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Highlight Review

Recent Progress in Living Cationic Polymerization of Vinyl Ethers

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Abstract

Recent advancements in living cationic polymerization of vinyl ethers are reviewed, especially focusing on newly developed initiating systems using various Lewis acid catalysts. In concert with the diversification of efficient metal halide catalysts, several types of initiators (cationogens) have been shown to mediate living polymerization, in which the nature of the central metals is responsible for the polymerization behavior. Other types of initiating systems, e.g., living cationic polymerization using metal oxides as solid catalysts and Lewis acid-free systems, are also summarized, as well as the applications of the polymerization for the synthesis of functional poly(vinyl ether)s.

◆ Introduction

Living polymerization, first achieved for anionic polymerization of styrene in 1956,[1] is the principal method for the synthesis of well-defined polymers. Living cationic polymerization (Figure 1) was developed in 1984 for isobutyl vinyl ether (IBVE) with the HI/I_2 system of Higashimura et al.[2] and in 1986 for isobutene with the tertiary ester/BCl_3 system of Kennedy et al.[3] The basic concept for control of polymerization is to construct a dormant–active equilibrium where the concentration of the propagating cationic species (active species) is kept much lower than that of the covalently bonded species (dormant species).[4] The instability of the propagating carbocation requires forcibly moderating reaction conditions to induce the equilibrium. This is different from living anionic polymerization, which is mediated by a relatively stable carbanion satisfying the octet rule. A variety of systems have been established for living cationic polymerization, as shown in Scheme 1 [only those for the polymerization of vinyl ethers (VEs) are listed], and are now categorized into three main methods: control by (i) nucleophilic counteranions, (ii) added weak Lewis bases such as esters or ethers, and (iii) added salts including quaternary ammonium salts.

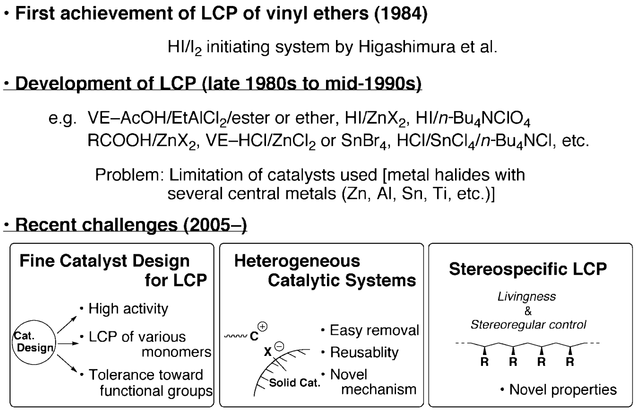
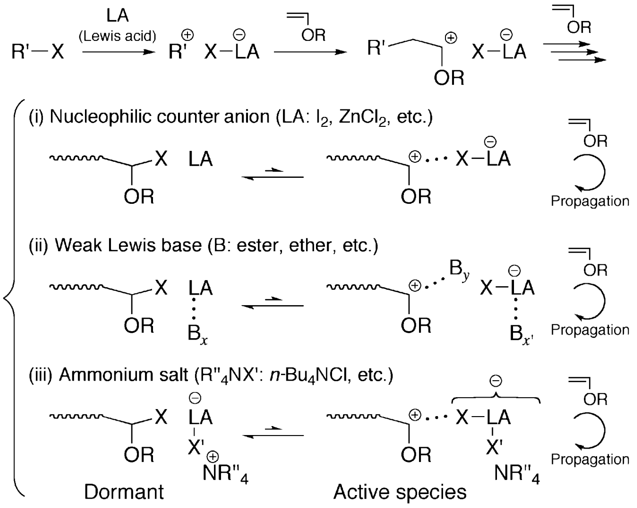


Figure 1. Developments and challenges in living cationic polymerization (LCP) of vinyl ethers.



Scheme 1. Methods leading to living cationic polymerization of vinyl ethers: control by (i) a nucleophilic counteranion, (ii) a weak Lewis base, and (iii) an ammonium salt.

