Chem. Rev. **2009,** *109,* 5245–5287

A Renaissance in Living Cationic Polymerization

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Received June 22, 2009

Contents

1. Introduction

Cationic polymerization has a long history, and the first research into cationic polymerization on record was con-

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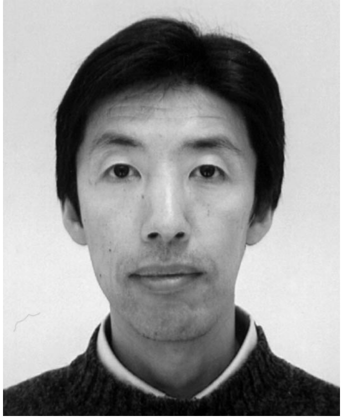
10.1021/cr900225g CCC: $71.50

Sadahito Aoshima is a Professor of Macromolecular Science at Osaka University in Japan. He was born in Mito, Japan, in 1959, and received his B.S. (1981), M.S. (1983), and Ph.D. (1987) degrees in polymer chemistry from Kyoto University under the supervision of Professor Toshinobu Higashimura. After subsequent postdoctoral research with Professor Higashimura, he started his academic carrier at Tokyo University of Science in 1988. During 1993–1994, he spent a year at Cornell University as a visiting scientist, working with Professor Jean M. J. Fréchet. In April 2000, he moved to Osaka University as an Associate Professor and was promoted to a full professorship in October 2000. His recent research interests focus on the development of living cationic polymerization and the precise synthesis of various stimuli-responsive polymers.



Shokyoku Kanaoka was born in Osaka, Japan, in 1965. He studied polymer chemistry at Kyoto University, receiving his B.S. in 1988, his M.S. in 1990, and his Ph.D. in 1993. In graduate school, he worked under the supervision of Professor Toshinobu Higashimura and Professor Mitsuo Sawamoto. After a subsequent postdoctoral appointment at California Institute of Technology, working with Professor Robert H. Grubbs, he joined the faculty at the University of Shiga Prefecture in 1995 as an assistant professor. In 2002, he moved to Osaka University, where he was promoted to associate professor in 2004. His research interests include the development of new initiating systems for living cationic polymerization and the precision synthesis of sequence- and/or shape-controlled polymers with various functional groups, among which star-shaped and multibranched polymers have been the main subjects of his research.

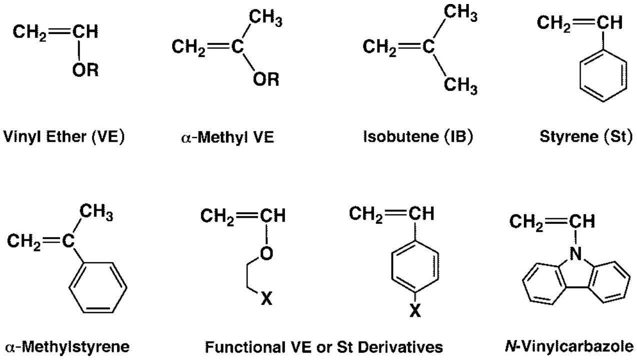
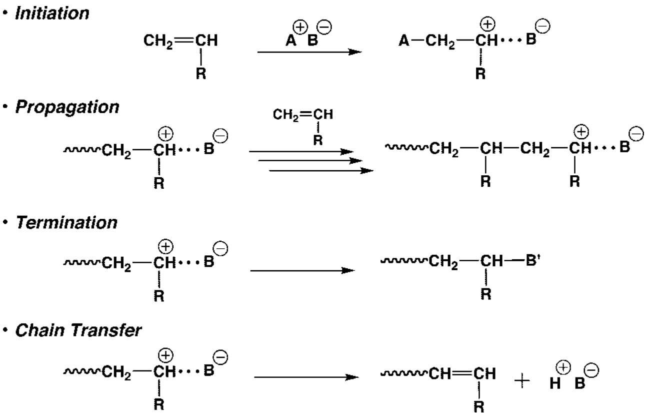


Figure 1. Typical monomers for cationic polymerization.

Scheme 1. Elementary Reactions for Cationic Polymerization



ducted in the late 18th century. Since then, polymerization reactions of various monomers (Figure 1) have been examined, for which numerous types of initiators have been developed.[1−3] It was in the early 20th century that kinetic studies on the polymerization began to be reported.[4] Then considerable research had been performed from different aspects,[1−3,5] including the possibilities of controlling reactions. However, no result demonstrated hope of progress in controlling the reaction until 1960s. In the reactions, highly active and inherently unstable growing species caused a variety of side reactions, such as β-proton elimination (Scheme 1), irrespective of monomers, which appeared too formidable to be overcome. Thus, it came to be considered that controlled reactions in cationic polymerization would be impossible even after living polymerization was first reported in anionic polymerization.[6]

The pessimistic outlook was shattered by the discovery of long-lived cationic species in polymerization of styrene derivatives in the late 1970s.[7,8] Then the unreachable dream turned into a real possibility. Following this event, long-lived species were also observed in the polymerization of vinyl ethers[9] and isobutene.[10] Finally, the first major breakthrough was made in the 1980s by Higashimura and Sawamoto with living polymerization of alkyl vinyl ethers,[11,12] followed by Kennedy and Faust with living polymerization of isobutene.[13,14] The next decade witnessed the vigorous growth of the field of living cationic polymerization. A variety of initiating systems were developed for different types of monomers, and this enthusiasm is well documented elsewhere.[15−19] The discovery of living cationic polymerization brought another revolutionary change in polymer chemistry because the method of keeping originally unstable growing species from undergoing side reactions is now applied to various polymerization mechanisms.

As the momentum of the catalyst development was beginning to wane, precision synthesis of a new class of functional polymers became focused, especially in the 90s. For example, polyisobutene-related polymers were shown to be far superior as elastmers[20,21] and biomaterials.[20,22,23] Similar trends were observed with other monomers. With vinyl ethers, various functional block copolymers and star-shaped polymers were prepared.[24,25] Thus, living cationic polymerization apparently became a tool for precision synthesis of functional polymers with well-defined and complex structures.

However, there was still much to be challenged in living cationic polymerization in terms of the reaction itself, such as polymerization under aqueous conditions; stereoselective polymerization; fast living polymerization, especially for polar functional monomers; and determination of absolute rate constants. Some of those formidable tasks were achieved in the past decade. Since the early development of living cationic polymerization is referred thoroughly elsewhere,[15−19] the first part of this review focuses on recent progress in living polymerization reactions for three types of monomers: vinyl ethers (VE), isobutene (IB), and styrenes (St). Critical studies in the "pre-living" era are also outlined to acquire a better understanding of the reaction mechanisms for various living cationic polymerization systems.

Living cationic polymerization was the first controlled polymerization reaction that permitted precision synthesis of various functional polymers; hence, there are enormous examples of well-defined functional polymers that cannot be highlighted in a single review. Thus, the recent most active areas are outlined here: stimuli-responsive polymers; precise synthesis and properties of sequence controlled polymers (block and star-shaped polymers). In addition, related polymers prepared by other polymerization mechanisms are described for better understanding of the significance of the developments.

2. Historical Background of Living Cationic Polymerization

Before starting this review, we would like to define the terms long-lived, quasiliving, and living to avoid confusion. Although definitions may be varied by authors and may be controversial, we used these three words according to the following definitions. In polymerization with long-lived species, a clear increase in molecular weight against monomer conversion is observed, but noticeable side reactions occur. Thus, a broad molecular weight distribution (MWD) is usually obtained. The relationship between molecular weight and monomer conversion can be either nonlinear or linear. Controlled polymerization is interchangeably used for this type of reaction in the text. Quasiliving is used, especially for isobutene polymerization, in which there is no transfer but only reversible termination. Thus, quasiliving is a better control version among reactions with long-lived species. However, MWDs of product polymers are still relatively broad because of slow initiation. Living is used for the polymerization that produces well-defined polymers with narrow MWDs, which is attained by fast and quantitative initiation and propagation free from permanent termination.

To achieve living cationic polymerization, controlled initiation and propagating steps are essential.[26] After the discovery of living anionic polymerization in the 1950s, critical research on controlled initiation and propagation was performed in cationic polymerization in the "pre-living" era. In retrospect, those studies became the basis of the development of living cationic polymerization of various monomers. Therefore, some critical research is first highlighted briefly in this review.

2.1. Well-Defined Initiation

A clear scheme of initiating reaction in cationic polymerization was first described by Kennedy.[27,28] During his studies on polymerization of IB using Ziegler−Natta related catalysts, Et_2AlCl was shown to polymerize IB only when a small amount of water or a Brönsted acid, such as HCl, was contained in the reaction mixture. It was postulated that protons liberated from water by its reaction with the Lewis acid or released from an acid initiated cationic polymerization of IB. The logical consequence from this result was the use of *tert*-butyl chloride, as an initiator, combined with Et_2AlCl, since *tert*-butyl chloride is regarded as the adduct of IB with HCl. With this initiating system, polymerization also proceeded smoothly. In this case, Et_2AlCl abstracts the chlorine atom of *tert*-butyl chloride, producing a carbocation; hence, it is called a cationogen. The survey of various haloalkanes revealed that *tert*-butyl chloride produced polymers most efficiently.[27] This indicated that the stability of a produced carbocation from a cationogen (haloalkane) affects the polymerization reaction significantly. It would not be an overstatement to say that the study demonstrated a critical strategy for controlled polymerization, because the combinations of a proactive species with a catalyst (activator) are now used not only in living cationic polymerization but also in controlled/living radical polymerization.

2.2. Choice of Counteranion: Selective Dimerization

In order to suppress frequent transfer and/or termination reactions, the choice of counteranions and Lewis acid is very important. A controlled reaction by a counteranion was first demonstrated in selective cationic oligomerization of styrenes.[29] In styrene polymerization, linear and cyclic dimers are accompanied by polymers. The yield of dimers generally reduced in a polar solvent, irrespective of the acid catalyst. In contrast, selective dimerization was observed in a nonpolar solvent when a suitable catalyst was used. For example, the treatment of styrene with acetyl perchlorate yielded linear dimer selectively in benzene at 70 °C.[30,31] Similar trends were observed with several styrene derivatives.[29] In a nonpolar solvent, the strong interaction of the counteranion inhibited propagation. Under these circumstances, the β-proton elimination was promoted at a higher temperature, and selective dimerization proceeded.

2.3. Long-Lived Species: Appropriate Lewis Acid

The importance of the choice of acid catalysts (activator) was shown in cationic polymerization of styrene and its derivatives. It was then known that molecular weight of product polymers became higher when a polar solvent was used. The more dissociated growing species is favorable for a propagating reaction. Thus, Higashimura and co-workers examined cationic polymerization of styrene using various acid catalysts. The polymerization with acetyl perchlorate in dichloromethane gave a polymer with a bimodal molecular weight distribution (MWD).[32] The amount of higher and lower molecular weight fractions increased on increasing the ratio of nitrobenzene and benzene, respectively, to CH_2Cl_2. These results suggested that polymerization proceeded independently from different types of growing chain ends. Bimodal distributions were also observed with product polymers of *p*-methylstyrene and *p*-methoxystyrene (pMOSt) prepared with iodine.[33] Since an electron-donating substituent stabilizes carbocation, it was considered less difficult to suppress side reaction in the pMOSt polymerization. Thus, cationic polymerization of pMOSt was studied in detail using iodine as a catalyst.[7] Polymerization in CCl_4 at 0 °C produced polymers with unimodal MWDs. The peak molecular weight of the product polymers increased linearly with monomer conversion. Thus, the existence of long-lived active species was demonstrated clearly in cationic polymerization for the first time. At −15 °C, the M_n of product polymers increased in nearly direct proportion to monomer conversion after addition of the second feed of pMOS.[8] Moreover, block copolymers with isobutyl VE (IBVE) were obtained under similar conditions, although blocking efficiency was low.[8] Similarly, the formation of long-lived growing species was confirmed in polymerization of VEs using iodine.[9]

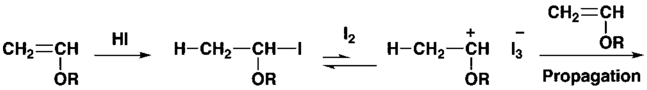
In the meantime, Kennedy et al. found that almost no chain transfer reaction occurred when IB was polymerized with BCl_3 in CH_2Cl_2 in the presence of a slight amount of water at −78 °C under high vacuum.[34] The absence of chain transfer was confirmed by a straight line from the origin in the Mayo plot, which plots $1/DP_n$ against $1/[M]$ ([M]: monomer concentration), and is a diagnostic tool as to whether chain transfer and/or termination occur. The polymerization was initiated by the proton released from water reacting with BCl_3. Other kinetic studies suggested that only termination reaction as well as propagation occurred in this polymerization system. However, monomer conversion reached over 90% under optimum conditions. From these results, the capping reaction of carbocation with the chloride anion liberated from the boron atom was proposed. The combination of cumyl chloride with BCl_3 induced quantitative polymerization of IB, and product polymers had C−Cl bonds at their terminal chain ends.[35] Furthermore, the synthesis of block copolymers with styrene was examined by reactivating the terminal C−Cl bonds of once-isolated polyisobutene.[36] Although the term “living polymerization” was not used in the papers, this series of the studies on IB polymerization with BCl_3 led to development of quasiliving polymerization systems.

Inspired by the above-mentioned results, Kennedy considered that living polymerization could be achieved if termination is completely reversible throughout reaction. Thus, polymerization of α-methylstyrene was examined with a cumyl chloride/BCl_3 initiating system in CH_2Cl_2/methylcyclohexane (25:75).[10] At −50 °C, chain transfer was suppressed, especially when monomer was added incrementally. As a result, the molecular weight of product polymers increased linearly with monomer conversion in the early stage of the polymerization. In addition, product polymers had relatively narrow MWDs ($M_w/M_n = 1.3-1.6$). In the same paper, an equilibrium of the formation and dissociation of the terminal C−Cl growing bonds was first illustrated in a scheme. Similar phenomena were observed with other monomers including IB. In the IB polymerization with cumyl chloride/$TiCl_4$ in hexane/CH_3Cl (60:40),[37] the linear relationship between the molecular weight of product polymers and monomer conversion was observed, although the polydispersity was high. This first example of controlled polymerization of IB mediated with long-lived species was a critical step to living cationic polymerization of IB.

2.4. The Breakthrough

The two systems that allowed controlled polymerization still had drawbacks. With the I_2-catalyzed sytem, slow initiation (addition of a vinyl group with I_2) gave a polymer with a broad MWD. The BCl_3-mediated quasiliving system never overcame chain transfer completely. However, the two initiating systems were modified, permitting excellent living polymerization.

Scheme 2. Living Cationic Polymerization of Vinyl Ethers



Scheme 3. Equilibrium between Dormant and Active Species

Hydrogen iodide was used as an initiator in VE polymerization to increase the rate of the initiating step. The fast initiation realized ideal living cationic polymerization of alkyl VE in hexane at −15 °C (Scheme 2).[11,12] Thus, homopolymers and block copolymers with narrow MWDs were first synthesized in cationic polymerization. This system indicated that a suitably nucleophilic anion played a key role in controlling polymerization.

With the BCl_3 system, stabilization of a counteranion was examined to eliminate chain transfer reaction. A tertiary ester was used as an initiator for polymerization of IB using BCl_3. Cumyl acetate and 2,4,4-trimethylpentyl acetate induced living polymerization in CH_2Cl_2/hexane at −30 °C.[13,14] After the two major breakthroughs, numerous studies on living cationic polymerization were performed all over the world, especially in the next decade.[15−19]

The key to achieving living polymerization is to exploit equilibria between active (ionic) and dormant (covalent) species (Scheme 3), which have been performed by three general methods: (A) with nucleophilic counteranions; (B) with added bases (nucleophiles); and (C) with added salts. Efficient and fast initiation is another decisive factor for ahieving living polymerization. To this end, initiators (cationogens), from which carbocations with a structure similar to that from a monomer, are used (Figure 2) as well as protonic acids.

3. Design of Initiating Systems for Living Polymerization

3.1. Living Cationic Polymerization of Vinyl Ethers

3.1.1. Early Development

After the discovery of the HI/I_2 system, combinations of protonic acids (or an adduct of a vinyl ether with a protonic acid) with weak Lewis acids were followed. Typical examples are hydrogen halides[38−42] and acetic acids[43,44] in conjunction with zinc halides,[38−42,44] zinc acetates,[43] and $SnBr_4$.[42] Living systems were expanded to strong Lewis acids by using additives, such as Lewis bases and salts. Added bases (nucleophiles) including esters[45,46] and ethers[47,48] were shown to assist strong Lewis acids to induce living polymerization. Nucleophiles were also found to be effective for controlling reactions in the polymerization using a protonic acid without a metal halide.[49,50] The addition of a tetraalkylammonium salt attained an appropriate equilibrium between the active and dormant species for living polymerization.[42,51,52]

3.1.2. “Classical” Base-Assisting System

Significant progress was reported recently with living cationic polymerization in the presence of an added base.

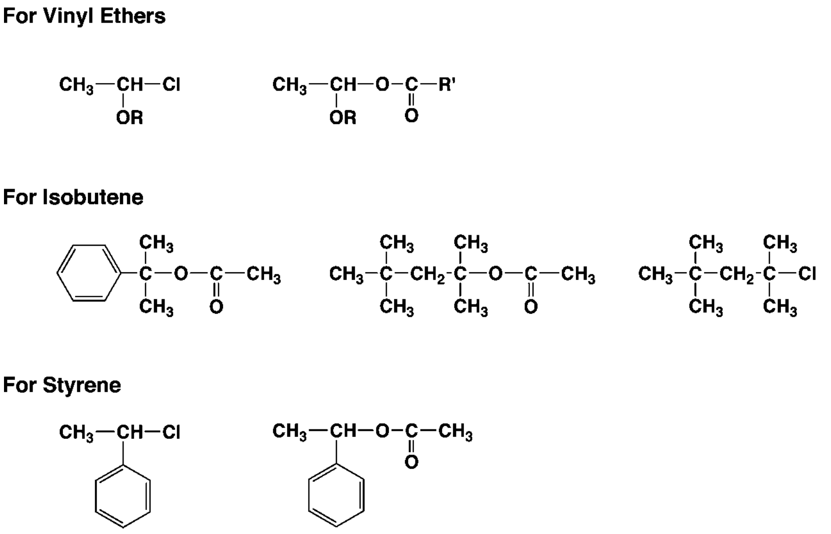


Figure 2. Typical initiators (cationogens) for living cationic polymerization.

This base-assisting system consists of a strong Lewis acid and a Lewis base, such as esters and ethers.[53] A strong Lewis acid itself induces conventional or nonliving cationic polymerization. In sharp contrast, the combinations of esters with $EtAlCl_2$ and the adduct of IBVE with acetic acid (IBEA) permitted living cationic polymerization of VEs to yield well-defined polymers with low polydispersity.[45,46] In a "classic" base-assisting living cationic polymerization, $EtAlCl_2$ was used in nonpolar solvent such as hexane or toluene at or above 0 °C.[45−48] The aluminum-based systems were efficient for polymerizing not only alkyl VEs but also functional monomers. However, polymerization reactions were significantly retarded or inhibited with monomers with some polar functional groups, such as esters and nitrogen-containing functions.[54] The retardation is caused by the strong interaction of an electron-rich moiety in a polar group with the Al atom. This drawback was a great obstacle in the development of various stimuli-responsive polymers. Thus, there was a keen need to survey efficient and active initiating systems for living cationic polymerization of functional VEs.

