe, T.; Takagi, K.; Endo, T. Block Copolymerization of Alkoxyallenes by the Living Coordination System with a □-allylnickel Catalyst. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33* (14), 2487−2492.

(125) Takagi, K.; Tomita, I.; Nakamura, Y.; Endo, T. Living Coordination Polymerization of Alkoxyallenes by π-Allylnickel Catalyst. 2.1 Effect of Anionic Ligands on Polymerization Behavior and Polymer Structure. *Macromolecules* **1998**, *31* (9), 2779−2783.

(126) Kino, T.; Taguchi, M.; Tazawa, A.; Tomita, I. Living Coordination Polymerization of Allene Derivatives in Protic Solvents: Remarkable Acceleration of Polymerization and Increase of 1,2-Polymerization Selectivity. *Macromolecules* **2006**, *39* (22), 7474−7478.

(127) Yamauchi, A.; Shirai, A.; Kawabe, K.; Iwamoto, T.; Wakiya, T.; Nishiyama, H.; Inagi, S.; Tomita, I. Well-Defined Polymer Microspheres Formed by Living Dispersion Polymerization: Precisely Functionalized Crosslinked Polymer Microspheres from Monomers Possessing Cumulated Double Bonds. *NPG Asia Mater.* **2016**, *8*, 1−12.

(128) Sakai, K.; Nishiyama, H.; Inagi, S.; Tomita, I.; Hibi, Y.; Komura, M.; Nose, K.; Iyoda, T. Synthesis of Well-Defined Block Copolymer Composed of Flexible Amphiphilic Poly(Ethylene Glycol) and Hydrophobic Liquid Crystalline Segments by Living Coordination Polymerization of Allene Derivatives and Its Application to Thin Film with Perpendicularly. *J. Polym. Sci.* **2020**, No. January, 1−8.

(129) Havinga, R.; Schors, A.; Visser, J. W. Preparation and Properties of Polyallenes. II. Phase Transitions of Polyallene. *J. Macromol. Sci., Chem.* **1968**, *2* (1), 21−30.

(130) Huisgen, R.; Otto, P. The Mechanism of Dimerization of Dimethylketene. *J. Am. Chem. Soc.* **1968**, *90* (19), 5342−5343.

(131) Elam, E. U. Ketenes. XI. Preparation of β-Lactone Dimer by Dimerization of Dimethylketene in the Presence of Derivatives of Trivalent Phosphorus. *J. Org. Chem.* **1967**, *32* (1), 215−216.

(132) Hasek, R. H.; Clark, R. D.; Elam, E. U.; Martin, J. C. The Chemistry of Dimethylketene Dimer. IV. The Polyester and β-Lactone Dimer of Dimethylketene. *J. Org. Chem.* **1962**, *27* (1), 60−64.

(133) Staudinger, H. Ketene: Uber Additions Und Polymerisationreaktionen Des Dimethylketens. *Helv. Chim. Acta* **1925**, *8* (1), 306−332.

(134) Natta, G.; Mazzanti, G.; Pregaglia, G.; Binaghi, M.; Peraldo, M. Crystalline Polymers of Dimethylketene. *J. Am. Chem. Soc.* **1960**, *82*, 4742−4743.

(135) Pregaglia, G. F.; Binaghi, M.; Cambini, M. Polydimethylketene with Carbon- Oxygen Backbone Stnicture. *Makromol. Chem.* **1963**, *67* (1), 10−30.

(136) Yamashita, Y.; Miura, S.; Nakamura, M. Ambident Nature of the Polydimethylketene Anion. *Makromol. Chem.* **1963**, *68* (1), 31−47.

(137) Natta, G.; Mazzanti, G.; Pregaglia, G.; Binaghi, M. Alternating Copolymers of Dimethylketene with Ketones. *J. Am. Chem. Soc.* **1960**, *82* (20), 5511−5512.

(138) Natta, G.; Mazzanti, G.; Pregaglia, G. F.; Pozzi, G. Alternating Copolymers Having a Stereoregular Polyester Structure. *J. Polym. Sci.* **1962**, *58* (166), 1201−1210.

(139) Tsunetsugu, T.; Arimoto, K.; Fueno, T.; Furukawa, J. Polymerization of Methylphenylketone and Its Copolymerization with Benzaldehyde. *Makromol. Chem.* **1968**, *112* (1), 210−219.

(140) Yamashita, S.; Nunomoto, Y. Polymerizability of Diphenylketene. *Kogyo Kagaku Zasshi* **1968**, *71* (12), 2067−2072.

(141) Dyer, E.; Sincich, E. Anionic Copolymerization of Isocyanates With Ketenes. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11* (6), 1249−1260.

(142) Sudo, A.; Uchino, S.; Endo, T. Development of a Living Anionic Polymerization of Ethylphenylketene: A Novel Approach to Well-Defined Polyester Synthesis. *Macromolecules* **1999**, *32* (5), 1711−1713.

(143) Sudo, A.; Uchino, S.; Endo, T. Application of Ketenes to Well-Defined Polyester Synthesis. III. Living Anionic Polymerization of Ethyl(4-Methoxyphenyl)Ketene—Development of Polyester Having Masked Phenol Side Chain. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39* (10), 1596−1600.

(144) Hayki, N.; Desilles, N.; Burel, F. Polyester Obtained by Anionic Polymerization of Ethylketene. *Macromol. Chem. Phys.* **2011**, *212* (4), 375−382.

(145) Nagai, D.; Sudo, A.; Endo, T. Stereocontrolled Anionic Alternating Copolymerization of Ethylphenylketene with Benzaldehyde by a Bisoxazoline Ligand. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42* (21), 5384−5388.

(146) Nagai, D.; Sudo, A.; Endo, T. Anionic Alternating Copolymerization of Ketene and Aldehyde: Control of Enantioselectivity by Bisoxazoline-Type Ligand for Synthesis of Optically Active Polyesters. *Macromolecules* **2006**, *39* (26), 8898−8900.

(147) Egret, H.; Couvercelle, J. P.; Belleney, J.; Bunel, C. Cationic Polymerization of Dimethyl Ketene. *Eur. Polym. J.* **2002**, *38* (10), 1953−1961.

(148) Tidwell, T. T. *Ketenes II*, 2nd ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2006.

(149) Xiang, Y.; Burrill, D. J.; Bullard, K. K.; Albrecht, B. J.; Tragesser, L. E.; McCaffrey, J.; Lambrecht, D. S.; Pentzer, E. Polymerization of Silyl Ketenes Using Alkoxide Initiators: A Combined Computational and Experimental Study. *Polym. Chem.* **2017**, *8* (35), 5381−5387.

(150) Xiang, Y.; Rheingold, A. L.; Pentzer, E. B. Synthesis of Highly Functionalized 2-Pyranone from Silyl Ketene. *ACS Omega* **2018**, *3* (8), 9419−9423.

(151) Xiang, Y.; Mitchell, S.; Rheingold, A. L.; Lambrecht, D. S.; Pentzer, E. Oligomerization of Silyl Ketene: Favoring Chain Extension over Backbiting. *Macromolecules* **2019**, *52* (16), 6126−6134.

(152) Mitchell, S. M.; Xiang, Y.; Matthews, R.; Amburgey, A. M.; Pentzer, E. B. Lewis Acid-Activated Reactions of Silyl Ketenes for the Preparation of α-Silyl Carbonyl Compounds. *J. Org. Chem.* **2019**, *84* (22), 14461−14468.