Alkyl VE can be polymerized to give high molecular weight polymers only by cationic processes (except for radical alternating copolymerization with electron-deficient monomers such as maleic anhydride). Coordination polymerization has also been examined using complexes with late-transition metals, but undesired reactions (β-OR elimination) and/or intercurrent cationic polymerization preclude its control.[5] In addition to the industrial importance of poly(VE)s as adhesives or coating materials, those with various functional side chains such as oxyethylene, carboxy, and azo groups have recently been attracting much attention as smart materials.[6] The synthesis of such polymers with well-regulated primary structures is critical for the precise control of their properties.

Living cationic polymerization of VEs presents several challenges, as shown in Figure 1, including the diversification of the initiating systems. New initiating systems should contribute

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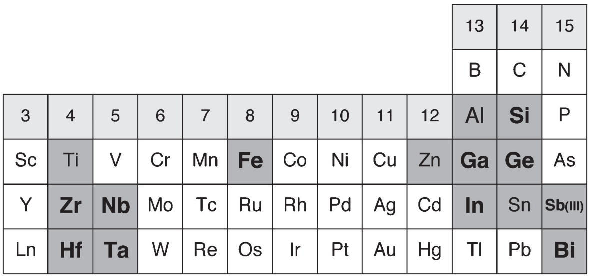


										13	14	15
										B	C	N
3	4	5	6	7	8	9	10	11	12	Al	**Si**	P
Sc	Ti	V	Cr	Mn	**Fe**	Co	Ni	Cu	Zn	**Ga**	**Ge**	As
Y	**Zr**	**Nb**	Mo	Tc	Ru	Rh	Pd	Ag	Cd	**In**	Sn	**Sb(III)**
Ln	**Hf**	**Ta**	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	**Bi**

Figure 2. Central metals of metal halides used for living cationic polymerization of vinyl ethers (shaded elements; bold ones: recent achievements).

to producing novel functional polymers if those systems have features such as tolerances toward various polar functional groups and improved activities. In addition, there were no initiating systems using solid acid catalysts for living cationic polymerization. Heterogeneous catalysts are especially useful for their removability and reusability. Improvement of the regularity in stereospecific polymerization and the development of stereospecific living cationic polymerization are also attractive issues in this field.

In this highlight review, we will discuss recent progress in initiating systems for living cationic polymerization of VEs. Particular attention will be paid to newly developed systems using various Lewis acid catalysts and the accompanying diversification of effective initiators (cationogens).

◆ *New Phases in Catalyst Development: Explosive Growth of Available Metal Halides for LCP*

After the first achievement of living cationic polymerization of VEs by HI/I_2, several kinds of metal halides (MX_n; M: Zn, Al, Sn, and Ti) were used as catalysts (Figure 2).[4,7–9] In attempting to produce well-regulated stimuli-responsive poly(VE)s with functional pendant chains, our group noticed the superiority of $SnCl_4$ to Et_xAlCl_{3-x} ($x = 1$ or 1.5) in terms of catalytic activity in the presence of an added base.[10] The "rediscovery" of the conventional but competent Lewis acid spurred us to investigate the possibility of living polymerization with various metal halides.

Rigorous research revealed that diverse metal halides induced living cationic polymerization of IBVE in conjunction with IBVE–HCl adduct as a cationogen (Figure 2).[11] Most of the metal halides require additives for well-controlled reactions, and some of them exhibit their preference for additives. A classification of the Lewis acids based on their suitable additives is listed in Figure 3. Polymerizations using catalysts including $FeCl_3$ and $GaCl_3$ are controlled in combination with an added weak Lewis base, ester or ether, whereas those such as $NbCl_5$ and $TaCl_5$ require an added salt (tetraalkylammonium halide) for control. Since the latter two are pentachlorides, their chemistry is likely to be related to the stability of the hexachloride anions generated via the abstraction of the initiating/propagating end chlorine atoms. Both a weak Lewis base and an added salt were efficient for living polymerization using $SnCl_4$ and $TiCl_4$, although $SnCl_4$ was also reported to induce controlled reactions without an additive under some conditions.[12,13]