3.1.3. Recent Progress in Friedel−Crafts Catalysts

It is well-known that there is much in common between catalysts for cationic polymerization and the Friedel−Crafts and its analogous reactions. In fact, most Friedel−Crafts catalysts serve as catalysts for cationic polymerization.[2] Although Friedel−Crafts reactions give the impression of old and established chemistry, not a few studies on catalyst development have recently been reported. A major focus on those studies is to achieve the acylation and/or reactions of substrates with heteroatoms, such as heterocyclic compounds, using a catalytic amount of a Lewis acid. With a conventionally used acid including $AlCl_3$, an equimolar amount of the acid to a substrate is required due to the complex formation of a product and/or a substrate with the acid. As a result, significant byproducts are produced in industrially used Friedel−Crafts processes. Thus, solid acids[55−57] and various Lewis acids have been studied recently.

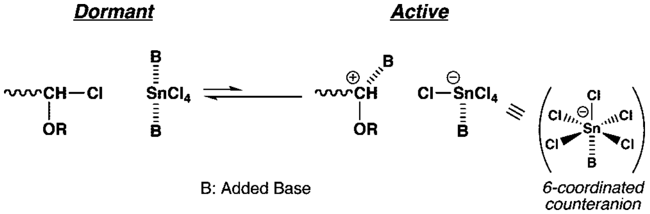
Successful catalytic processes were achieved using metal triflates in the 1990s. Efficient acylation proceeded with a catalytic amount (1−10%) of triflates of Ti,[58] Hf,[59,60] Sc,[61,62] and lanthanides.[62] Very recently, metal halides with late period metals, including Rh,[63] Ir,[63] In,[64,65] Pt,[63,66] and Bi,[67] were shown to be effective for acylation and/or alkylation of heterocyclic compounds. For catalytic processes, weaker interaction of central metals with the carbonyl group or polar functional groups as well as sufficient reactivity is required. This progress suggested that more reactive catalysts could be developed for cationic polymerization of functional monomers. However, catalyst development had been subdued in the late 1990s for living cationic polymerization, in contrast to Friedel−Crafts reactions.

3.1.4. Fast Living Polymerization Using $SnCl_4$

Excellent examples of the importance of the interaction between Lewis acids and a basic compound for successful living polymerization have been demonstrated using base-assisting living cationic polymerization systems.[53] In this system, an added base interacts with growing active centers and/or a Lewis acid, achieving a suitable equilibrium between the dormant and active species. Thus, a combination of a Lewis acid and a base is critical for attaining living polymerization. The first successful example was aluminum-based metal halides reported in 1986,[45] and almost no other metal halides have been reported until recently. In view of the HSAB principle[68,69] and some classifications from results of organic reactions,[70−72] a survey of Lewis acids has been performed very recently. According to the book "Friedel−Crafts and Related Reactions" by Olah, $SnCl_4$ and $FeCl_3$, compared with $AlCl_3$, have a strong affinity for Cl atoms, especially in a carbonyl-containing solvent.[73] In addition, Sn^{4+} and Fe^{3+} are considered softer than Al^{3+}, although they are still classified as hard acids.[74]

Based on these facts, $SnCl_4$ in conjunction with an added base was employed for the cationic polymerization of IBVE: the polymerization was examined using the adduct of IBVE with HCl (IBVE-Cl)/$SnCl_4$ (or IBEA-$EtAlCl_2$/$SnCl_4$) in toluene at 0 °C in the presence of ethyl acetate.[75] The polymerization was accelerated by a factor of 10^3, compared to the system with $EtAlCl_2$, proceeding quantitatively without an induction period within only 2 min. Despite the significantly large rate of the reaction, polymerization was well controlled, giving a polymer with an extremely narrow molecular weight distribution ($M_w/M_n \leq 1.05$). The $SnCl_4$-induced polymerization rate for O- or N-containing monomers was shown to be 10^3−10^5 times larger than the rates using the conventional Et_xAlCl_{3-x} ($x = 1$ or 1.5) initiating systems.[75]

Scheme 4. Dormant and Active Species in the Polymerization Using $SnCl_4$ with a Base



The difference in reactivity is attributed to the hardness of the Lewis acid, as also described below. $SnCl_4$ is considered a soft acid, whereas Al-based Lewis acids are classified as hard counterparts.[68] Since it is less hard than aluminum-based acids, $SnCl_4$ was likely to interact weakly with an added base and polar functional groups and attack the relatively soft chlorine atom at the growing end more readily than its aluminum counterpart. The counterion was also a key to the high reactivity of the reaction system. $SnCl_4$ is transformed into a stable hexacoordinated anion with one additional base coordinated after it extracts the chlorine atom of the growing end (Scheme 4). On the other hand, the counterion from $AlCl_3$ was considered to be tetrahedral and unstable.[53,76] The active species from $SnCl_4$ with the stable anion was more favorable than in the Al system. The formation of the stable anion caused the shift of an equilibrium between the active and dormant species to the active side, leading to fast polymerization. Furthermore, molecular orbital calculations using Gausian 03 showed that the activation energy ΔE in the Sn system is 10 kcal/mol lower than that in the Al system.[76]

3.1.5. Versatility of $SnCl_4$

$SnCl_4$ also realized living polymerization of various monomers containing VEs with polar side groups,[54,75,76] cyclic enol ethers,[77] and α-methyl VEs[78] (see polymerization of styrene and its derivatives in section 3.3). In each case, the use of $SnCl_4$ significantly accelerated the reaction and/or rendered polymerization much favorable over side reactions such as oligomerization, inducing smooth living polymerization to give polymers with low polydispersity. In the polymerization of α-methyl VEs, for example, no living polymerization was reported due to frequent *β*-proton elimination. In fact, $EtAlCl_2$ yielded only oligomers at 0 °C even in the presence of an added base.[78] In contrast, $SnCl_4$ produced polymers in good yield at 0 °C, although the molecular weight was low. At −78 °C, living polymerization was achieved with $SnCl_4$ in the presence of ethyl acetate.[78] The $SnCl_4$/base initiating system was also shown to induce living cationic polymerization of a cyclic diene. Tetrahydroindene was polymerized using $SnCl_4$ in toluene in the presence of ethyl acetate at −78 °C to produce polymers with a narrow MWD ($M_w/M_n = 1.1-1.4$).[79]

3.1.6. Effectiveness of a Strong Base with $SnCl_4$

In general, base-assisting systems for living polymerization can contain either a weak Lewis base or a strong version. The combination of a large quantity of weak bases such as esters and ethers with Et_xAlCl_{3-x} or $SnCl_4$ allowed the living cationic polymerization of VEs.[45−47,53,75] Isobutene was polymerized in a living fashion using a catalytic amount of some strong bases such as amides and dimethyl sulfoxide (DMSO) combined with BCl_3 or $TiCl_4$,[14,80] reported by Kennedy el al. These base-assisting living polymerization systems were reported over a decade ago. A recent advance was $SnCl_4$-induced living cationic polymerization of VEs in the presence of a strong base.[81] Even aliphatic amines and *N*-substituted anilines were found to be effective for inducing living cationic polymerization of alkyl VEs when combined with $SnCl_4$ in toluene at 0 °C. The systems required much less quantity of bases than weak base systems to achieve living polymerization. Strong bases also helped $TiCl_4$ and $ZnCl_2$ induce living polymerization, while $EtAlCl_2$, $FeCl_3$, and $GaCl_3$ in their presence induced only nonliving polymerization. In addition, amine derivatives allowed living polymerization even in the presence of a catalytic quantity. These strong bases are likely to convert a small amount of nonliving species to living species through the interaction with Lewis acids. This is an interesting rare case that a terminator for polymerization reactions metamorphoses into a helpful ingredient for living cationic polymerization at a low concentration.

3.1.7. Ultrafast Living Polymerization

Another softer Lewis acid, $FeCl_3$, was also found to be a good example of fast living polymerization of IBVE.[82] Although having advantages, such as low toxicity, for industrial use,[83,84] $FeCl_3$ has never been used for living cationic polymerization of any monomer, although there have been several examples of its use in cationic polymerization of VEs,[85] styrenes,[86] and dienes.[87] The combination of $FeCl_3$ with a weak Lewis base did also result in fast living polymerization of IBVE. For example, cationic polymerization of IBVE was completed in 15 s using IBVE-Cl/$FeCl_3$ in toluene in the presence of 1,4-dioxane at 0 °C, yielding a polymer with a very narrow MWD ($M_w/M_n = 1.06$).[82]

It was reported that the rate of living cationic polymerization of IBVE was correlated with the basicity of an added base when the Al-based initiating systems were used: the weaker the base, the faster the polymerization.[88] Similar trends were observed with $SnCl_4$ and $FeCl_3$. An alternative weaker base, ethyl chloroacetate, realized very fast polymerization with $SnCl_4$ in toluene, being completed within 2 s (determined using a high-resolution digital video camera).[89] Moreover, 1,3-dioxolane, a weaker base than 1,4-dioxane, induced faster polymerization with $FeCl_3$, complete in 2−3 s.[82] In both cases, product polymers had a very narrow MWD, irrespective of the monomer conversion.

3.1.8. Base-Assisting Living System with Various Lewis Acids

The results obtained using $SnCl_4$ and $FeCl_3$ suggested that various other Lewis acids, especially metal halides, could induce living polymerization of VEs if accompanied with appropriate added bases. Thus, various metal halides comprising several main group elements and transition metals were examined. In the presence of an appropriate added base, ester, or ether, the living polymerization of IBVE proceeded for almost all Lewis acids (MCl_n; M = Fe, Ga, Sn, In, Zn, Al, Hf, Zr, Bi, Ti, Si, Ge, Sb) used in conjunction with the IBVE-HCl adduct in toluene at 0 °C.[90] All MWDs of the product polymers were very narrow, with polydispersity ranging from 1.02 to 1.10. Significant differences in the polymerization rate with these Lewis acids were observed. For example, some acids, such as $FeCl_3$, induced very rapid polymerization completed in the order of seconds, whereas it took more than a few weeks for others such as $SiCl_4$ and $GeCl_4$ to complete living polymerization. The difference in activity is most likely based on the strength of the interaction between the Lewis acid and the propagating end chloride anion and/or the basic carbonyl (or ether) oxygen atom of the added base. These results suggested that the chlorophilic or oxophilic nature of each metal halide is a decisive factor. Despite the diversity of polymerization manners, all the product polymers had similar tacticities, about 70% of *meso* dyads.

The differences in polymerization activity were quite significant for all the metal halides examined. The order of polymerization rate in the presence of ethyl acetate was as follows:

$$GaCl_3 \sim FeCl_3 > SnCl_4 > InCl_3 > ZnCl_2 > AlCl_3 \sim HfCl_4 \sim ZrCl_4 > EtAlCl_2 > BiCl_3 > TiCl_4 \gg SiCl_4 \sim GeCl_4 \sim SbCl_3$$

This order corresponds to the strength of metal halides for extraction of the chloride anion from trityl chloride in a carbonyl compound, PhCOCl;[73] the amount of cations generated from trityl chloride in the presence of ethyl acetate is as follows:

In PhCOCl

$$FeCl_3 > SnCl_4 > ZnCl_2 > TiCl_4 > AlCl_3$$

In ethyl acetate

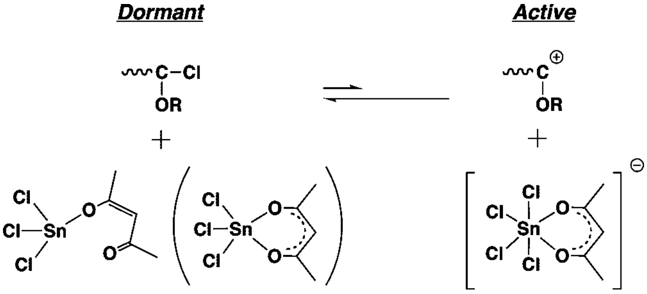
$$FeCl_3 \sim GaCl_3 > InCl_3 > AlCl_3$$

These results indicate that some metal halides such as $SnCl_4$ and $ZnCl_2$ are more likely to interact strongly with a chlorine atom (chloride anion) than with a carbonyl (or ether) oxygen atom, while others, including $TiCl_4$ and $AlCl_3$, would interact more strongly with the oxygen atom. Thus, the activity of each metal halide for base-present living cationic polymerization is determined by the balance between the interaction with the propagating end chlorine atom and the carbonyl (or ether) oxygen atom of the added base, namely, the "relative" strength based on the degree of chlorophilicity and oxophilicity. The differences in reactivity between metal halides with central metals of the same group are also attributed to the balance between chlorophilicity and oxophilicity.

3.1.9. Ligand Design for Living Polymerization

In contrast to the above-mentioned metal halides, any added base was not effective for achieving living polymerization when metal pentachlorides were used. With $NbCl_5$ and $TaCl_5$, addition of a salt (nBu_4NCl) resulted in well-controlled reactions.[90] With another pentachloride, $MoCl_5$, polymerization was not controlled at all, yielding polymers with broad MWDs.[90] For $MoCl_5$, however, unexpected additive did good for livingness in the reaction. It was a combination of an alcohol with $MoCl_5$ that induced living cationic polymerization of IBVE. For example, $MoCl_5$ and methanol allowed living polymerization of IBVE in the presence of ethyl acetate.[91] Furthermore, other Lewis acids were also shown to induce the methanol-initiated living polymerization. The Lewis acids examined in the study were classified mainly into three categories in terms of polymerization behavior: those producing long-lived species (e.g., $MoCl_5$, $NbCl_5$, and $ZrCl_4$), inducing uncontrolled polymerization (e.g., $GaCl_3$ and $FeCl_3$), or showing no activity (e.g., $ZnCl_2$ and $InCl_3$). The exchange reaction between the methoxy group of methanol and the chloride anion of a metal chloride to generate HCl, a true initiator, was confirmed in living polymerization systems. Only C−Cl dormant terminals were observed with the more chlorophilic Lewis acids, whereas the rapid equilibrium between the C−Cl ends and acetal structures is involved in the propagation reaction with the more oxophilic Lewis acids.

Scheme 5. Dormant and Active Species in the Polymerization Using a Complex of acac with $SnCl_4$



A similar initiating step was observed using the $SnCl_4$/acetylacetone (acac) initiating system.[92] On mixing acetylacetone with an equimolar $SnCl_4$ in toluene in the presence of ethyl acetate at 0 °C, they reacted readily and formed a complex species with a proton released. The polymerization began immediately after the addition of monomer to the $SnCl_4$/acac solution to give living polymers. In the dormant-active equilibrium, acac most likely formed a bidentate chelate-type counteranion (Scheme 5). An increase in *meso* content in the main chain was observed when an acac derivative with a bulky group, such as a phenyl ring, was employed. In both cases, moderation of Lewis acidity by the ligand exchange with methanol or acac was a critical step for achieving living polymerization.

3.1.10. Copolymerization of Aromatic Aldehydes with Vinyl Ethers

The differing features are opening possibilities for living cationic polymerization of a new class of monomers. A recent example is controlled cationic copolymerization of benzaldehyde or its derivatives with VEs. Copolymerization of benzaldehyde with IBVE was successfully performed using ethanesulfonic acid and $GaCl_3$ in toluene in the presence of 1,4-dioxane at −78 °C.[93,94] Furthermore, product polymers had very narrow MWDs ($M_w/M_n < 1.1$), although a small amount of cyclic oligomers were also obtained. Each of the reaction parameters (Lewis acid, solvent, added base, temperature) was indispensable for achieving the controlled copolymerization. In addition, nearly alternating and controlled copolymerization proceeded when *p*-methoxybenzaldehyde was used instead of benzaldehyde. The treatment of the product copolymer with hydrochloric acid yielded a single low molecular weight compound selectively.[93,94]

3.1.11. Heterogeneously Catalyzed Living Polymerization

In view of increasing environmental demands, solid catalysts have been of great interest in organic and polymer chemistry for years. The feasibility of living polymerization of VEs using a solid acid, such as metal oxides, was examined recently. There are, in fact, several examples of heterogeneous cationic polymerization using solid acids, including metal oxides, heteropoly acids, and ion-exchange resin,[95−100] but none were living polymerization.

Aoshima and co-workers reported the first example of heterogeneous living cationic polymerization of IBVE using Fe_2O_3 in conjunction with the IBVE-HCl adduct in toluene in the presence of an added base at 0 °C. Ethyl acetate and 1,4-dioxane are effective bases for homogeneous living cationic polymerization of VEs with various metal halides. In the presence of such a base, Fe_2O_3 induced living cationic polymerization of IBVE to produce polymers with very narrow MWDs.[101,102] In addition, M_n of the product polymers increased in direct proportion to the monomer conversion, and their MWDs were very narrow throughout the polymerization [$M_w/M_n \leq 1.1$]. Although stereoselectivity was expected, the product polymers were similar in steric structure to those obtained by soluble catalysts. Controlled polymerization also occurred even at higher temperature (30 °C). This is the first example of heterogeneously catalyzed living ionic polymerization.

The catalyst was separated from the mixture by centrifugation, and this used catalyst was able to catalyze living polymerization under the same conditions, yielding a polymer with narrow MWD. The ease of the catalyst separation permitted repeating reuse of the catalyst. Up to the fifth use, the catalyst maintained its reactivity to give well-defined polymers with very narrow MWD.[101]

3.1.12. Metal-Halide-Free System: HCl and Heteropoly Acids

Metal halide-free systems were reported very recently. Sugihara et al.[103] and our group[104] found that an HCl/diethyl ether or HCl/1,4-dioxane initiating system induced living cationic polymerization of various VEs in nonpolar solvent such as hexane and toluene. This is the first example of metal-free living cationic systems since living polymerization of *N*-vinylcarbazole using hydrogen iodide alone,[105] and living polymerization of IBVE using HI with an ammonium salt[106] or trifluoromethanesulfonic acid with dimethyl sulfide (Me_2S)[49,50] were reported.

A metal halide-free system was also achieved using heteropoly acids.[107] Cationic polymerization of IBVE was examined using a Keggin type heteropoly acid, $H_3PW_{12}O_{40}$, in CH_2Cl_2 at 0 °C in the presence of various added bases. In the presence of 1,4-dioxane or THF, the polymerization was complete instantly and the obtained polymers had very broad MWDs. In contrast, polymerization in the presence of Me_2S in ethyl acetate at −30 °C proceeded in a living fashion and gave a polymer with a narrow MWD ($M_w/M_n < 1.1$). It should be noted that the reaction mixtures were heterogeneous because of the very poor solubility of $H_3PW_{12}O_{40}$ to ethyl acetate. This is another successful heterogeneous living cationic polymerization.