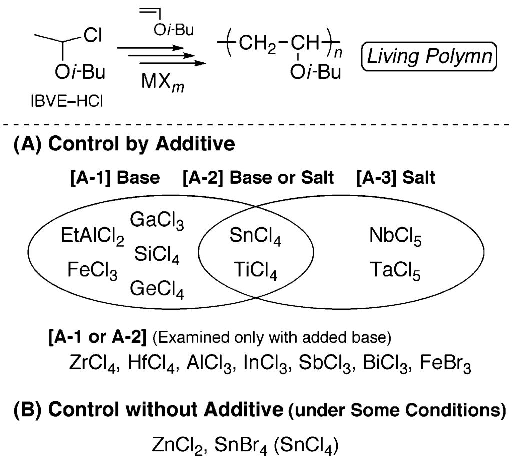


Figure 3. Classification of metal halides for living cationic polymerization of vinyl ethers.

The large difference in activity among the metal halides is also an important feature. Very fast living polymerization completed in seconds was induced by $FeCl_3$ in the presence of a cyclic ether with a suitable basicity,[14] which is similar to the case of the $SnCl_4$/ethyl chloroacetate system.[15] In contrast, a reaction using $SiCl_4$ or $GeCl_4$ requires more than several weeks under similar polymerization conditions. Polymerization activities in the presence of a weak Lewis base are closely related to the balance between the interactions with the chlorine atoms (chloride anion) of the initiating/propagating ends (chlorophilicity) and the interactions with the basic oxygen atoms of Lewis bases (oxophilicity). Similar trends are found in comparison of Lewis acidity based on spectroscopic techniques and organic reactions.[16–18] HSAB theory[19] also explains the trends among metals in the same group: the lower a metal (a softer acid) is in the periodic table, the stronger is the interaction with the chloride anion (a softer base compared to the oxygen atom).

The diversification in efficient metal halide catalysts expands the availability of living cationic polymerization, e.g., polymerization of monomers with various functional groups, initiations from various cationogens as described in the following section, and synthesis of polymers with unique primary structures. A new index for the nature of Lewis acids may also be established based on these polymerization behaviors. In addition, other metal halides which have not been examined due to their poor solubility in polymerization solvents can surely be utilized by modifying the ligands to exhibit novel features.

◆ *Quest for New Initiators (Cationogens)*

In general, highly efficient and rapid initiation reactions, indispensable for living cationic polymerization, are achieved by strong protic acids (HCl, HI, carboxylic acids, phosphoric acids, etc.) or their adducts with VE (Figure 4).[4] The carbon–heteroatom bonds of in situ formed or prepared adducts are easily cleaved to generate a carbocation with the help of a Lewis acid catalyst. However, these cationogens possess disadvantages such as corrosiveness, toxicity, and/or require troublesome synthesis.

Despite the drawbacks of existing cationogens, development of suitable cationogens for controlled reaction of VEs has long

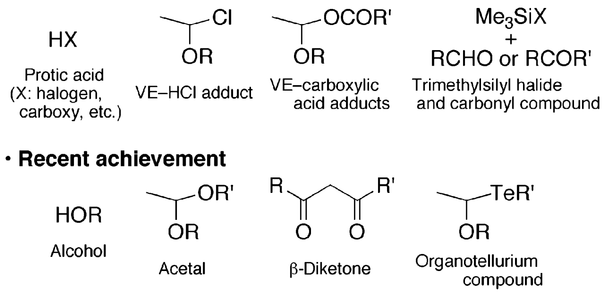
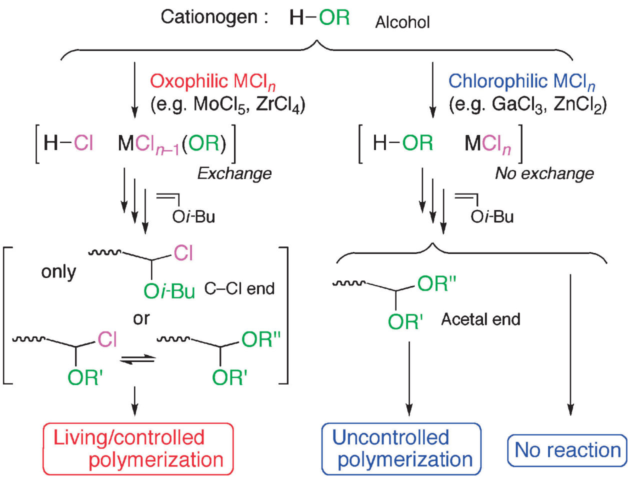


Figure 4. Cationogens (initiators) for living cationic polymerization of vinyl ethers.



Scheme 2. Cationic polymerization using alcohol as cationogen.

been considered to be a closed matter. This invisible wall was broken by several recent studies on living polymerization using uncommon cationogens. Simple alcohols, less acidic hence much easier to handle, were recently shown to function as good cationogens for living cationic polymerization of VEs.[20,21] Suitable metal chlorides were crucial for the controlled reactions, i.e., the polymerization behaviors were categorized into three main groups depending on the metal chloride used: (i) living/controlled polymerization mediated by living/long-lived species, (ii) uncontrolled polymerization, and (iii) no reaction. The differences were attributed to the types of the propagating species (Scheme 2), which were suggested by the in situ ^{1}H NMR analysis of the polymerization media. With $NbCl_5$ or $ZrCl_4$, both of which catalyzed well-controlled reactions in conjunction with alcohols, only C–Cl ends or both C–Cl and acetal ends, respectively, were observed during the polymerizations using methanol as a cationogen. The MALDI-TOF-MS analysis of the product polymers also supported their existence. In contrast, only acetal ends were present in a reaction mixture using a Lewis acid that induced uncontrolled polymerization, i.e., $GaCl_3$. Thus, the generation of the C–Cl propagating ends is indispensable for controlled reactions. The bonds stem from the exchange between the chloride anion of a metal chloride and the alkoxy group of an alcohol to generate the alkoxy-modified metal chloride and HCl (or the adduct of VE and HCl). The balance between the oxophilicity and the chlorophilicity of the metal chlorides is possibly related to the occurrence of the exchange reactions. It should be noted that the reaction using $ZrCl_4$ proceeded in an unprecedented fashion, where the two types of propagating species were involved but the polymers had very narrow molecular weight distributions (MWDs). In addition, the alcohol-mediated systems will be surely applied as easy catalyst modification methods.

Living polymerization of VEs using alcohols is also reported based on another concept. A combination of $BF_3{\cdot}OEt_2$ and Me_2S induces living polymerization in conjunction with various alcohols as cationogens, in which no exchange reaction occurs.[22] This is different from the metal chloride systems. The easy abstraction of the alkoxy groups by the boron catalyst and the strong stabilization of the propagating carbocations by the sulfide result in controlled reactions.

Polymerization of VEs using acetals, which are regarded as adducts of VE with alcohols, proceeded in similar manners to those using alcohols when combined with appropriate metal chlorides[23] (living polymerization using acetals/trimethylsilyl iodide/$ZnCl_2$ or ZnI_2 has been achieved by transforming the carbon–alkoxy bond into a carbon–iodine one[24]). Star-shaped polymers were also produced quantitatively by activating the acetal ends of separately prepared poly(VE)s and subsequent polymer-linking reactions using divinyl monomers.