3.2. Living Cationic Polymerization of Isobutene

3.2.1. Early Development

Isobutene (IB), being polymerizable only cationically, has been investigated extensively, since polyisobutene (PIB) is of interest as a commercial material. After the discovery of its living polymerization, initiating systems for IB were vigorously investigated by many groups.[26] The first living system gave relatively broad MWD polymers,[13,14] in contrast to the VE case.[11,12] Thus, producing PIB with a narrow MWD was the next target. Combinations of BCl_3 or $TiCl_4$ with a small amount of strong Lewis bases ([Lewis acid] ≫ [base]), such as DMSO and *N*,*N*-dimethylacetamide (DMA), were found to be effective for the better control of the reaction.[108] For example, living polymerization was achieved using dicumyl chloride/BCl_3/DMSO, dicumyl alcohol/BCl_3/DMSO, or 2-chloro-2,4,4-trimethylpentane (TMP-Cl)/$TiCl_4$/DMA, yielding polymers with narrow MWDs. Without the base, only ill-defined reactions occurred with these three initiating systems. Basic compounds moderate Lewis acidity and/or stabilize carbocations, producing living growing species. It is interesting to note that similar base-assisting living systems were independently developed for VEs[45−47] and IB around the same time.

A proton trap also improved the molecular weight distribution of product polymers. With BCl_3[108] or $TiCl_4$,[109] narrowly distributed PIB was obtained in the presence of 2,6-di-*tert*-butylpyridine (DTBP). DTBP had no interaction with carbocations and only scavenged protic impurities, which was confirmed by the fact that the polymerization rate was not influenced by the excess of DTBP and the polymerization was of first order with respect to both monomer and the Lewis acid.

3.2.2. Departure from BCl_3 and $TiCl_4$ Systems: Fast Living Polymerization

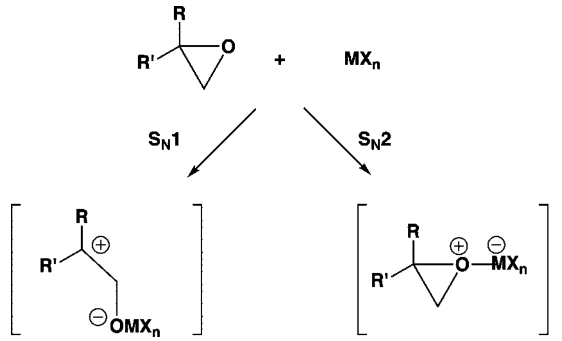
Apparently only two Lewis acids had been used for living cationic polymerization of IB.[110] Cheradame and co-workers reported the first example of living polymerization using Et_2AlCl.[111] Another feature of this system was the use of a halogen-free cationogen. A bifunctional azide-containing compound induced living polymerization in CH_2Cl_2 at −50 °C, although the MWDs of the product polymers were less narrow ($M_w/M_n = 1.3−1.4$). A better system was provided by Shaffer et al.[112,113] Me_2AlCl permitted living polymerization in conjunction with conventional tertiary alkyl chlorides, such as TMP-Cl, without any additional ingredient, yielding high molecular weight polymers with narrower MWDs ($M_w/M_n \sim 1.2$).

A detailed kinetic study was conducted with nonliving systems by Faust et al.,[114] comparing between polymerization rates with Et_2AlCl, $EtAlCl_2$, and $TiCl_4$. This study showed that $EtAlCl_2$ induced faster polymerization than $TiCl_4$ in hexanes/CH_3Cl (60/40 v/v) at −80 °C. Polymerization with $EtAlCl_2$ was also examined in dichloromethane or CH_3Cl at low temperatures.[115] TMP-Cl was larger in ionization equilibrium constant than tBuCl. The feasibility of living cationic polymerization with aluminum-based Lewis acids was examined in hexanes/CH_3Cl (60/40 v/v) at −80 °C in the presence of DTBP.[116] $MeAlCl_2$ induced rapid and less controlled reaction, completed within 30 s, whereas slow and well-controlled polymerization proceeded using Me_2AlCl. In sharp contrast, $Me_{1.5}AlCl_{1.5}$ attained very fast and well controlled polymerization, completed within 30 s. Despite such rapid reaction, product polymers had very narrow MWDs ($M_w/M_n < 1.1$).[116] $MeAlBr_2$ and $Me_{1.5}AlBr_{1.5}$ were also effective for fast living polymerization of IB.[117]

3.2.3. Kinetic Studies

Numerous experiments to determine propagation rate constants for various monomers have been conducted in cationic polymerization.[118−120] One reason why one cannot reach solid conclusions is that rate constants vary depending on experimental methods.[119,120] In IB polymerization, for example, gravimetric analysis was conventionally used to

Scheme 6. Possible Initiation Steps with an Epoxy Initiator



determine monomer consumption, which would make errors in determining a larger reaction rate. It was demonstrated that real-time FTIR monitoring was a powerful tool to determine propagation rate constants in living IB polymerization.[121,122] Reactions were monitored by FTIR with a fiber optic immersion attenuated total reflection (ATR) IR probe (FTIR-ATR) for polymerization using the 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene (t-Bu-m-DCC)/2,4-dimethylpyridine/$TiCl_4$ (1:2:20) system in hexane/methyl chloride (Hx/MeCl) (60:40 v/v) at −80 °C,[121] or using TMP-Cl/$TiCl_4$ in Hx/MeCl 60/40 v/v cosolvents at −80 °C.[122] Whether the disappearance of the 887 cm^{-1} wag[121] of the $=CH_2$ group or the C=C stretching[122] at 1656 cm^{-1} was followed, the data acquired via FTIR-ATR agreed well with data obtained by conventional gravimetric analysis. Copolymerization reactivity ratios for IB and isoprene were also determined using the real-time FTIR technique.[123] The study showed the possibility of determining reactivity ratios based on a single experiment.

A competitive reaction method has been shown to be effective for determining the absolute rate constants of propagation for ion pairs and free ions in the living cationic polymerization of IB.[124,125] Polymerization of IB was carried out in Hx/MeCl (60/40 v/v) at −80 °C in the presence of a capping agent, such as allyltrimethylsilane. ^1H NMR analysis confirmed the absence of uncapped terminals and side reactions.[125] The rate constant for ion pairs was (4.2−4.7) × 10^8 L mol^{-1} s^{-1}, and that for free ion was (6.2−6.5) × 10^8 L mol^{-1} s^{-1}.[125] These values were in good agreement with those determined by another group using a similar method.[126]

3.2.4. New Catalyst Systems

All the cationogens used in the IB living polymerization were alkyl halides except for pseudohalide compounds.[111,127] A new initiator was reported by Puskas's group almost a decade ago. Substituted epoxides were found to initiate cationic polymerization of IB in conjunction with $TiCl_4$.[128] For example, the combination of α-methylstyrene epoxide (MSE) with $TiCl_4$ initiated controlled polymerization of IB in Hx/MeCl (60/40 v/v) at −80 °C, although initiator efficiency was about 35%. Controlled polymerization also proceeded from a hexafunctional epoxy initiator with higher initiator efficiency (see below).[128] The mechanism of the initiation step was studied using the real-time FTIR analysis. With a $TiCl_4$-mediated system, S_N1 and S_N2 pathways were competitive (Scheme 6),[129] while S_N1 became favorable using BCl_3.[130]

Design of a Lewis acid and/or a counteranion is critical to controlling polymerization or preparing high molecular weight polymers. Thus, several recent examples of initiating systems are mentioned in this section, although they are not living systems. The first successful use of metallocene-type catalysts for the IB polymerization was reported by Baird et al.[131] Isobutene polymerization was initiated by adding (η^5-$C_5(CH_3)_5$)$Ti(CH_3)_3$ and $B(C_6F_5)_3$ (1:1) to solutions of IB in toluene at −78 °C, yielding IB homopolymers with high molecular weight (up to 5 × 10^5, M_w/M_n ∼ 2). High molecular weight polymers were also obtained at higher temperatures, such as −20 °C.[132] Because of its noncoodinating nature, the couteranion, $MeB(C_6F_5)_3^-$, hardly caused termination and/or chain transfer. The polymerization was initiated either from protons generated from water by the reaction with $B(C_6F_5)_3$ or from the metal cation center (**1**: Figure 3).[132] Copolymerization with isoprene (IB:IP 99:1) was also induced by the same catalyst, producing a copolymer with 1 mol % of IP units. The structure of the product was identical to commercial butyl rubber, confirmed by ^1H and ^{13}C NMR.[132] An interesting feature of this catalyst is that it is effective not only for cationic polymerization of styrene and α-methylstyrene at low temperature but also for the Ziegler−Natta polymerization of ethylene and styrene at temperatures above 0 °C.[133−135] Cationic zirconocene hydrides were also effective for IB cationic polymerization.[136] For example, the cationic zirconocene trihydrides $[Cp'_4Zr_2H(\mu\text{-}H)_2]^+X^-$ ($Cp' = C_5H_4SiMe_3$, $X^- = [B(C_6F_4R)_4]^-$) generated from $[Cp'_2ZrH_2]_2$ (**2**: Figure 3) with various trityl salts of weakly coordinating anions, were also shown to induce the polymerization of IB to give high molecular weight polymers (M_w ∼ 5 × 10^5 at −35 °C)[136] and its copolymerization with IP.[137]

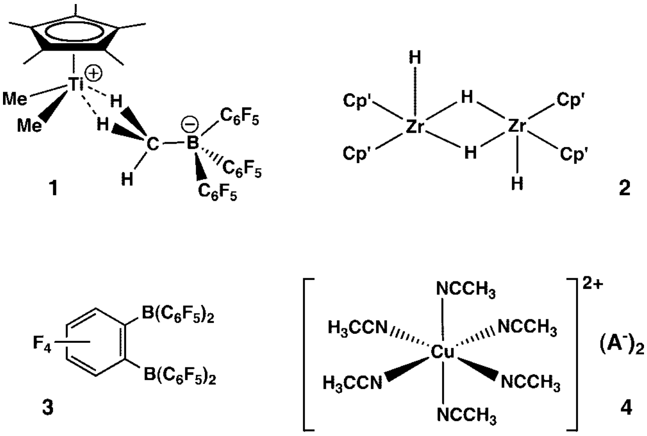


Figure 3. New types of catalysts for IB polymerization.

Since a noncoordinating anion has proven to be good for preparing high molecular weight polymers,[131,132,136−138] more simple systems containing a noncoordinating anion were examined.[139−141] Kennedy and co-workers reported that the *in situ* $(CH_3)_3Si[B(C_6F_5)_4]$ initiating system produced high molecular weight PIB at unusually high temperatures for IB cationic polymerization. The catalyst also induced copolymerization with IP, yielding copolymers with over 10 mol % of IP units.[140] Another system consists of a carboxylic acid and a borane.[141] The reactions of an electrophilic borane $B(C_6F_5)_3$ with a variety of carboxylic acids RCO_2H gave 1:1 and 1:2 adducts $[RCO_2H][B(C_6F_5)_3]$ and $[RCO_2H]$-$[B(C_6F_5)_3]_2$. Among the obtained adducts, the 1:2 adduct of *n*-decanoic (stearic) acid was an excellent initiator for the IB cationic polymerization and copolymerization of IB with IP in methylene chloride and methyl chloride. High molecular weight PIB was obtained in high yield at −30 to −40 °C, and IB-IP copolymers are obtained. The high molecular weight and monomer conversion were likely attributed to the weakly coordinating anion $[n\text{-}C_{17}H_{35}CO_2\{B(C_6F_5)_3\}_2]^-$. A chelating diborane anion can be a form of weakly coordinating anion. The combination of cumyl chloride with diborane **3** (Figure 3) permitted cationic polymerization of IB in hexane in the presence of DTBP at −78 °C,[142] yielding polymers with less controlled structures ($M_w = 1.5-7.8 \times 10^4$, $M_w/M_n = 1.7-2.1$). Unexpectedly, the diborane anion formed the contact ion pair with cumyl cation in hexane.[143] This closely located anion was likely responsible for chain transfer. Similar diboranes were shown to be effective for suspension polymerization in aqueous LiCl, sulfuric acid, or fluoroboric acid suspension.[144] Nuyken et al. reported polymerization using a copper-based catalyst with a noncoordinating anion (**4**: Figure 3).[145] This system achieved faster reaction than the Mn-based systems[146,147] they reported before.

Solid catalysts were found to induce the IB cationic polymerization in heterogeneous systems.[99,100,148] A proton exchanged montmorillonite clay called "H-Maghnite" attained cationic polymerization of IB in bulk or in solutions (hexane or CH_2Cl_2) at −7 °C. The M_w values of the obtained polymers were similar, while the MWDs of the products were much narrower in solutions ($M_w/M_n < 1.2$) than in bulk ($M_w/M_n = 4.2-4.6$).[148] H-Maghnite was also shown to catalyze ring-opening polymerization of THF,[149] ε-caprolactone,[150−152] and oxetanes[153,154] and polymerization of α-methylstyrene.[155] Interestingly, this catalyst produced poly(α-methylstyrene) with higher molecular weight above 0 °C, whereas only oligomers were obtained with metal halides.[156] Furthermore, the resulting polymers had narrow MWDs ($M_w/M_n \sim 1.2$).[155] Heteropoly acid salts, $M_{0.5}H_{0.5}PW_{12}O_{40}$ (M = Cs, NH_4), were also found to be active catalysts for the IB polymerization and gave PIB with high terminal vinylidene content (75−80%) and large polydispersity, which is claimed good for dispersants.[99] There have been few examples of IB polymerization using group 3 and lanthanide compounds.[157] It was recently demonstrated that Y, Dy, or Sm supported on SiO_2 exhibited the ability to induce IB cationic polymerization in heptane at −30 °C, although polymer yield was low (∼10%).[100]

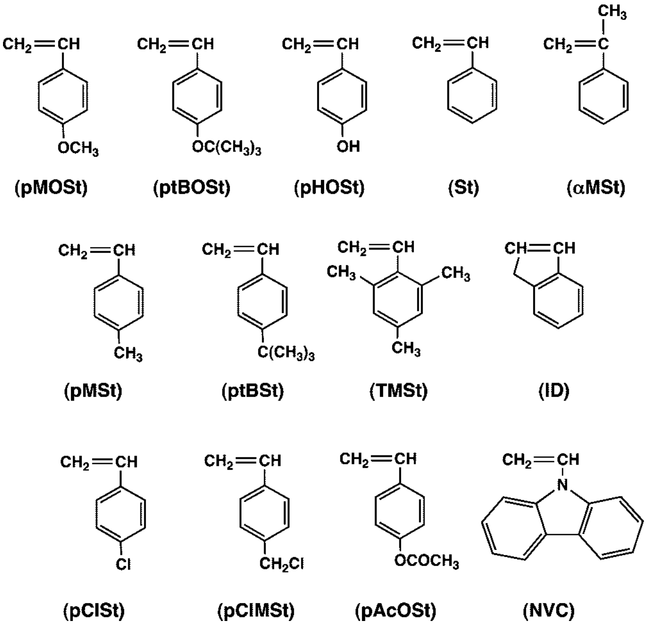


Figure 4. Styrene monomers.

3.3. Living Cationic Polymerization of Styrenes

The cationic polymerization of styrenes (Sts) is generally more difficult to control than those of VEs and IB. This is because the growing species frequently induce chain transfer reactions such as β-proton elimination and intra- and/or intermolecular Friedel−Crafts alkylation. As a result, the development of living cationic polymerization of Sts has lagged behind those for VEs and IB. However, since the late 1980s, a large number of living polymerization systems for Sts (Figures 4 and 5) have been developed.

3.3.1. p-Alkoxy Sts [p-Methoxy St (pMOSt), p-tert-Butoxy St (ptBOSt), and p-Hydroxy St (pHOSt)]

p-Alkoxy Sts are one of the most reactive monomers among Sts in cationic polymerization, and their polymerization behavior is known to be similar to that of VEs. The first evidence for living cationic polymerization of pMOSt was reported in 1979, in which the formation of a long-lived propagating species with I_2 was observed, but the MWDs were not very narrow.[8] In 1988, the living cationic polymerization of pMOSt was successfully achieved with HI/ZnI_2 initiating systems in toluene at −15 to +25 °C.[158,159] The MWD of the polymers was very narrow, and the M_n's were in good agreement with calculated values and increased linearly with monomer conversion. The living polymerization could also be performed in a more polar solvent (CH_2Cl_2) with a small amount of nBu$_4$NI salt, while, in the absence of salt, broader MWDs were observed. Furthermore, various HI adducts of VEs having a functional group (**5**, Figure 6) were found to induce living polymerization with ZnI_2, yielding an end-functionalized poly(pMOSt) or its macromonomer.[160] Triarmed star polymers of pMOSt were prepared using a trifunctional initiator (**6**, Figure 6) with ZnI_2 in toluene at 0 °C, to give polymers with very narrow MWDs ($M_w/M_n \leq 1.1$). In combination with quantitative capping by 2-hydroxyethyl methacrylate, a triarmed poly(pMOSt) having three methacrylate groups was also obtained.[161] In the case of ptBOSt, under similar conditions, living polymerization was achieved with HI/$ZnCl_2$ in toluene or in CH_2Cl_2 (with nBu$_4$NCl) at temperatures up to +25 °C,[162] to give poly(ptBOSt), its hydrolyzed product poly(pHOSt), and various α-functionalized poly(ptBOSt)s with narrow MWDs.[163] The pMOSt-Cl/$SnBr_4$ initiating system with DTBP has been used in CH_2Cl_2 at −60 to −20 °C to give polymers with M_ns up to 1.2×10^5 and $M_w/M_n \sim 1.1$.[164] Quite recently, we polymerized pMOSt with a $SnCl_4$-based initiating system in CH_2Cl_2 at 0 °C in the presence of ethyl acetate as an added base.[165] With the IBEA-$EtAlCl_2$/$SnCl_4$ initiating system, very rapid polymerization occurred and the reaction was completed within 30 s. The M_n values of the product polymers increased in direct proportion to the monomer conversion, and had quite narrow MWDs (≤1.05). Living cationic polymerization of ptBOSt was also achieved with the same initiating system in toluene at 0 ∼ +40 °C. Although toluene may undergo Friedel−Crafts side reactions, the initiating system induced living cationic polymerization even at +40 °C. Furthermore, this $SnCl_4$-based initiating system is available to Sts with a variety of reactivities, as shown in Table 1. Depending on the substituents, the optimum polymerization conditions were slightly different. In spite of the rate differences (from 20 s to over 200 h for completion of the polymerization), by using IBEA-$EtAlCl_2$/

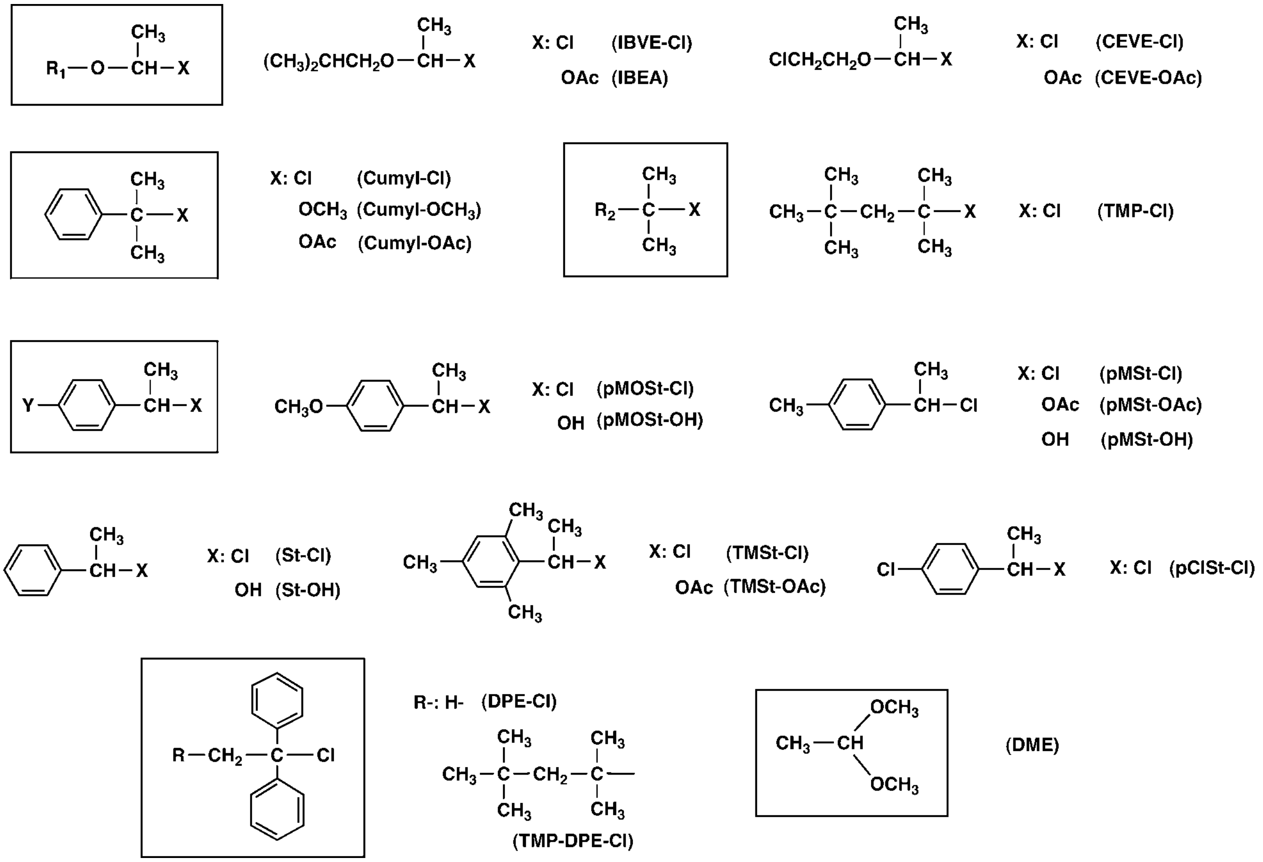


Figure 5. Initiators for living cationic polymerization of styrenes.

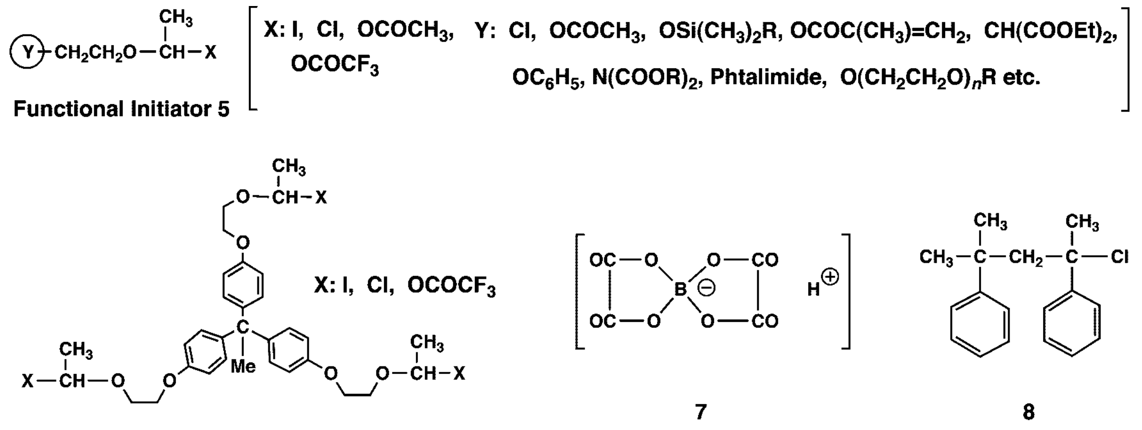


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Figure 6. Other initiators and catalysts.

Table 1. $SnCl_4$ with Added Base Induced Living Cationic Polymerization of Sts[a]

monomer	pMOSt	ptBOSt	pMSt	St	pAcOSt	pClSt	αMSt
substituent	OCH_3	$OC(CH_3)_3$	CH_3	H	$OCOCH_3$	Cl	CH_3(α)
polym $EtAlCl_2$	X	X	X	L	X	O	O
polym $SnCl_4$	O	O	O	O	O	O	O
time (conv ~90%)	20 s	40 s	1.5 h	50 h	120 h	>200 h	1.5 h
M_w/M_n	1.03	1.03	1.13	1.10	1.13	1.12	1.13

[a] O, living; L, long-lived; X, nonliving. Typical polymerization conditions: $[pMOSt]_0 = 0.38$ M, $[IBEA]_0/[EtAlCl_2]_0 = 4.0/2.5$ mM, $[SnCl_4]_0 = 10$ mM, $[CH_3COOEt] = 500$ mM, in CH_2Cl_2 or toluene at 0 °C.

$SnCl_4$ and an added base, very narrow polymers ($M_w/M_n = 1.03-1.13$) were obtained, as discussed later.

Controlled cationic polymerizations of pMOSt and ptBOSt were achieved even in the presence of a large amount of water by combination with the water adduct of pMOSt (pMOSt−OH) and BF_3OEt_2 as a water-tolerant Lewis acid in a CH_3CN/CH_2Cl_2 solvent mixture at 0 °C.[166] Under similar conditions, it was not necessary to protect the phenolic group of pHOSt to induce controlled polymerization.[167] In all cases, the M_n of the products increased in direct proportion to polymer yield with relatively narrow MWDs ($M_w/M_n \sim 1.4$). The C−OH bond is selectively activated by the oxophilic

Lewis acid BF_3OEt_2 to generate a carbocation species even in a homogeneous aqueous solvent. Other water-tolerant Lewis acids, e.g., lanthanide and related metal triflates such as ytterbium triflate [Yb(OTf)$_3$], in conjunction with IBVE-Cl, pMOSt-Cl, or sulfonic acids as initiators, also induced controlled cationic polymerizations of pMOSt in aqueous media at room temperature.[168,169] The MWDs are relatively narrow ($M_w/M_n \sim 1.4$), and the M_n's increase in proportion to monomer conversion. The success in controlled cationic polymerizations in aqueous media is attributed to the stability of Yb(OTf)$_3$ as well as the dormant C−Cl polymer ends in water. As in the characteristic mechanism, the propagating species would be formed in the organic phase via entrance of a water-soluble Lewis acid from the aqueous phase. Emulsion cationic polymerization of pMOSt or ptBOSt in water was also achieved with lanthanide triflates [Ln(OTf)$_3$; Ln = Yb, Sc, Dy, Sm, Gd, and Nd].[170] Even in the presence of a large amount of surfactants, Ln(OTf)$_3$ in conjunction with pMOSt-Cl induced cationic polymerizations in aqueous media at 30 °C, to give polymers of controlled molecular weights and narrow MWDs ($M_w/M_n \sim 1.4$). Recently, various types of polymerizations[171−173] such as solution, emulsion, miniemulsion, and dispersion polymerizations were investigated and found to give controlled/living polymers.

3.3.2. Styrene (St)

Living cationic polymerization of St, which lacks an electron-donating substituent, has been difficult to achieve, because St is much less reactive and forms a much less stable propagating carbocation than pMOSt or VEs. In 1988, Kennedy et al.[174] and Matyjaszewski et al.[175] reported that pMSt-OAc/BCl_3 and similar systems in CH_3Cl below −30 °C induced living polymerization. The M_n of the resulting polymers increased linearly, but their MWDs were very broad. Living polymers with controlled M_n's and narrow MWDs ($M_w/M_n = 1.1-1.2$) were first obtained by Higashimura et al. using $CH_3SO_3H/SnCl_4$[176] and St-Cl/$SnCl_4$[177] in the presence of nBu$_4$NCl (an added salt) in CH_2Cl_2 at −15 °C. The M_n's are directly proportional to monomer conversion and close to the calculated value, and they further increase after monomer-addition experiments. The use of an added salt with a common counterion suppressed the ionic dissociation of the propagating carbocation.[178] Similar living polymerization systems were later investigated using a careful selection of solvent polarity in the presence or absence of a proton trap.[179,180] The effect of nBu$_4$NCl on the kinetics and the MWD in the cationic polymerization by St-Cl/$SnCl_4$ was also investigated by ^{119}Sn NMR etc.[181] As an extension of this polymerization system, VE-based functional initiators were found to initiate living polymerizations with $SnCl_4$ catalyst and to give α-functional polymers containing a macromonomer.[182] On the other hand, we have investigated the effects of added bases on the behavior of Sn-induced polymerization.[53] Recently, base-assisted living polymerization was achieved using St-Cl/$SnCl_4$ in the presence of dual added bases, DMA and Et_2O, in CH_2Cl_2 at −15 °C, to give polymers with a narrow MWD ($M_w/M_n = 1.1-1.2$).[183]

Living polymerizations with Ti-based initiating systems were also investigated, e.g., TMP-Cl/$TiCl_4$ or pMSt-Cl/$TiCl_4$, with an added base (DMA) and/or a proton trap[184] in methylcyclohexane (MCH)/CH_3Cl at −80 °C,[185] and St-Cl/$TiCl_3$(iPrO) with added salt in CH_2Cl_2 at −78 ∼ −40 °C.[186] The living polymerization of St was also achieved with St-Cl/$TiCl_4$ in the presence of an added base (Bu_2O) in $C_2H_4Cl_2$/hexane at −15 °C,[187] but the MWDs were not so narrow ($M_w/M_n \sim 1.5$). For the Al-based initiating system, the formation of a long-lived propagating species was obtained using IBEA/$EtAlCl_2$ with $CHCl_2COOMe$ in C_6H_5Cl at −15 °C.[188] Although the polymerization of St retarded above 60% conversion in virtually every case, the system is effective to give well-controlled graft copolymers, PVA-g-PSt.

BF_3OEt_2 was successfully used for controlling the cationic polymerization of not only pMOSt[166] but also St[189] in the presence of water. For example, the controlled cationic polymerization of St was achieved with an alcohol (St−OH, pMSt−OH) as an initiator coupled with BF_3OEt_2 even in the presence of a large amount of water. The M_n's of the resulting polymers increased in direct proportion to monomer conversion and agreed well with the calculated values, although the MWDs were broad ($M_w/M_n \sim 2$). In the proposed polymerization mechanism, BF_3OEt_2 selectively and reversibly activates the terminal C−OH bond derived from the initiator to generate the growing cationic species. This was confirmed by ^{1}H NMR and MALDI-TOF-MS analysis. On the other hand, $B(C_6F_5)_3$ has been widely used as an activator for various organic reactions and metallocene Ziegler−Natta polymerizations, because of its water-tolerant Lewis acidity. Recently, Ganachaud et al. have shown that the living polymerization of St[190] and pMOSt[191] could be performed in CH_2Cl_2 at 20 °C even in the presence of water with the pMOSt−OH/$B(C_6F_5)_3$ initiating system, which was successfully applied in an aqueous suspension or dispersion polymerization.[190] The polymerization proceeded through the generation of a carbocation by hydroxide abstraction of the propagating PolySt−OH by the borane agent. Using a new Lewis acid initiator that is relatively easy to handle, bisoxalatoboric acid (**7**), the controlled cationic polymerization of St has been achieved at room temperature in an ionic liquid under mild reaction conditions.[192] The obtained polymers had low polydispersities, but low molecular weights. Baird et al.[134] and Shaffer et al.[132] have shown that Cp*$TiMe_3$ in combination with $B(C_6F_5)_3$ (**1**) and related systems can induce cationic polymerization of St. These results would generalize the concept of noncoordinating anion [$MeB(C_6F_5)_3^-$] based initiators for cationic polymerization.

3.3.3. α-Methyl St (αMSt)

It is difficult to control the cationic polymerization of αMSt due to steric hindrance, its low ceiling temperature, and the presence of five acidic β-protons susceptible to elimination. The living cationic polymerization of αMSt was first established with CEVE-Cl and $SnBr_4$ in CH_2Cl_2 at −78 °C.[193] Polymers with high M_n (up to 1.1×10^5) and narrow MWD ($M_w/M_n = 1.1$) were obtained. The living nature was confirmed by monomer addition experiments, and the selective incorporation of the initiator fragment was detected by ^{1}H NMR spectroscopy. The living polymerization of αMSt has also been achieved using 1,1-diphenylethene (DPE)-capped TMP-Cl (TMP-DPE-Cl)/$SnBr_4$ or $SnCl_4$,[194] and DPE-Cl or an HCl adduct of an αMSt dimer (**8**)/BCl_3 in MCH/CH_3Cl at −80 to −60 °C in the presence of DTBP.[195,196] The polymers obtained were in good agreement with calculated M_n's and had narrow MWDs ($M_w/M_n = 1.1-1.2$).

A recent interesting case was added base (ethyl acetate)-containing living cationic polymerization of αMSt with the (CEVE-OAc)-$EtAlCl_2$/$SnCl_4$ initiating system in CH_2Cl_2 at −78 °C.[165] This initiating system even permitted the random copolymerization of αMSt with another St derivative at 0

°C, where only oligomers were obtained in homopolymerization of αMSt. For copolymerization with ptBOSt, which is more reactive than αMSt, the obtained random polymers had a narrow MWD and their M_n values increased in direct proportion to monomer conversion ($M_n \geq 2.4 \times 10^4$).

3.3.4. Other St Derivatives [p-Alkyl St, Indene (ID), p-Chloro St (pClSt), p-Chloromethyl St (pClMSt), p-Acetoxy St (pAcOSt)] and N-Vinylcarbazole (NVC)

For St derivatives having moderately electron-donating alkyl substituents such as *p*-methyl St (pMSt), *p-tert*-butyl St (ptBSt), 2,4,6-trimethyl St (TMSt), ID, and electron-withdrawing substituents such as pClSt, pClMSt, and pAcOSt, various types of living cationic polymerization have been reported. The earlier living-like polymerization systems for pMSt were acetyl perchlorate (a catalyst) with $n\mathrm{Bu_4NClO_4}$ (an added salt),[197] and R-OAc/BCl_3 (R-OAc = Cumyl-OAc, TMSt-OAc, and pMSt-OAc).[198] Later, homopolymers and/or block copolymers with a very narrow MWD were obtained by living cationic polymerization using HI/$ZnCl_2$ or ZnI_2 in toluene or CH_2Cl_2 below 0 °C,[199] VE-HCl adduct/$SnCl_4$ in CH_2Cl_2 at −15 °C with $n\mathrm{Bu_4NCl}$ (an added salt),[182] TMP-Cl/$TiCl_4$:Ti(*i*PrO)$_4$ with DMA or Et_3N (an added base),[200] pMSt-Cl/$SnCl_4$ with DTBP (a proton trap) in CH_2Cl_2 at −70 to −15 °C,[201] and TMP-Cl/$TiCl_4$ with DTBP (a proton trap) in CH_3Cl/MCH at −80 °C (for ptBSt).[202] We have reinvestigated the living polymerization of pMSt with $SnCl_4$-based initiating systems in the presence of an added base. Living polymerizations using IBEA-$EtAlCl_2$/$SnCl_4$ with ethyl acetate (an added base) in CH_2Cl_2 at 0 °C,[203] or 1,1-dimethoxyethane [$CH_3CH(OCH_3)_2$]-$TiCl_4$/$SnCl_4$ with ethyl acetate (an added base) and DTBP (a proton trap) in CH_2Cl_2 at 0 °C,[204] were found to give living polymers with a very narrow MWD ($M_w/M_n \sim 1.1$). Quite recently, the latter initiating systems containing acetal-$TiCl_4$/$SnCl_4$ turned out to be available for living polymerization of other Sts and VEs. TMSt is known to prevent intra- and intermolecular alkylation chain transfer reactions in the cationic polymerization due to its ring substituents. Living polymerization was initiated by Cumyl-OAc/BCl_3 in CH_3Cl at −30 °C[205] and TMSt-Cl/BCl_3 in CH_2Cl_2 at −70 ∼ −20 °C,[206] to give polymers with low polydispersity ($M_w/M_n = 1.02-1.2$).

The polymerization of ID has been of interest because of the high glass transition temperature (T_g) of polyID (200 °C) and its potential use in thermoplastic elastomers. Sigwalt et al. and Kennedy et al. have investigated several living polymerizations of ID with Cumyl-OCH_3 or TMP-Cl/$TiCl_4$ or $TiCl_3$(BuO) in the presence of additives such as DMSO, DMA, Et_3N, DTBP,[207−210] or Cumyl-Cl/BCl_3,[209] to give controlled polymers. For example, polyID of $M_n = 1.3 \times 10^4$ with a narrow MWD ($M_w/M_n \sim 1.2$) was obtained with the Cumyl-Cl/BCl_3 initiating system in CH_3Cl at −80 °C. Triblock copolymer, PID-*b*-PIB-*b*-PID, was also produced with TMP-Cl/$TiCl_4$ using the sequential monomer addition method, and the polymer exhibited excellent thermoplastic elastomeric character.[211]

In the case of pClSt, which has relatively low reactivity due to the electron-withdrawing substituent, living polymerization was achieved in CH_3Cl/MCH at −80 °C with TMP-Cl/$TiCl_4$ with added DMA and DTBP as a proton trap[212] or with $n\mathrm{Bu_4NCl}$ salt,[213] pMSt-Cl, or pClSt-Cl/$TiCl_4$ with DTBP.[214] We have obtained poly(pClSt) of a narrow MWD ($M_w/M_n \leq 1.2$) using St-Cl/$SnCl_4$ with added $n\mathrm{Bu_4NCl}$ in CH_2Cl_2 at −15 ∼ +25 °C[215] or IBEA-$EtAlCl_2$/$SnCl_4$ with $Cl_2CHCOOCH_3$ (an added base) in CH_2Cl_2 at 0 °C.[183]

The living cationic polymerization of Sts with polar and electron-withdrawing groups, except for pClSt, is difficult because of their lower polymerizabilities and side reactions of the polar groups with Lewis acids. Controlled cationic polymerization of pClMSt was achieved with St−OH/BF_3OEt_2 as an activator/catalyst.[216] This study was designed to make linear and controlled polymers from unprotected pClMSt by cationic polymerization based on the selective activation of C−O terminals. Thus, the authors employed a highly oxophilic Lewis acid, BF_3OEt_2. The polymerization was initiated by the BF_3OEt_2-induced selective activation of the C−O bond of St−OH and proceeded via similar activation of the resulting ∼C−OH dormant polymer terminal. The linear structures that formed via reactions of the chloromethyl pendent groups were confirmed by ^{1}H NMR spectroscopy. In contrast, for St-Cl/$SnCl_4$-based initiating systems, which are available for living polymerizations of St or pClSt, low M_n's based on SEC and broad NMR absorptions were observed and suggested a branched structure, in which a part of the chloromethyl group in pClMSt initiated cationic polymerization. We have investigated pAcOSt, of which living cationic polymerization has not yet been reported. The resulting poly(pAcOSt) was further transformed into poly(HOSt)s by alkaline hydrolysis. Among various Lewis acids, $SnCl_4$ was shown to induce living cationic polymerization of pAcOSt in the presence of ethyl acetate (an added base) in CH_2Cl_2 at 0 °C, yielding a polymer with low polydispersity ($M_w/M_n \sim 1.1$).[183,217] Random and block copolymers of pAcOSt and other Sts were also prepared. More importantly, the resulting poly(HOSt) with a narrow MWD showed a sensitive pH-responsive transition from a clear solution to an opaque one upon decreasing pH (around pH 10).