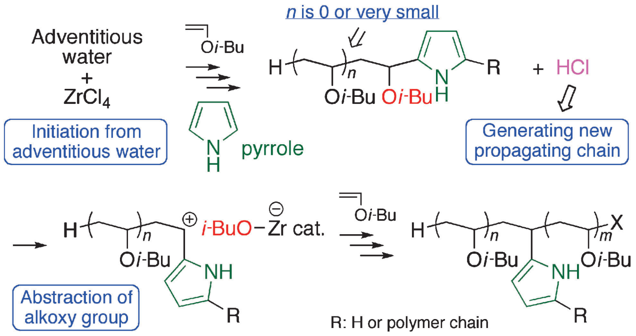
Similar initiation reactions occur with β-diketones such as acetylacetone.[25] Metal chlorides, including $SnCl_4$, react with acetylacetone in a one-to-one ratio to exchange the chloride anion with the acetylacetonate (acac) group. The reaction results in the generation of HCl and subsequent living cationic polymerization catalyzed by the acac-complex [living polymerization using HI/M(acac)$_n$ (M: Zn, Fe, and Al) was reported in the 1990s[26]]. The strong coordination ability of the acac group also enables the exchange of Lewis acids with large chlorophilicities, such as $GaCl_3$ and $FeCl_3$, which induce no exchange reaction with alcohols,[20] to mediate controlled reactions.

Organotellurium compounds, which have been shown to act as mediators for living radical polymerization,[27] have also been found to function as good cationogens for cationic polymerization.[28] In combination with a metal triflate, $In(OTf)_3$, living polymerization of IBVE proceeds by scission of the carbon–tellurium bonds of the initiating/propagating ends. The softness of the tellurium atom is possibly responsible for the controlled reactions in the absence of additives.

Chain Multiplying Controlled Polymerization Using Pyrrole

Controlled reactions using the above-mentioned cationogens containing oxygen atoms indicated the possibility of compounds with other heteroatoms as similar cationogens. Pyrrole, a heteroaromatic compound possessing a nitrogen–hydrogen bond, has a smaller pK_a value (23.0) than that of methanol (29.0) in DMSO,[29] although the compound is also reported to show nucleophilicity large enough to function as a quencher for the cationic polymerization of isobutene.[30,31] Thus, cationic polymerization of VEs using pyrrole in conjunction with various metal chlorides was examined.

With a few kinds of metal chlorides, such as $ZrCl_4$, cationic polymerization of IBVE using pyrrole proceeded in a controlled fashion to produce polymers with narrow MWDs and the M_n



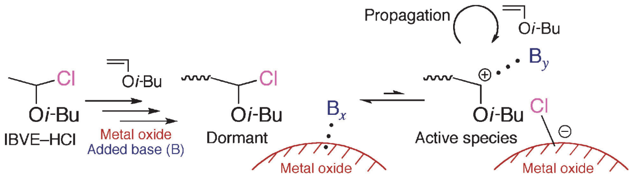
Scheme 3. Chain multiplying controlled cationic polymerization using pyrrole as "initiator-like" chain transfer agent.

values expected from the amount of pyrrole used.[32] However, no acid generation was confirmed in the reaction between pyrrole and the Lewis acid. The polymerization was initiated not from pyrrole but from adventitious water which could not be completely removed (Scheme 3). Pyrrole reacts with the propagating carbocation at its 2- and 5-positions smoothly, accompanying the emission of HCl. In addition to the generation of a new propagating chain from the HCl molecule, further reactions also proceed from the resulting chain ends with alkoxy and pyrrolyl groups via the activation of the carbon–alkoxy bond. Such a role of pyrrole as an unusual transfer agent, where one reaction between the carbocation and pyrrole produces two propagating species, resulted in cationogen-like behavior. This polymerization method, mechanisms of which involve the activation of the VE-side chains, can be a tool for the synthesis of polymers with novel architectures.