NVC is among the most reactive monomers in cationic polymerization due to its electron-donating nitrogen and a large conjugating substituent. However, there are very few reports available on its living polymerization. NVC was polymerized effectively using only HI without I_2 or any Lewis acid activators either at −40 °C in toluene or at −78 °C in CH_2Cl_2 with a small amount of $n\mathrm{Bu_4NI}$.[105] The M_n's of the polymers obtained were directly proportional to the monomer conversion or to the monomer/HI feed ratio and in good agreement with the calculated values. The polymers exhibited narrow MWDs ($M_w/M_n = 1.2-1.3$). Recently, we have investigated the polymerization of NVC with $ZnCl_2$ in the presence of a relatively strong Lewis base THF in toluene at 0 °C, to give controlled polymers with a narrow MWD ($M_w/M_n \leq 1.2$).[218]

4. New Monomers

4.1. Naturally Occurring Monomers and Their Derivatives

From the viewpoint of environmentally benign and sustainable chemistry, biobased polymers from renewable resources have recently been attracting much attention. For example, Kamigaito et al. used anethole and isoeugenol (Figure 7) as naturally occurring St derivatives. The controlled cationic copolymerization of these *β*-methyl St (*β*MSt) derivatives with pMOSt was achieved by the alcohol/BF_3OEt_2 system, whereas their homopolymerization did not proceed.[219] For both monomers, the M_n's of the copolymers

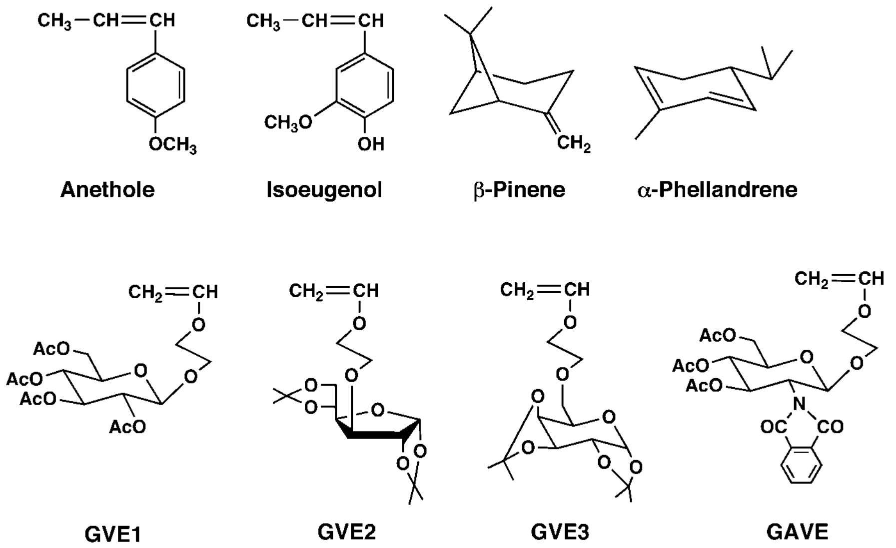


Figure 7. Naturally occurring monomers.

increased in direct proportion to the monomer conversions, retaining relatively narrow MWDs. Furthermore, the measurement of monomer reactivity ratios and MALDI-TOF-MS analysis of copolymers of isoeugenol and pMOSt showed them to be of an alternating fashion. Thus, the aqueous-controlled cationic copolymerization of naturally occurring monomers proceeded with the alcohol/BF_3OEt_2 system to give well-defined phenolic alternating copolymers, which are regarded as linear lignin analogues.

β-Pinene (Figure 7) is one of the main constituents of natural turpentines. Its polymers are used commercially as resins in many applications, but living polymers could not be obtained. The first example of living cationic isomerization polymerization of β-pinene was reported with an HCl adduct of CEVE (CEVE-Cl)/$TiCl_3$(*i*PrO) in conjunction with *n*Bu_4NCl as an added salt in CH_2Cl_2 at $-40 \sim -78$ °C.[220] The M_n of the polymers increased in direct proportion to the monomer conversion. ^1H NMR analysis of the polymers showed that the poly(β-pinene) chains contained the initiator-derived (CEVE-type) headgroup, a *tert*-chloride tail group, and isomerized β-pinene repeat units with a cyclohexane ring. Block-copolymers, graft-copolymers, and end-functionalized polymers were obtained by this living polymerization system (see also sections 6.1 and 7). Living copolymerization with IB was also achieved with St-Cl/$TiCl_4$:Ti(*i*PrO)$_4$ in conjunction with *n*Bu_4NCl under similar conditions,[221] in which both monomers exhibited almost equal reactivity. The MWD was relatively narrow, and the M_n of the copolymers increased in direct proportion to the total monomer conversion. Furthermore, to extend commercial utilization of these polymers, relatively high molecular weight polymers of β-pinene and α-phellandrene with an alicyclic structure were produced. The polymerizations proceeded smoothly with $EtAlCl_2$ or $Et_{1.5}AlCl_{1.5}$ in CH_2Cl_2/MCH (1/1) at -78 °C.[222] The key to achieving relatively high molecular weight polymers is considered to be the judicious choice of Lewis acids and solvents. The polymers were then hydrogenated to give terpene-based alicyclic polymers with a high T_g and degradation temperature. The polymers have good properties for optoelectronic materials, such as low dielectric constants, nonhygroscopicities, and good transparencies.

Recently, there has been increasing interest in glycopolymers containing sugar moieties which act as specific biological functional groups similar to those of naturally occurring glycoconjugates.[223] The sugar portions of the glycopolymers are expected to play essential roles as recognition sites between cells due to their multivalent interactions or as factors controlling the generation of biological functions. A few VE derivatives having protected monosaccharide pendants have been prepared by conventional cationic polymerization, but well-controlled polymers were not obtained, because the sugar moiety consists of multiple polar groups, even if they were masked with protecting groups. Recently, for the preparation of well-defined glycopolymers, various living/controlled polymerization techniques such as radical, anionic, and cationic polymerization were investigated.[223] In the field of cationic polymerization, Miyamoto and Minoda et al. succeeded in polymerizing carbohydrate-carrying VEs, GVE1, and GVE2 (Figure 7), in a living manner.[224−226] The polymerizations of GVE1 and GVE2 were investigated with the two initiating systems. Living cationic polymerization of GVE1 having an acetyl-protected glucose was achieved by $CF_3COOH/EtAlCl_2$ in the presence of 1,4-dioxane as an added base at 0 °C. In contrast, HCl/ZnI_2 at -15 °C was more suitable for the controlled polymerization of GVE2 having an isopropylidene-protected glucose. Homopolymers and various block copolymers with narrow MWDs ($M_w/M_n \sim 1.1$) and controlled molecular weights were obtained (see also section 6.1). Deffieux et al. have investigated the living cationic polymerization of another saccharidic VE (GVE3, Figure 7) using a 1,1-diethoxyethane-Si$(CH_3)_3I/ZnCl_2$ initiating system. They studied the detailed kinetics carefully by ^1H NMR, dilatometry, and MALDI-TOF-MS.[227] D-Glucosamine-containing glycopolymers with well-controlled structures and molecular weights were also synthesized via living cationic polymerization of monomers protected by acetyl and phthaloyl groups (GAVE, Figure 7).[228] Living polymerization was achieved with an adduct of CF_3COOH and IBVE/$EtAlCl_2$ in the presence of 1,4-dioxane (added base) in toluene, to give polymers with very narrow MWDs ($M_w/M_n \sim 1.1$). Quantitative deprotection with hydrazine monohydrate afforded the corresponding water-soluble polymers with pendant D-glucosamine residues, which exhibited unique characteristics useful in the fields of biotechnological, pharmacological, and medical materials.

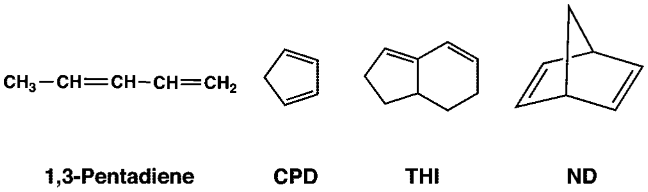


Figure 8. Diene monomers.

4.2. Diene Monomers

To date, linear dienes have not been polymerized by controlled or living procedures, because frequent side reactions can occur such as cross-linking, isomerization, cyclization, and chain transfer reaction. Cheradame et al. reported a series of kinetic studies on the polymerization of 1,3-pentadiene initiated by $AlCl_3$ in a nonpolar solvent.[229] They showed the complexation of propagating species with the polymer at −10 °C, which limited the polymer conversion. The long-lived character of the active centers was shown by deactivating polymerizations with an excess of dimethyl sulfide, in which the formation of sulfonium ion was evidenced by ^{1}H NMR spectroscopy.

On the other hand, precise control of molecular weights and MWDs in cationic polymerization of several cyclic diene monomers such as cyclopentadiene (CPD), tetrahydroindene (THI), and norbornadiene (ND) has recently been achieved with various initiating systems. The cyclic dienes gave rigid main chains of directly linked, unsaturated rings. Their hydrogenated saturated hydrocarbon polymers have attracted much attention as new materials with high T_g's and low dielectric constants.

CPD is a simple and representative cyclic diene that has been polymerized via a cationic addition mechanism with conventional acid catalysts since the 1920s.[3] However, the precise control of CPD cationic polymerization has been difficult, in terms of molecular weights and mainchain microstructure (1,2- and 1,4-enchainments). Sawamoto et al. have synthesized poly(CPD) with controlled molecular weights and narrow MWDs via cationic polymerization of CPD with a three-component initiating system consisting of an HCl adduct of CPD or VE (initiator), $SnCl_4$ (Lewis acid catalyst), and n-Bu_4NCl, Et_2O, or ethyl acetate (added salt or base) in CH_2Cl_2 at −78 °C.[230] The control of the regioselectivity of CPD was also examined with various initiating systems.[231] For example, weak Lewis acids such as ZnX_2 (X: Cl, Br, I) gave the highest 1,4-content (64, 70, and 76%, respectively), whereas $SnCl_4$, $TiCl_4$, and other strong Lewis acids resulted in less controlled microstructures. More recently, with the pMOSt−OH/$B(C_6F_5)_3$ initiating system, Kostjuk et al. reported the controlled cationic polymerization of CPD under mild experimental conditions such as open air and room temperature.[232] ^{1}H NMR analysis indicated that the polymerization proceeded via reversible activation of the C−OH bond. It was shown that the nature of the solvent affected the regioselectivity of poly(CPD), and aqueous suspension polymerization was preliminarily performed.

A bicyclic conjugated diene, THI (bicyclo[4.3.0]-2,9-nonadiene), has recently been employed as a novel diene monomer to produce polymers with new rigid hydrocarbon backbones consisting of bicyclic structures of five- and six-membered rings. Its hydrogenated product has unique physical and chemical properties and particularly good mechanical, electrical, and optical characteristics. The development of the living or controlled cationic polymerization of THI would expand its use considerably. The living cationic polymerization of THI was achieved using the CEVE-HCl/$SnCl_4$ initiating system in the presence of an added base such as ethyl acetate.[79,233] The M_n of the obtained polymers increased in direct proportion to the monomer conversion, and the MWDs were narrow throughout the reactions ($M_w/M_n \sim 1.2$). Living cationic block copolymerization with IBVE led to di- and triblock copolymers consisting of hard nonpolar THI and soft polar IBVE segments for possible application as a thermoplastic elastomer. The subsequent hydrogenation of poly(THI) resulted in a saturated alicyclic hydrocarbon polymer with a relatively high T_g (220 °C) and improved pyrolysis temperature (10% weight loss at 480 °C).[233]

The carbocationic polymerization of ND involves both double bonds by transannular rearrangement, to give a rigid and high-T_g (~320 °C) tricyclic repeat structure, in a range suitable for thermoplastic applications. Kennedy et al. have investigated the cationic polymerization of ND with the TMP-Cl/$TiCl_4$ system. By the use of a proton trap or an added base at −35 to −60 °C, the M_n increased linearly with conversion up to approximately 45%.[234] The chain consisted of about equal amounts of exo/exo and exo/endo connected tricyclic repeat units. Furthermore, two structurally related three-arm star block polymers, tCumyl(PIB-*b*-PND)$_3$ and tCumyl(PND-*b*-PIB)$_3$, were synthesized and characterized.[235]

4.3. Vinyl Ethers (VEs)[236]

Minoda et al. have synthesized poly(VE)s carrying pendant cellobiose heptadecanoate residues (**9**) by cationic polymerization using IBVE-Cl/ZnI_2 in toluene at −15 °C.[237] Although monomeric and some oligomeric byproducts also resulted, polymers with controlled architecture and low polydispersity ratio ($M_w/M_n \sim 1.15$) were obtained. Their mesomorphic properties were examined by DSC, polarization microscopy, and X-ray diffraction. The mesophase of the polymers proved to be quite similar to that of the star-shaped triplet derivative, i.e., (i) discotic columns built up by a regular stacking of the pendant cellobiose heptadecanoate residues, (ii) an extended conformation of each polymer main chain, and (iii) three discotic columns. Other types of VEs having various polar functional groups and bulky substituents (Figure 9) were allowed to polymerize cationically, to give living polymers. Hashimoto et al. reported living polymerization of VE having urethane (**10**)[238] and cyclic acetal (**11**)[239] groups. Although each monomer has an acid-sensitive polar group, both cationic polymerizations proceeded in a living fashion under the appropriate conditions. For example, in the former case, a judicious choice of substituents linked to the urethane nitrogen, the initiating system (HCl/$ZnCl_2$), and a lower polymerization temperature (−30 °C) were found to be important to induce living polymerization of VE with a urethane group. For the latter monomer, various types of initiating systems, including additives (DTBP and added base), were examined. The cyclic acetal in **11** worked well as an effective protecting group under such living polymerization conditions. Feit et al. have presented a route to comb-shaped poly(VE)s with oligooxyethylene carbonate pendant groups (**12**) by living cationic polymerization using CF_3SO_3H with $S(CH_3)_2$ in CH_2Cl_2 at −23 °C.[240] Fluorine-containing polymers have unique properties such as low surface energy, high contact angle, high biocompatibility, and lipo- and hydrophobicity. Yamaoka and Matsuoka et al. reported the living polymerization of fluorine-containing VE

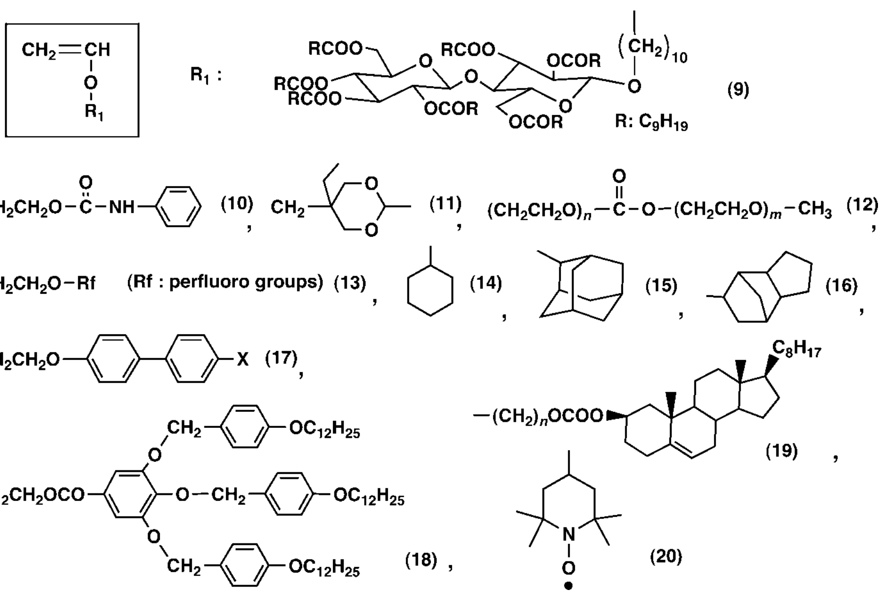


Figure 9. Vinyl ether monomers.

(**13**), 2-(2,2,2-trifluoroethoxy)ethyl VE, with *n*-butyl VE-Cl/ $ZnCl_2$. The synthesis of various block copolymers (see also section 6.1) and the properties of their aqueous solutions were also investigated.[241−243]

In general, poly(VE)s with linear alkyl chains are usually sticky liquids or gums at room temperature (except for the long alkyl VEs), because of low T_g's, and hence, they present problems for use as commodity plastics. However, a series of VEs with an aliphatic (poly)cyclic unit formed plastic resins or films exhibiting high T_g and high thermal stability. Living cationic polymerization of VE containing cyclohexyl (**14**),[244,245] 2-adamantyl (**15**),[246] tricyclodecane (**16**),[247,248] or tricyclodecene[247] units was achieved with VE-Cl or VE-I/ $ZnCl_2$ in the presence or absence of $n\text{Bu}_4\text{NI}$ in CH_2Cl_2 at $-50 \sim -30$ °C, VE-Cl or VE-I with $n\text{Bu}_4\text{NI}$ in CH_2Cl_2 at $-50 \sim -30$ °C, IBEA/$\text{Et}_{1.5}\text{AlCl}_{1.5}$ with ethyl acetate (added base), or HCl/$ZnCl_2$ in toluene at 0 or −30 °C. The M_n's of the obtained polymers increased in direct proportion to monomer conversion and produced polymers with narrow MWDs ($M_w/M_n = 1.03-1.1$). The T_g's and thermal decomposition temperatures (T_d) of the polymers were 178 and 323 °C [for poly(2-adamantyl VE)], and 95 and 346 °C [for poly(tricyclodecane VE)], respectively. Furthermore, a series of diblock copolymers with a stimuli-responsive segment were synthesized to prepare a new class of smart films.[245,248] The resulting films showed reversible thermosensitive behavior.

Long alkyl chains and mesogenic groups are known to have stronger interactions, especially in water, compared with other hydrophobic groups, and many studies on the self-association behavior of the polymers with these groups have been reported. Vinyl ethers carrying a variety of mesogenic substituents (**17**) have been polymerized by HI/I_2, HI/ZnI_2, CF_3SO_3H with $S(CH_3)_2$, or $EtAlCl_2$ with added base in CH_2Cl_2, to give narrowly distributed homopolymers and random and block copolymers.[249−253] For example, Percec et al. have systematically studied the effects of the degree of polymerization and the spacer length on the mesogenic phase formation or phase diagrams.[251−253] They also studied the cationic polymerization of dendritic VE macromonomers (**18**), though the livingness was not established, to give well-controlled polymers with relatively narrow MWDs.[254] Furthermore, the characterization by various methods showed that the obtained polymers displayed an enantiotropic columnar hexagonal mesophase and an enantiotropic nematic mesophase, and the self-assembly mechanism, which resembled that of tobacco mosaic virus, was demonstrated. We have investigated the living cationic polymerization of VEs with a crystalline octadecyl chain (ODVE) or liquid crystalline mesogenic structures (**19**), using appropriate combinations of Lewis acids with added bases, to give each homopolymer with a narrow MWD and well-defined random and block copolymers with various pendants.[255−257]

As a new cathode-active material for organic radical batteries, poly(VE) having a TEMPO radical (**20**) was first prepared.[258] The direct polymerization of the radical monomer was carried out using BF_3OEt_2 in CH_2Cl_2 at −25 °C, although they are not living systems, to give reddish polymers which were soluble in THF, chloroform, DMF, and DMSO. The spin concentration of the obtained polymers was determined by ESR measurement to be 2.75×10^{21} spins·g^{-1} (100% spin per repeating unit). No decrease in spin concentration was observed, even when storing polymer samples for more than a year under aerobic conditions at room temperature. The electrochemical properties of the polymers were also examined by cyclic voltammetry measurements. The extreme stability, the high capacity, and excellent charge/discharge properties demonstrated a wide range of potential applications of **20** as a new power source.

5. Stimuli-Responsive Polymers

Stimuli-responsive polymers, whose properties and shape change in response to an external stimulus, have recently been attracting attention from academic researchers.[258−261] For constructing "intelligent" stimuli-responsive systems, the polymer primary structures would affect the sensitivity, reversibility, and self-assembly of such polymers. Therefore, we have begun to demonstrate the usefulness and possibilities of living polymerization for systematic investigations on stimuli-responsive polymers by the living cationic polymerization of VEs (Figure 10). The strategy and results are described in the latter part of this section (cf. see sections 5.2−5.4).

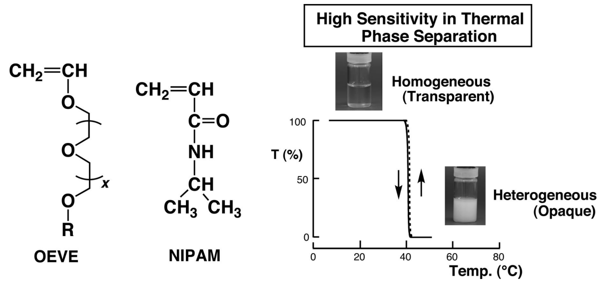


Figure 10. Representative two monomers for stimuli-responsive living polymers and a typical example of thermally induced phase separation of poly(OEVE) ($x = 1$; R = C_2H_5) in water (1 wt %).

5.1. Stimuli-Responsive Polymers: Poly(NIPAM) and Other Polymers

Before showing examples of the synthesis of stimuli-responsive poly(VE)s by living cationic polymerization, we shortly summarize the work done on poly(*N*-isopropylacrylamide) [poly(NIPAM)],[262,263] because it is the most well-known thermoresponsive polymer and has been synthesized intensively throughout the world since the recent discovery of its living radical polymerization.[264] The study of the living polymerization of NIPAM was delayed in comparison with that of other monomers due to various side reactions and solubility problems with the polymer. In 2000, the RAFT[265,266] living radical polymerization of NIPAM was first reported by AIBN employing benzyl dithiobenzene or cumyl dithiobenzoate RAFT agents **21** by Rizzardo et al.[267] (Figure 11). Müller et al.[268] demonstrated the benzyl and cumyl dithiocarbamate(**22**)-mediated polymerization of NIPAM. McCormick et al. achieved controlled RAFT polymerization of NIPAM at room temperature using trithiocarbonate RAFT agent **23** with an azo initiator in DMF or aqueous media, to give a living polymer having an extremely narrow MWD.[269] Yamago et al. demonstrated the effectiveness of organotellurium or organostilbine compounds **24** and **25** as the chain transfer agents for living polymerization of various monomers, including NIPAM, using an azo-initiator.[270] The simultaneous control of the stereostructure and molecular weight was reported by Okamoto et al.[271,272] Subsequently, other living polymerizations of NIPAM have also been reported. NMP has been carried out by Hawker and Fréchet et al.[273] with initiator **26**, a hydrogen alkoxyamine derivative, instead of the TEMPO-based systems, to give poly(NIPAM) with a narrow MWD, along with its block copolymers with PSt, and star block copolymers having poly(NIPAM) and PSt segments.[274] Masci et al.[275] and Stöver et al.[276] reported the successful living radical polymerization of NIPAM with a combination of alkyl 2-chloropropionate (**27**) initiator, copper(I) chloride catalyst, and Me_6TREN (**28**) ligand. Recently, the reaction conditions using CuCl/Me_6TREN have been determined to be single-electron-transfer living radical polymerization (SET-LRP).[277] The specific polymerization of NIPAM via SET-LRP has been reported to give a series of well-defined double-hydrophilic graft copolymers.[278]

Living radical polymerization has allowed the synthesis of diblock copolymers using many monomer combinations, as shown in Figure 12.[279] These block copolymers **29**−**35** formed polymer micelles in water in response to variations in temperature. For example, the diblock copolymer, poly(NIPAM)−poly(acrylic acid) (**29**), with low polydispersities was synthesized by RAFT polymerization by Müller et al., and its thermally- or pH-induced micelle formation in aqueous solution was investigated by DLS, NMR, IR, and cryo-TEM techniques.[280] Block copolymers with hydrophobic [PSt (**30**) or poly(MMA) (**31**)],[281,282] biodegradable [poly(ethylene oxide) (PEO, **32**),[283] poly(lactic acid)s (PLA, **33**),[284] and poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC, **34**)],[285] and thermoresponsive segments have also been synthesized. Furthermore, dual thermosensitive block copolymers **35** containing zwitterionic segments which exhibit upper critical solution temperatures (UCST) have been prepared.[286] Upon heating, the dual thermosensitive block copolymers exhibited switching between the interior and exterior of the aggregates. Furthermore, various types of branched polymers have been designed and prepared, such as dendrimers,[287] star-shaped polymers,[288] hyperbranched polymers,[289] and graft copolymers, onto various polymers[290] or inorganic substrates.[291]

Well-controlled thermoresponsive polymers other than poly(NIPAM) were also synthesized by different living polymerization systems. Particularly, PEO-related triblock copolymers were synthesized by anionic ring-opening polymerization,[292] e.g., PEO-poly(propylene oxide)-PEO (PEO-PPO-PEO),[293] PEO-PLA-PEO,[294] PEO-PPO,[295] and PEO-poly(butylene oxide) (PEO-PBO)[296] (Figure 13). They are well-known for their many commercial applications as emulsifiers, dispersants, and stabilizers. As other thermoresponsive polymers, polymethacrylate having oxyethylene groups on the side chains (**36**)[297] and various temperature-responsive polymers having an ether bond in the main and side chains (**37**)[298] have also been examined by living anionic and ring-opening cationic polymerization, respectively.

Ionic liquids have attracted attention because of their unique properties such as thermal and chemical stability, negligible volatility, nonflammability, and high ionic conductivity. Watanabe et al. found that a certain combination of macromolecules in ionic liquids exhibited LCST- (lower critical solution temperature-) or UCST-type phase separation.[299] poly(NIPAM) exhibited UCST-type phase separation in ionic liquids[300] such as [C_2mim][NTf_2], and the thermosensitivity has recently been utilized in a thermoreversible ionic gel with high ion conductivity by the use of ABA triblock copolymers, poly(NIPAM)−PEO−poly(NIPAM).[301] On the other hand, poly(benzyl methacrylate) (**38**, Figure 13) and its analogous copolymers exhibited the LCST-type phase separation in common hydrophobic ionic liquids such as [C_2mim][NTf_2].[302,303] The phase separation behavior is now under investigation from a thermodynamic viewpoint.

5.2. Thermoresponsive Poly(VE)s with Oxyethylene Pendants and Related Poly(VE)s

About 20 years ago, we discovered the thermoresponsive properties of poly(VE)s with oxyethylene pendants [poly(OEVE), Figure 14][304,305] in water.[306−308] This phase transition was found to be quite sensitive: clear aqueous solutions of these poly(OEVE)s transformed into turbid solutions, with complete transition within 1 °C at a heating rate of 1 °C/min. The behavior was completely reversible upon heating and cooling without hysteresis.[306,309−311] For example, an aqueous solution of a poly(EOVE) underwent phase separation sensitively at 20 °C. The phase separation temperature (T_{PS}) of poly(OEVE)s can be controlled by varying the length of the pendant oxyethylene units and/or an ω-alkyl group.[306] Aqueous solutions of poly(MOVE) and poly(EOEOVE) underwent phase separation sensitively at 63 and 41 °C, respectively. The critical temperature was also controllable

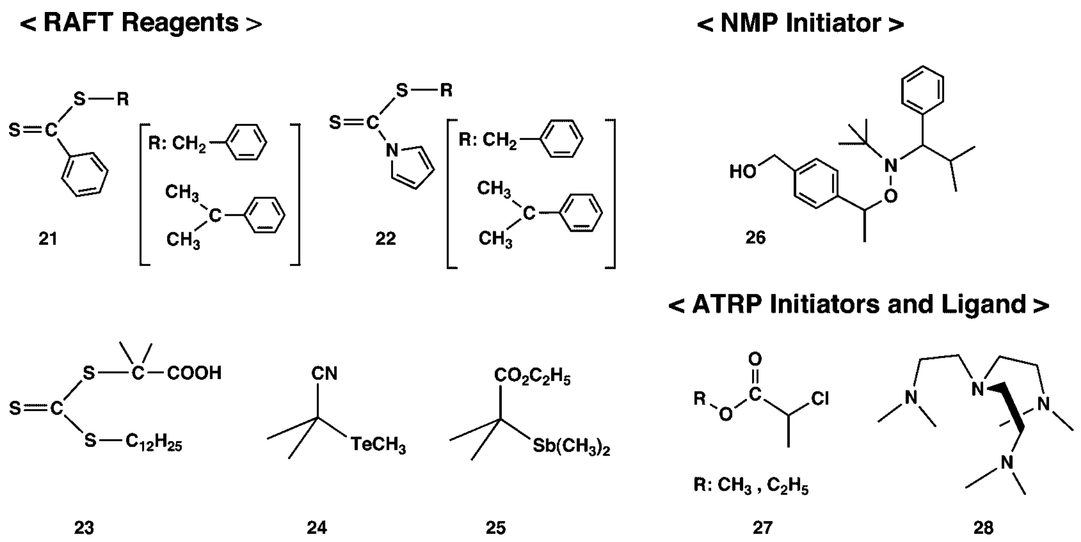


Figure 11. RAFT reagents, an NMP initiator, ATRP initiators, and ligands for living/controlled polymerization of NIPAM.

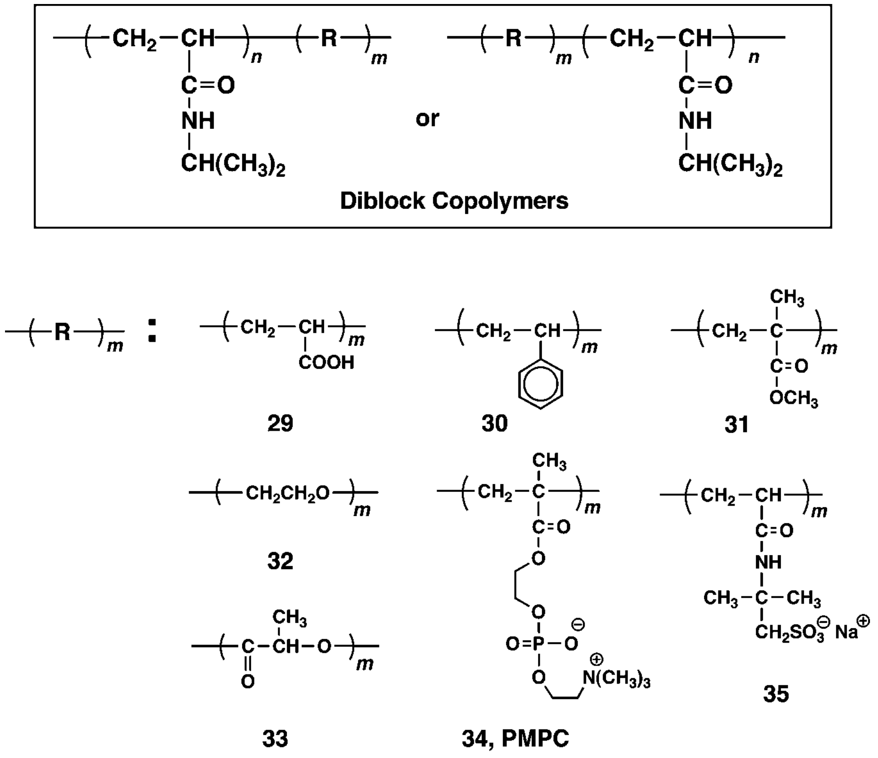


Figure 12. Poly(NIPAM) diblock copolymers.

by regulating the composition of a random copolymer of OEVE with another thermosensitive OEVE, a hydrophilic, or a hydrophobic monomer. For example, the T_{PS} of a random copolymer of EOVE and MOVE lies between those of the two homopolymers at 20 and 63 °C, respectively. It should also be noted that high sensitivity in phase transition was observed only by polymers with narrow MWDs.[306]

The polymerization of an alcohol-type monomer having a fine balance between hydrophilicity and hydrophobicity was also carried out to produce another type of polymer with thermosensitivity in water.[312] For example, a hydroxybutyl group is a rearrangement of an ethoxyethyl unit and is expected to have a similar overall amphiphilic balance. Aqueous solutions of **39** and **40**[313] underwent rapid phase separation at 42 and 20 °C, whereas those with shorter or longer spacers were soluble and insoluble in water, respectively. These results show that an appropriate hydrophilic/hydrophobic balance was required for achieving thermosensitivity. On the other hand, we have also investigated random copolymers of hydrophobic and hydrophilic units to synthesize more generalized thermoresponsive polymers,[314] because the pendant design of poly(OEVE) is often cumbersome. Thermoresponsive behavior has been observed for a series of copolymers containing hydrophilic (HOVE: $CH_2=CH-O-CH_2CH_2OH$) and hydrophobic alkyl VE units, which were prepared via living cationic polymerization in the presence of an added base. The thermally induced phase separation was sensitive and reversible, similar to those of poly(OEVE)s. The T_{ps} of the random copolymers can be controlled by varying the composition ratio of HOVE with a hydrophobic VE or the structure of the hydrophobic VEs. Furthermore, it was found that the randomness of sequence distribution was the key to realizing such highly sensitive phase separation. Random copolymers involving block

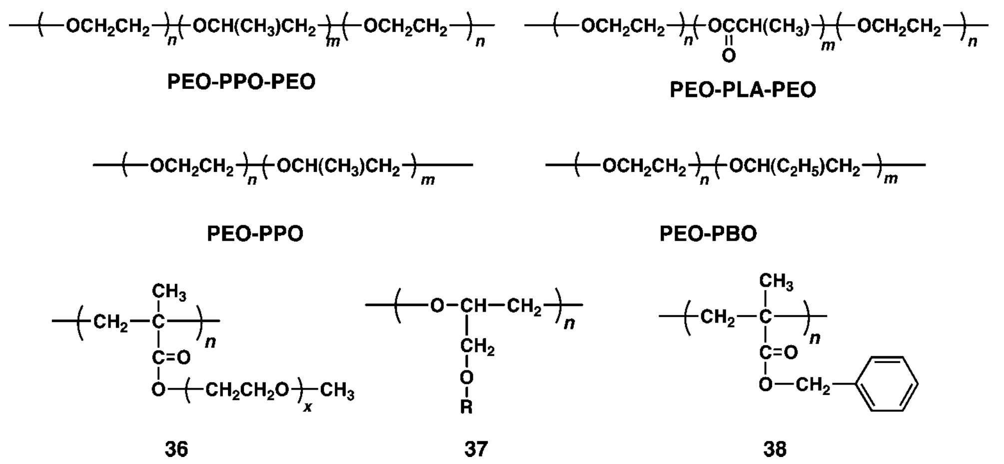


Figure 13. Other stimuli-responsive living polymers.

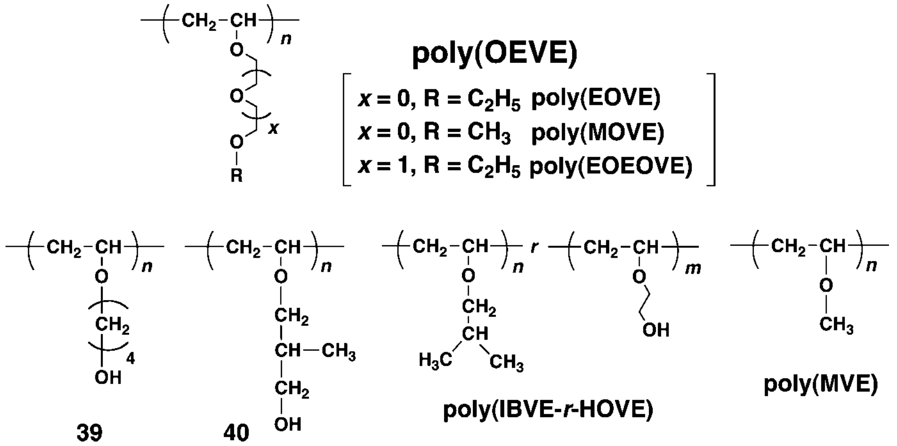


Figure 14. Thermoresponsive poly(VE)s for LCST-type phase separation in water.

segments, which were separately prepared by continuous living polymerization (see section 6.3.2), exhibited different phase separation behavior from those of random and block copolymers. The phase separation was not sensitive, and clear hysteresis was observed between the heating and cooling cycles, in spite of the same composition and its ratio as thermosensitive random copolymers.

Methyl VE (MVE), whose polymer is known to show thermosensitive LCST-type behavior in water for a long time,[262] has been polymerized using the HI/I_2 initiating system, to give living polymers with narrow MWDs ($M_w/M_n \sim 1.10$).[12] The block copolymers with cetyl VE and pMOSt were prepared using the HI/I_2 or HI/ZnI_2 initiating system.[12,315,316] Living polymerization of MVE was also accomplished by the IBVE-Cl/$SnCl_4$ initiating system with $n$$Bu_4NCl$ as an added salt in CH_2Cl_2 at −78 °C,[317] 1,1-diethoxyethane-Si$(CH_3)_3$I/ZnI_2 in toluene at −40 °C,[318] or TMP-DPE-Cl/$TiCl_4$:Ti$(OEt)_4$ with DTBP as a proton trap in hexane/CH_3Cl at −78 °C,[319] to give MVE polymers with narrow MWDs. By using these initiating systems, various di- or triblock copolymers, random copolymers, and end-functionalized polymers were selectively obtained (cf. see sections 5.4 and 7). Furthermore, their aqueous solution behavior such as micelle formation, self-association, colloidal dispersion, and pressure-enhanced dynamic heterogeneity was investigated.