◆ Heterogeneous Living Cationic Polymerization Using Metal Oxides

Heterogeneous catalysts show great ability in their removal, reuse, and possibility of stereospecific reactions. Some of their merits also satisfy recent demands for environmentally friendly chemistry. However, no living cationic polymerization had been reported with heterogeneous catalysts, although there were a number of papers describing (nonliving) cationic polymerization using solid acids such as metal oxides,[33] metal sulfate–sulfuric acid complexes,[34,35] Ziegler-type catalysts,[36] and heteropolyacids.[37]

Successful heterogeneous living cationic polymerizations of VE were first demonstrated using several metal oxides coupled with suitable additives (Figure 5).[38,39] In the presence of a weak Lewis base (ester or ether), α-Fe_2O_3, a main component of red rust, catalyzed living polymerization of IBVE in conjunction with IBVE–HCl, to give polymers with very narrow MWDs ($M_w/M_n = 1.03$–1.1).[38] Furthermore, the catalyst was removed by centrifugation and could be reused as a living polymerization catalyst at least five times after simple washing and drying. Other types of iron oxides, γ-Fe_2O_3 and Fe_3O_4, also induced controlled reactions. In contrast to these catalysts, polymers with bimodal MWDs whose lower peaks were derived from long-lived species were produced with oxides containing other metals, such as Ga_2O_3, In_2O_3, and ZnO even in the presence of a weak Lewis base.[39] The combined use of another additive, *n*-Bu_4NCl or a pyridine derivative with bulky substituents, suppressed the production of the uncontrolled portions with higher molecular weight to induce controlled reactions.



Metal Oxide	Polymerization Behavior
α-Fe_2O_3, γ-Fe_2O_3, Fe_3O_4	Control by Weak Lewis Base
Ga_2O_3, In_2O_3, ZnO	Control by Both Weak Lewis Base and Ammonium Salt or Bulky Pyridine Derivative
Co_3O_4, Bi_2O_3	Bimodal MWDs (Including Long-lived Species)
Al_2O_3, ZrO_2, Nb_2O_5	No Polymerization

Figure 5. Living cationic polymerization using metal oxides: the polymerization behavior and the possible mechanism.

The mechanisms for the polymerization with metal oxides have not yet been revealed in detail (Figure 5). Only a small part of the catalyst, such as an edge and a corner or some nanosized electronically unsaturated particles, may be responsible for the catalytic activity, considering the polymerization results in the presence of a very small amount of a chloride anion donor (*n*-Bu_4NCl) or the effect of stirring on the polymerization rate.[39]

◆ Lewis Acid-free Initiating Systems

The first example of Lewis acid-free initiating systems was the combination of a very strong protic acid [trifluoromethanesulfonic acid (TfOH)] with a sulfide at low temperatures (−15–−40 °C).[40] In this system, the growing end is stabilized by the formation of a sulfonium salt from a carbocation and a sulfide as the dormant species. The strong interaction of the sulfur atom with the carbocation is the key to achieving living polymerization. A recent surprising case was the well-defined reactions of VEs with a combination of a less acidic protic acid and a weaker stabilizer, i.e., HCl and an aliphatic ether.[41] The aliphatic ether is proposed to assist the dissociation of HCl, in addition to stabilizing the propagating carbocations.[4,8]

Heteropolyacids, solid protic acids with large counteranions, can also mediate Lewis acid-free living cationic polymerization at low temperature (−30 °C) in the presence of a sulfide,[42] as is the case with the TfOH system.[40] The polymerization solvent was the decisive factor for inducing controlled reactions. In a polar and relatively basic solvent such as ethyl acetate, polymers with M_n values calculated assuming that all the protons initiated the polymerization were produced, in contrast to reactions in nonpolar and/or nonbasic solvents such as toluene and dichloromethane, which gave higher molecular weight polymers with obvious tailings in the GPC curves. This is possibly because the solid acid was swollen with the help of the solvent and the polymerization proceeded in a pseudoliquid phase.[43]

Controlled cationic polymerization of VEs using a strong protic acid or a "cation-pool" as an initiator has also been achieved with a microflow system.[44] The fast mixing of an initiator and a monomer and the efficient liberation of the reaction heat gave polymers with expected molecular weights and narrow MWDs, whereas the same components produced ill-defined polymers in a conventional batch system. This process is capable of producing block copolymers by successive mixing of the second monomer.