On the other hand, phase separation behavior of well-defined polymers in organic solvents has also drawn attention academically and industrially for years. For example, for LCST-type phase separation, various studies were reported with conventional polymers such as poly(St), poly(IB), poly(acrylic acid), and cellulose derivatives.[320,321] However, most of the systems required tough conditions, such as a high-pressure system in a sealed cell above the bp of a solvent, except for a few examples which had independently been reported in recent years.[322] For polymers which exhibit LCST-type phase separation behavior in organic solvents under mild conditions, we have designed well-defined poly(VE)s with ionic liquid type pendants.[323] The polymers have a poly(VE) backbone and imidazolium or pyridinium salt pendants, which were prepared via base-assisting living cationic polymerization of CEVE, followed by chemical modification of the pendants. Nuyken et al. reported the synthesis of block copoly(VE)s containing pendant pyrrolidonyl, succinimido, pyrazolyl, and imidazolyl groups as amphiphilic polymers, but no investigations on phase separation behaviors were conducted.[324] For example, the poly([Bulm][Cl]) ($M_n = 0.8 \times 10^4$, $M_w/M_n = 1.13$) was soluble in chloroform at ambient temperature, but the transparent solution became opaque sharply at 40 °C, as shown in Figure 15.[323] The solution became clear upon decreasing the temperature, without hysteresis. Poly([MePy][Cl]) with pyridinium salts exhibited similar phase transition characteristics. The dependencies of the molecular weight, the concentration, and the salt structures were demonstrated, and similar phase separation in various organic solvents was also induced by adding a good solvent to a nonsolvent. Upon heating, the interaction between a polymer pendant and a solvent becomes weaker by the cleavage of the hydrogen bond.

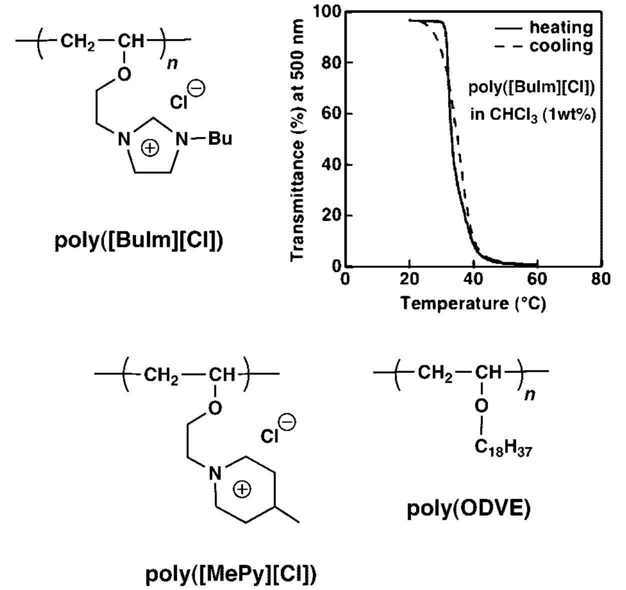


Figure 15. Thermoresponsive poly(VE)s for LCST or UCST-type phase separation in organic solvents.

UCST-type phase separation in organic solvents was also investigated as follows,[257,325−327] in which the driving forces for aggregation are strong hydrophobic interactions, such as crystallization of long alkyl chains.[255] The homopolymer of ODVE (C18 pendant) and its block copolymers, such as with methyl VE, have been investigated in detail, because of their characteristic solubilities and high emulsion stabilities.[318] We have prepared various types of poly(ODVE)s, not only homopolymers, but random, block, and gradient copolymers with very narrow MWDs.[255−257] Interestingly, sensitive UCST-type phase separation of homopolymers and random copolymers occurred for all solutions in various conventional organic solvents with wide-ranging polarities.[255] A calorimetric study indicated that the transition with poly(ODVE) involves crystallization of pendant octadecyl chains; no peak appeared in the thermogram for poly(dodecyl VE) containing long but amorphous alkyl pendants. Furthermore, the sequence distribution (block, periodic, statistic, and gradient) in the copolymers was found to affect the viscoelastic properties of the product gel significantly.[256,257] On the other hand, poly(VE)s with pendant cholesteryl[257,325,326] or biphenyl groups were also prepared and found to exhibit sensitive UCST-type phase separation in organic solvents.[257]

5.3. Other Stimuli-Responsive Poly(VE)s

Base-assisting living cationic polymerization is tolerant toward various polar functional monomers, selectively yielding a new series of well-defined stimuli-responsive polymers including pH-,[328] photo-,[54,329,330] solvent-,[331,332] and pressure-responsive[333,334] polymers (Figures 16 and 17).[307,308] For example, although a solution of **41** or **42** having an alkylene group ($\geq$C5) or a phenylene adjacent to the carboxy group was transparent at neutral or alkaline conditions, the transmittance of solutions of polymers **41** and **42** sharply changed at pH 5.6 and 6.5, respectively.[328] The polymer pK_a value, the solubility of the polymer, and introduction of hydrophobic units were found to be important to control the critical pH. Interestingly, random copolymers **43** and homopolymer **44** exhibited a sensitive phase transition in PBS even at pH 7.0, which is unusually high for carboxy-containing polymers.

Living cationic polymerization of AzoVE or its derivatives containing an azobenzene side group (**45**) known for *cis*−*trans* isomerization by light irradiation was achieved using various Lewis acids in the presence of an ester as an added base.[54,329,330] The characteristic phase transition behavior was observed sensitively and reversibly upon irradiation with UV or visible light. For example, random copoly(AzoVE)s containing both thermally responsive and azobenzene units (**46**) could control the solubility of polymers in water by irradiation with UV or visible light at a constant temperature (Figure 17). Sensitive phase separation was also induced by the addition of a small amount of water[308,332] or an organic compound[331] or by increased pressure.[333,334] For the former separation using polymer **47**, the addition of very small amounts of water (as little as 0.1%) induced a rapid phase transition or physical gelation of a silyloxy-containing diblock copolymer.[308]

5.4. Stimuli-Responsive Block Copolymers

We have been investigating poly(OEVE) systems in regard to the effects of molecular weight, MWD, and sequence distribution, etc.,[306] because PNIPAM could not be obtained by living polymerization at that time. Our findings were quite important for our understanding of the mechanism and for further design of stimuli-responsive polymer derivatives. Sharp and reversible phase separation might lead to well-defined construction of reversible self-association systems. We have thus synthesized multicomponent block copolymers with a stimuli-responsive moiety and examined their thermally induced self-association.[307,308,335−340] First, a diblock copolymer containing a thermosensitive poly(EOVE) segment and a polyalcohol poly(HOVE)[341] segment (**48**) was prepared by sequential living cationic polymerization.[337,338] The diblock copolymer was found to form micelles with a very narrow size distribution in water above the critical temperature, 20 °C,[339,340] as shown in Figure 18. The critical micelle temperature was in good agreement with the clouding point of the thermosensitive segment. The association−dissociation behavior was observed reversibly upon heating and cooling. More interestingly, the solution underwent rapid physical gelation at a higher concentration upon warming to the critical temperature.[337−340] The obtained transparent gel reverted with sensitivity to the solution state at the same temperature upon cooling, as confirmed by dynamic viscoelasticity measurements. Small-angle neutron scattering studies, dynamic light scattering studies, and cryo-TEM measurements indicated that physical gelation starts with thermally induced micellization, giving nearly monodisperse spherical micelles with core size 18−20 nm. Subsequent and immediate macrolattice formation with bcc symmetry transforms the solution into a physical gel. To achieve sharp self-association, highly controlled primary structures were found to play an important role, and the critical temperature of physical gelation could be varied by altering the combination of two segments in the diblock copolymer.

On the basis of this gelation mechanism, several stimuli-responsive gelation systems using diblock copolymers were created to respond to other stimuli as shown in Figure 19. Addition of a selected solvent or compound,[331,332] cooling,[256] pH change,[328] pressure,[333,334] and irradiation with UV light[54,329,330] were examined as stimuli. Furthermore, diblock copolymers with two different stimuli-responsive segments (**49**)[328,342] or with two thermosensitive segments (**50**)[336,343,344] possessing different T_{PS} values have also been synthesized

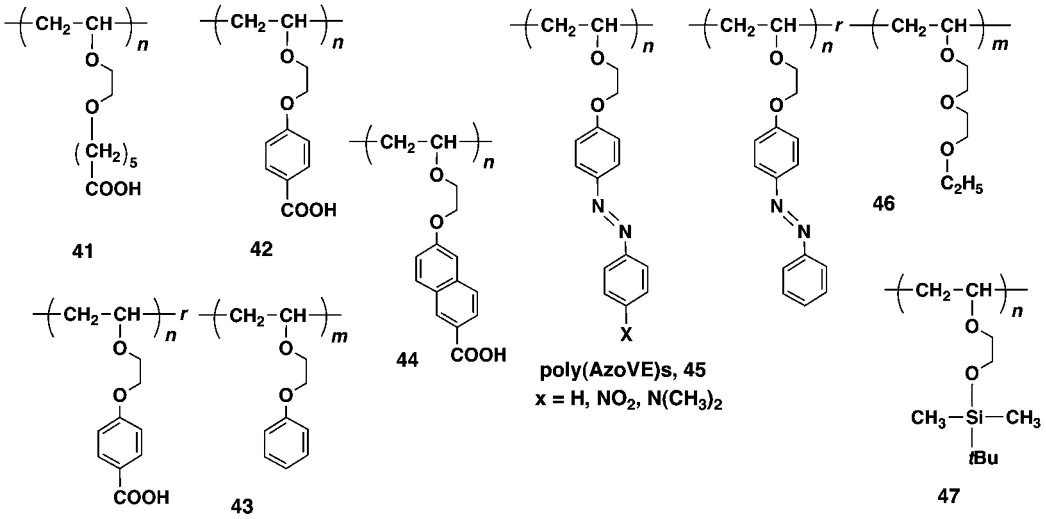


Figure 16. Various stimuli-responsive polymers.

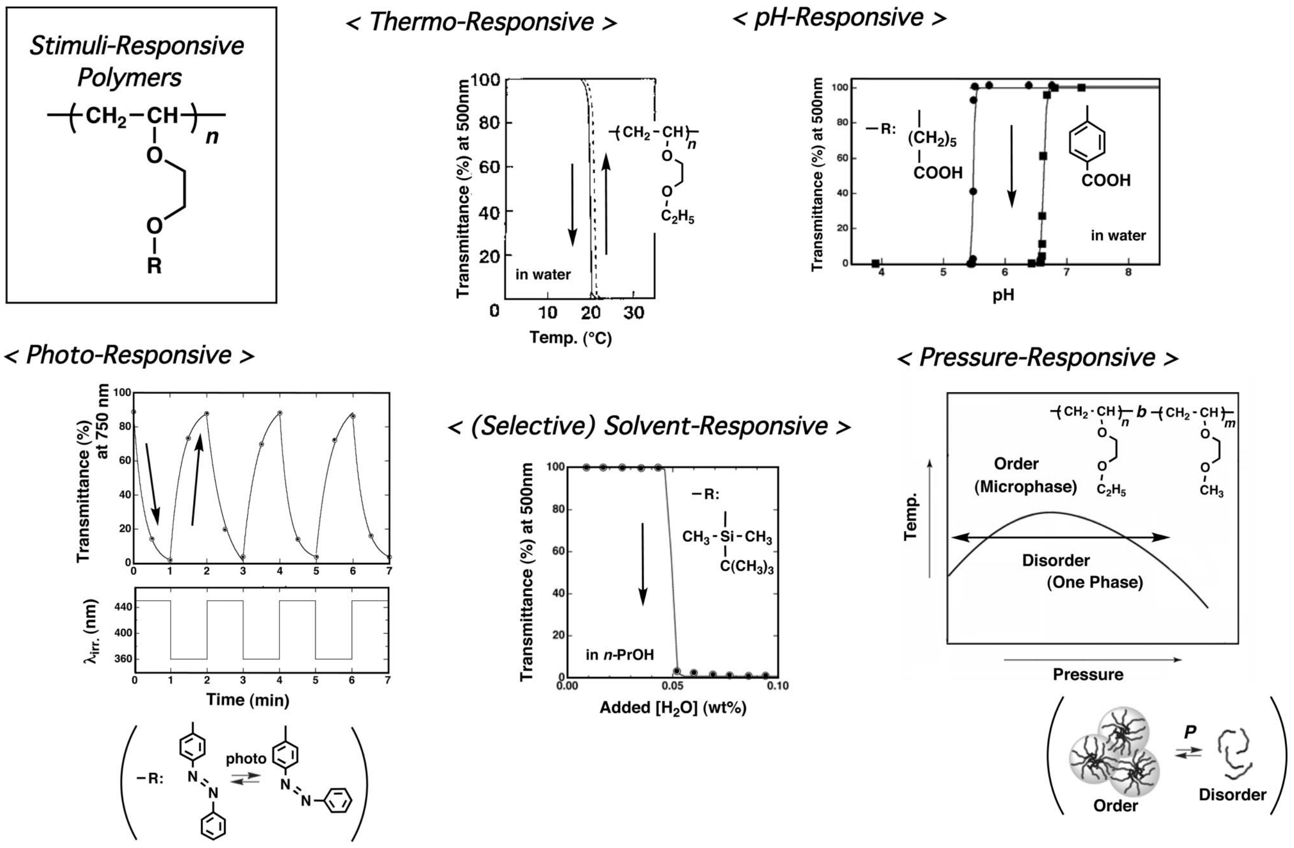


Figure 17. Typical example of the stimuli-responsive behavior of poly(VE)s in water.

and characteristic micelle formation and/or physical gelation was investigated. Stimuli-responsive ABC triblock copolymers (**51**) prepared by sequential living polymerization exhibited sensitive thermally induced physical gelation (open association) via formation of micelles, in which the ABC triblock copolymers exhibited Weissenberg effects in semidilute aqueous solution.[345] Further investigations for applications in the many fields have been examined as follows: cell attachment on the PET films coated with thermosensitive block copolymers,[346] thermosensitive liposomes,[347] characteristic smart films,[245,248] surface modification by diblock copolymers containing azobenzene,[348] and surface modified micelles with carboxy groups.[349,350]

Various types of block copolymers of poly(MVE), other themosensitive polymers, with hydrophilic or hydrophobic segments such as poly(vinyl alcohol) (**52**),[351] poly(methyl triethylene glycol VE: TEGVE) (**53**),[352,353] poly(IBVE) (**54**),[354−356] poly(St) (**55**),[317,357] poly(IB) (**56**),[319] and poly(ODVE) (**57**),[318] were selectively obtained (Figure 20) by using several living cationic polymerizations. For example, Armes et al. have prepared diblock copolymers of poly(MVE) and hydrophilic polymer poly(TEGVE) with a narrow MWD by IBVE-Cl/SnCl$_4$ with nBu$_4$NCl in CH$_2$Cl$_2$,[352,353] and they studied the aqueous solutions of these copolymers by various methods to elucidate the effect of temperature on thermally induced micellization. It was shown that the diblock copoly-

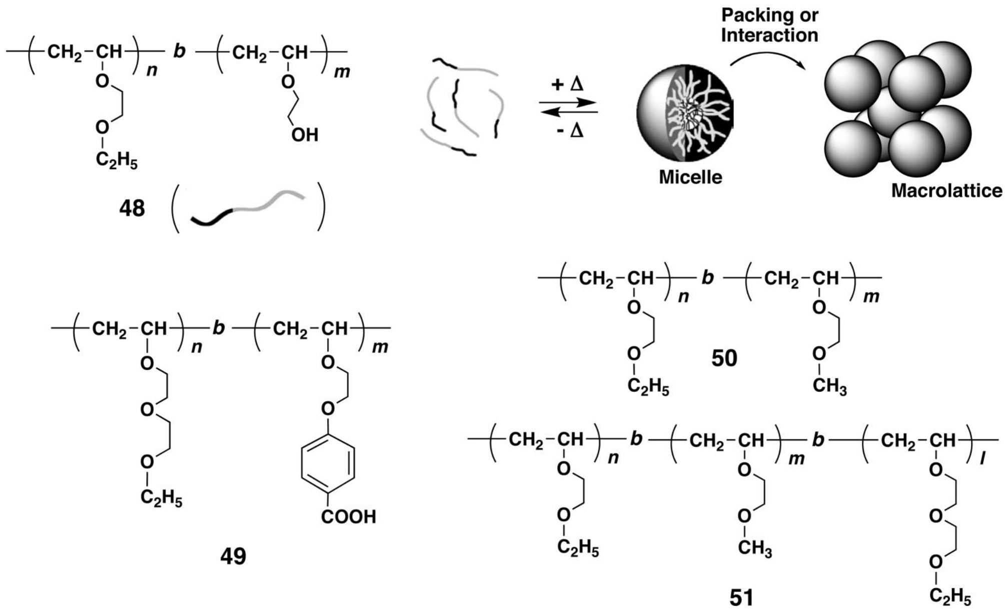


Figure 18. Block copoly(VE)s and the mechanism of thermally induced self-association.