♦ Possible Indication of Stereospecific Living Cationic Polymerization

One challenging but attractive issue in cationic polymerization of vinyl monomers is the complete control of stereoregularity. The highest stereoregulation ever achieved in cationic polymerization of VE is by a system with $TiCl_2(OAr)_2$, which gives poly(IBVE) with *m* value of 92%.[45] The value is not comparable to poly(methacrylate)s or poly(olefin)s obtained by anionic or coordination polymerization using designed catalysts, where regulation with more than 99% selectivity is possible. Another challenge in cationic polymerization is dual control of stereoregularity and molecular weight, i.e., stereospecific living polymerization.

Various metal sulfate–sulfuric acid complexes were reported to induce partly stereospecific cationic polymerization of VEs in the 1960s.[34,35] The catalysts produced mixtures of isotactic and atactic chains, although the molecular weights were uncontrolled. Recently, a possible indication of dual control of stereospecificity and molecular weight in polymerization of VEs was shown by a catalytic system using iron(II) sulfate (not as the complex with sulfuric acid).[46] In conjunction with a large amount of *t*-BuOH, the molecular weight of poly(VE)s increased with monomer conversion although the MWDs were broad. A molecular weight shift was also observed in the stereoregulated portion (13 wt %). These results should lead to stereospecific living cationic polymerization.

♦ Recent Progress in Functional Poly(VE)s

Poly(VE)s with functional side chains such as oxyethylene, azo, and carboxy groups exhibit responsive behaviors toward various stimuli (temperature, light, and pH).[6] The well-defined primary structures of polymers obtained by living cationic polymerization are responsible for the high sensitivities. For example, aqueous solutions of poly(VE)s with pendant oxyethylene side chains induce LCST-type phase-separation behaviors in response to subtle change of temperature. In addition, polymers with long alkyl chains, such as octadecyl VE, induce UCST-type phase-separation in various organic solvents. Recently, the remaining types of responsive behaviors, UCST-type phase-separation in aqueous media and LCST-type separations in organic solvents, were achieved with poly(VE)s possessing imidazolium salt structures in their side chains.[47,48] Suitable combinations of the alkyl substituents and the counteranions in the salt structures were crucial for each responsive behavior.

Living cationic polymerization is also utilized to synthesize various polymers with fine architectures, such as block, graft, and gradient copolymers. Star-shaped polymers are obtained by bundling living propagating chains with divinyl monomers, in which crosslinking reactions occur quantitatively to form a well-controlled polymer with a core and many arm chains.[49] Star-shaped polymers with poly(VE) arms with oxyethylene side chains and a hydrophobic core function as good stabilizers for gold nanoclusters.[50] The method to prepare star-shaped polymers was recently applied to a one-pot synthesis of flower-shaped polymers.[51] Crosslinking reactions of living polymers possessing propagating sites at both ends, which are generated from bifunctional initiators, yield a polymer with a core and many loop chains. The adjustment of the concentration of the propagating chains to be low enough to avoid flower–flower coupling reactions resulting in gelation, but high enough for efficient bundling, is essential for a clean synthesis. The polymer with no chain ends is expected to show characteristic behaviors distinguishable from those of star-shaped polymers.

♦ Summary

This highlight review article summarizes recent innovative changes in living cationic polymerization of VEs. The design of new initiating systems with various Lewis acid catalysts and the accompanying diversification of efficient cationogens have been achieved by utilizing the characteristics of the central metals. The combinations of metal halides and compounds with heteroatoms, such as alcohols, indicate a strong possibility toward more elaborate but easily accessible catalyst design for living cationic polymerization with high activity, high tolerance, and high selectivity. In addition, living polymerization using solid catalysts and Lewis acid-free systems are expected to contribute to industrial applications of living cationic polymerization. Developments in this field will not only open up a new avenue for the synthesis of a variety of well-defined polymers as smart materials but also provide a further understanding of the nature of Lewis acid catalysts.

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