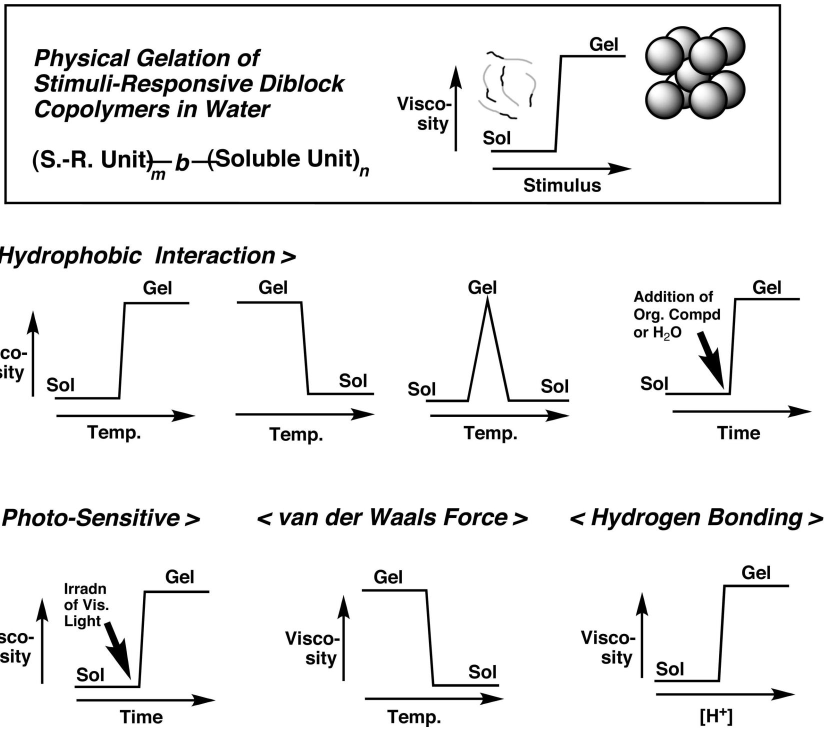


Figure 19. Typical examples of physical gelation of stimuli-responsive diblock copolymers.

mers were dispersed as single chains in water at room temperature, and micelles were formed at elevated temperatures above 50 °C (a unimer−micelle transition). The hydrodynamic sizes of the block copolymers ranged from 8.1 to 31 nm (by DLS), and the MVE block formed the micellar core. Micellization was reversible as shown by variable temperature ^{1}H NMR studies. Di- or triblock copolymers containing poly(MVE) and hydrophobic segments have been investigated by Goethals and Prez et al.[318,358] as nonionic surfactants or thermoresponsive colloidal stabilizers.[358] A series of end group modified poly(MVE)s was also prepared to clarify the effect of end groups on the phase separation behavior[359,360] and to prepare precursors for new types of block, graft, and star-shaped polymers.[360−362]

6. Block Copolymers

6.1. Di- and Triblock Copolymer Synthesis via Sequential Living Polymerization or Intermediate Capping Reaction

The oldest example of the synthesis of an AB block copolymer with a narrow MWD was in 1984.[12] For example, IBVE or MVE was first polymerized with the HI/I_2 initiating system in toluene at −35 °C to give a living polymer, followed by addition of the second monomer, a solution of cetyl VE (CVE: $CH_2{=}CH{-}O{-}C_{16}H_{33}$) (**58**) or pMOSt (**59**) in CCl_4, and the polymerization was completed at −15 °C. The narrow MWDs of the resulting polymers shifted toward

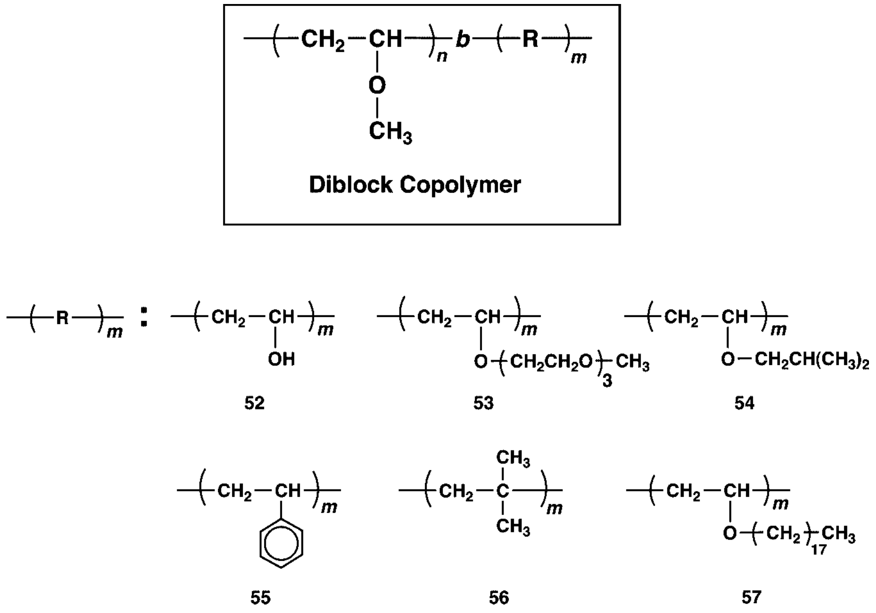


Figure 20. Poly(MVE) diblock copolymers.

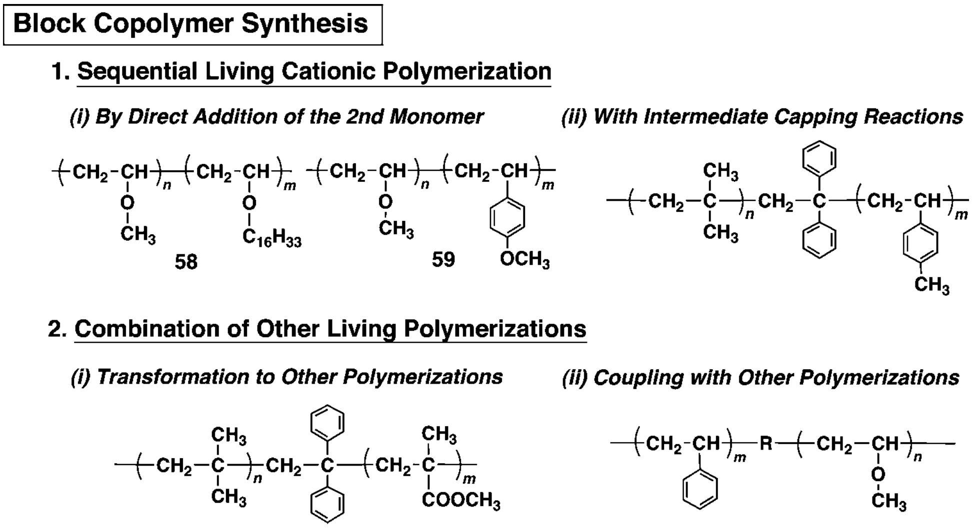
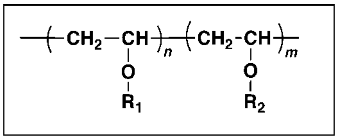


Figure 21. Block copolymer synthesis by living cationic polymerization.



R_1 or R_2 :

alkyl ($C_1 \sim C_{18}$), CH_2CH_2OH, $(CH_2)_3COOH$, $CH_2CH_2NH_2$

$CH_2C_6H_5$, $Si(CH_3)_2tBu$, H, CH_2CH_2Cl, $CH_2CH_2OCOCH{=}CH\text{-}C_6H_5$

$(CH_2CH_2O)_n\text{-}CH_3$, $(CH_2)_n\text{-}O\text{-}C_6H_4\text{-}C_6H_4\text{-}X$ (Mesogenic Group)

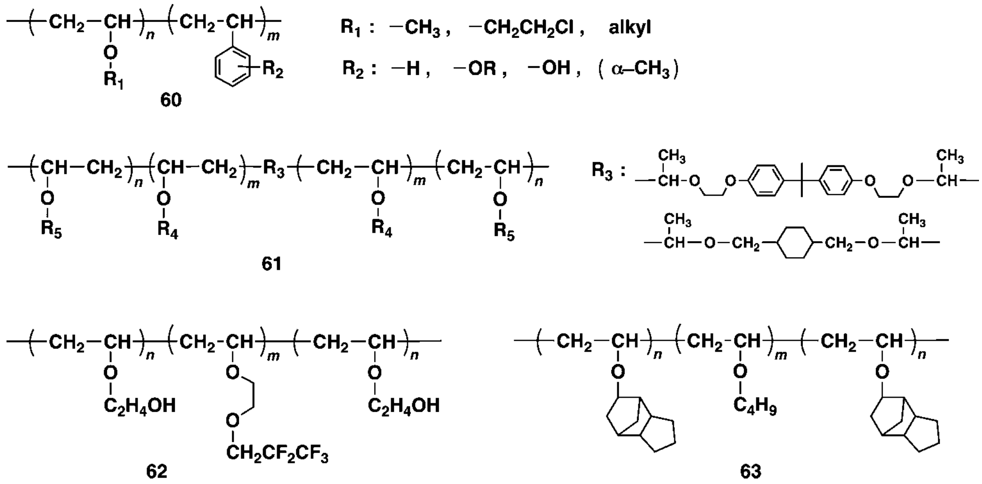
$CH_2CH_2\text{-}Y$ (Y: Glucose or Glicosamine Residues)

Figure 22. Poly(VE) diblock copolymers.

higher molecular weight without tailing [$M_w/M_n = 1.07$ for the precursor poly(MVE), 1.13 for poly(MVE)-*b*-poly(CVE)]. Furthermore, an extraction experiment with methanol showed the absence of the MVE homopolymer. Since this successful synthesis of a block copolymer, a large variety of block copolymers have been prepared via sequential living cationic polymerizations and/or an intermediate capping reaction,[363] as shown in Figure 21. Various transformations from cationic to other living polymerizations,[364] known as an alternative method for block copolymer synthesis, are described in a later section (see section 6.2).

6.1.1. Poly(VE)-Based Block Copolymers

For block copolymer synthesis of poly(VE)s, the sequential method is advantageous in that it offers an easy procedure, perfect blocking efficiency, and easier control of segment lengths in the product polymers. An important characteristic feature of VE polymerization is that the sequential living cationic polymerizations are achieved almost reversibly, although adjustment of reaction conditions or addition of extra catalysts or additives was sometimes needed. This is in sharp contrast to the block copolymerization of Sts or IB[363] (see section 6.1.2). Figure 22 summarizes typical examples of poly(VE)-*b*-poly(VE′) AB block copolymers. Higashimura et al. reported the sequential block copolymerization of various polar monomers with alkyl VE, to give amphiphilic diblock copolymers having hydrophilic segments including hydroxy,[365,366] carboxy,[367] and amino[368] pendant groups. Various protected monomers were employed, and appropriate initiating systems and reaction conditions were carefully



60

61

62

63

Figure 23. Other poly(VE) block copolymers.

chosen. For example, IBVE was first polymerized with HI/I_2, HI/ZnI_2, or HCl/$ZnCl_2$ in toluene at −40 °C, and AcOVE[365] or trialkylsilyl VE (SiVE)[369] was further polymerized to yield an AB diblock copolymer. Hydrolysis of the block copolymers yielded amphiphilic copolymers that lowered the surface tension of the aqueous solutions and the interfacial tension of the water/toluene interface.[365] PVA block copolymers were prepared by the sequential living polymerization of benzyl VE (BnVE)[370] or *tert*-butyl VE (tBuVE)[371] with IBVE by the IBEA/$EtAlCl_2$ initiating system in the presence of added bases below 0 °C in a nonpolar solvent (toluene or CCl_4). Debenzylation of the block copolymers was achieved by two methods [(i) HBr in toluene and (ii) Na in liquid NH_3] to give PVA block copolymers with narrow MWDs.

Other types of block copolymers containing poly(2-chloroethyl VE),[372] poly(2-vinyloxyethyl cinnamate),[373] liquid crystalline poly(VE)s,[374,375] and glycosidic poly(VE)s[376−380] were prepared based on this method.

For the synthesis of block copolymer poly(VE)-*b*-poly(Sts) (**60**, Figure 23) via sequential living cationic polymerization, some care is required, because the reactivities of most Sts are less than VEs.[15] For example, the living cationic polymerization of MVE was first carried out with the HCl/$SnCl_4$ initiating system in the presence of $n$$Bu_4NCl$ at −78 °C, and then the second monomer, St, was added. To accelerate the rate of polymerization, small amounts of $SnCl_4$ and the salt were added at −15 °C to give the target block copolymers quantitatively.[317]

ABA triblock copolymers (**61**−**63**, Figure 23) were prepared by using various initiators $X-R_3-X$ in Figure 23. For example, bifunctional initiator $X-R_3-X$ (X: $OCOCF_3$, in Figure 23) was prepared from the corresponding divinyl ether and trifluoroacetic acid in CCl_4 at 0 °C.[381] The $X-R_3-X$/$EtAlCl_2$ initiating system induced well-defined sequential living polymerization of IBVE and AcOVE at temperatures up to +40 °C in the presence of 1,4-dioxane, and subsequent hydrolysis led to ABA amphiphilic triblock copolymers where the hydrophilic poly(HOVE) segment could be in either the center or outer blocks. Other types of amphiphilic triblock copolymers including a perfluoro segment **62** have been prepared.[382] As a thermoplastic elastomer, Hashimoto et al. have demonstrated the preparation of new triblock copolymers composed solely of poly(VE)s backbones (**63**), and investigated their physical properties.[383]

6.1.2. PIB-Based Block Copolymers

Many groups have synthesized series of block copolymers of IB with Sts, VEs, and isoprene[140,384] (Figure 24). Some examples of PIB-based block copolymers are shown in Figure 24. In particular, the triblock copolymers PSts-*b*-PIB-*b*-PSts having rubbery PIB segments and glassy PSts segments (**64**) were investigated in detail to prepare thermoplastic elastomers.[384] The sequential living polymerization was initiated with a bifunctional initiator in conjunction with $TiCl_4$ in a moderately polar solvent mixture at a low temperature. The characteristic physical properties and morphologies of these triblock copolymers have also been demonstrated. For PαMSt-*b*-PIB (**65**), as an example of block copolymerization from a more reactive monomer to a less reactive one, BCl_3 (a weaker Lewis acid) was found to be suitable for the polymerization of αMSt and the quantitative crossover reaction, and the addition of $TiCl_4$ (a stronger Lewis acid) induced the polymerization of IB.[199,385]

In the case of sequential block copolymerization of IB with a more reactive second monomer such as αMSt,[386] pMSt,[387] or VE,[319,388,389] a new process was investigated that involved an intermediate capping reaction with diarylethylenes, followed by moderating the Lewis acidity before addition of the second monomer (**66**, **67**). Figure 24 shows typical examples. This method has been successfully employed in the di- or triblock copolymerization of IB with αMSt, pMSt, *p*-(*tert*-butyldimethylsillyoxy) St,[390] cyclohexyl VE,[391] MVE, and tBuVE. By using "grafting from" techniques including surface-initiated living cationic polymerization of IB with $TiCl_4$ in the presence of DTBP, organic−inorganic core−shell nanoparticles were produced.[392]

6.2. Synthesis of Block Copolymers via Combination of Other Living Polymerizations

Recently, by combining different living/controlled polymerization mechanisms such as radical, anionic, group transfer, ring-opening, and metathesis polymerizations, novel block polymers could be synthesized from new combinations of monomers. This chapter describes some representative examples of diblock, triblock, graft, and star-shaped copolymers.

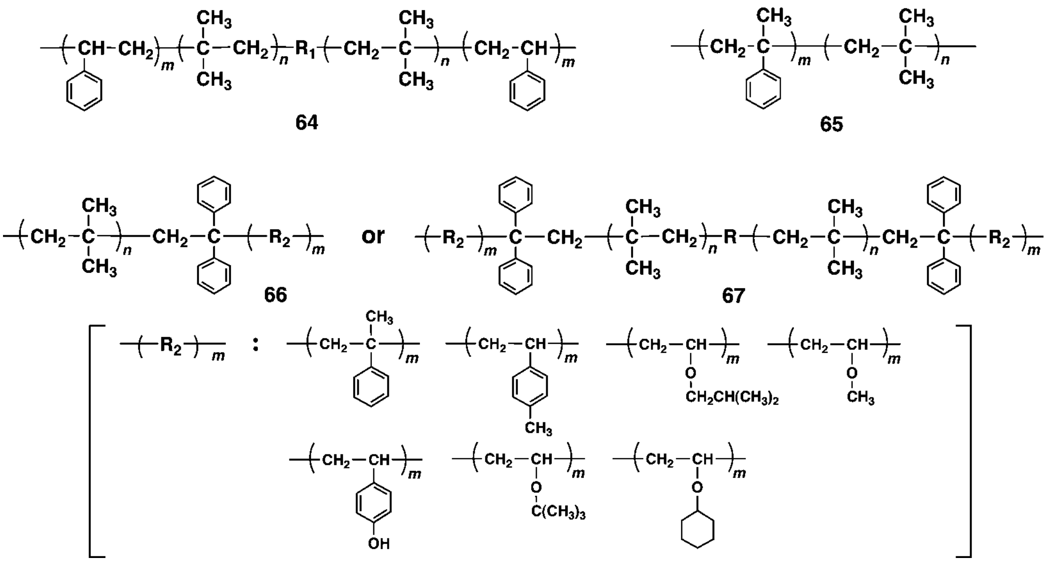


Figure 24. PIB block copolymers.

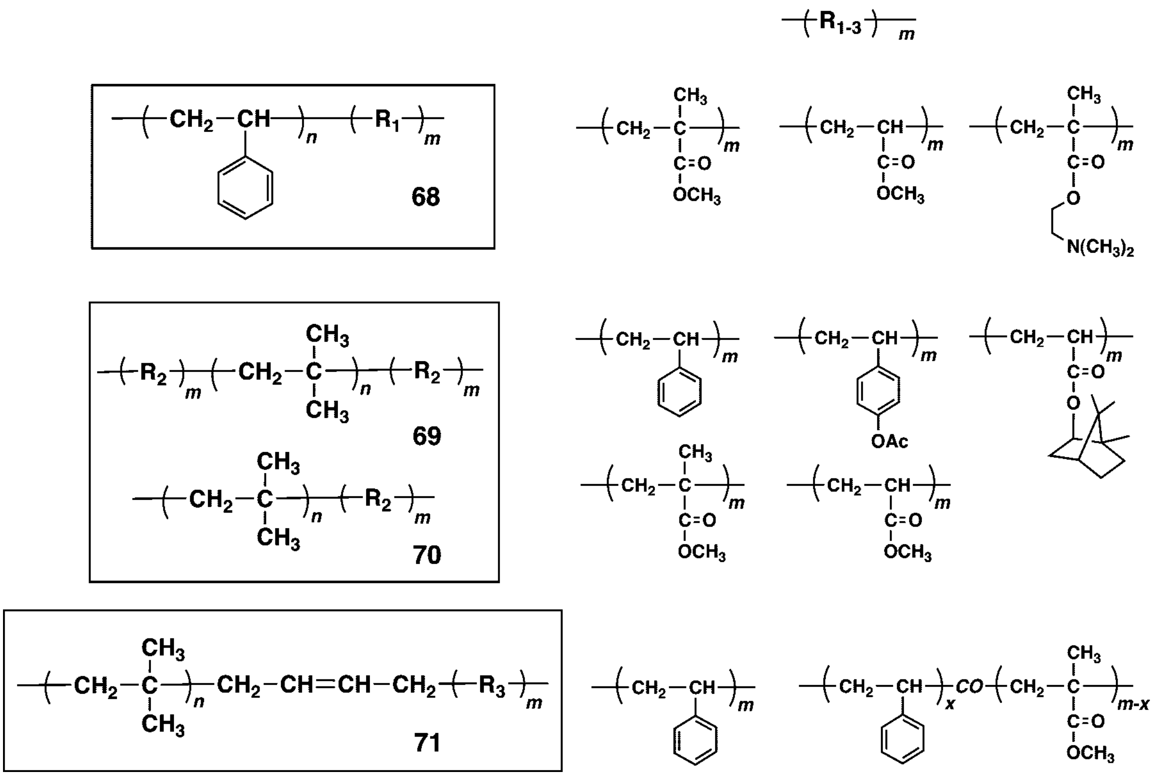


Figure 25. Block copolymers obtained via combination of cationic and radical polymerizations.

6.2.1. Radical Polymerization

Until the recent development of living radical polymerization, many transformations from cationic to (initer or iniferter) radical polymerization were investigated. Nuyken et al. investigated polymeric azo initiators having two poly(VE) segments and one central azo function.[393] The initiators were prepared by the living cationic polymerization of alkyl VE with an HI adduct of azo-containing divinyl ether as an initiator and $n\mathrm{Bu_4NClO_4}$ as a catalyst. The macro azo initiator was then used for thermally induced polymerization of MMA. The macro azo initiators containing PIB were prepared by the living cationic polymerization of IB using a bifunctional tertiary ether azo initiator and a Lewis acid catalyst.[394] The PIB macroinitiator was used for the radical polymerization of vinyl monomers such as St and MMA to give various block copolymers. As another transformation, polymers with a terminal trityl group or dithiocarbamate were first prepared and subsequently used to initiate radical polymerization of MMA or St via the initer mechanism for the preparation of block copolymers.[395−397] On the other hand, polymeric azo compounds were also prepared by the termination of living poly(VE) with an azo-containing alcohol.[398]

With the advent of living/controlled radical polymerization, the synthesis of well-defined block copolymers having various monomer units that do not undergo cationic polymerization has been expanded, as shown in Figures 25 and 26. PSt with chlorine termini, obtained by living cationic polymerization with R-Cl/Lewis acid, was subsequently used for the ATRP of acrylates and methacrylates, without any

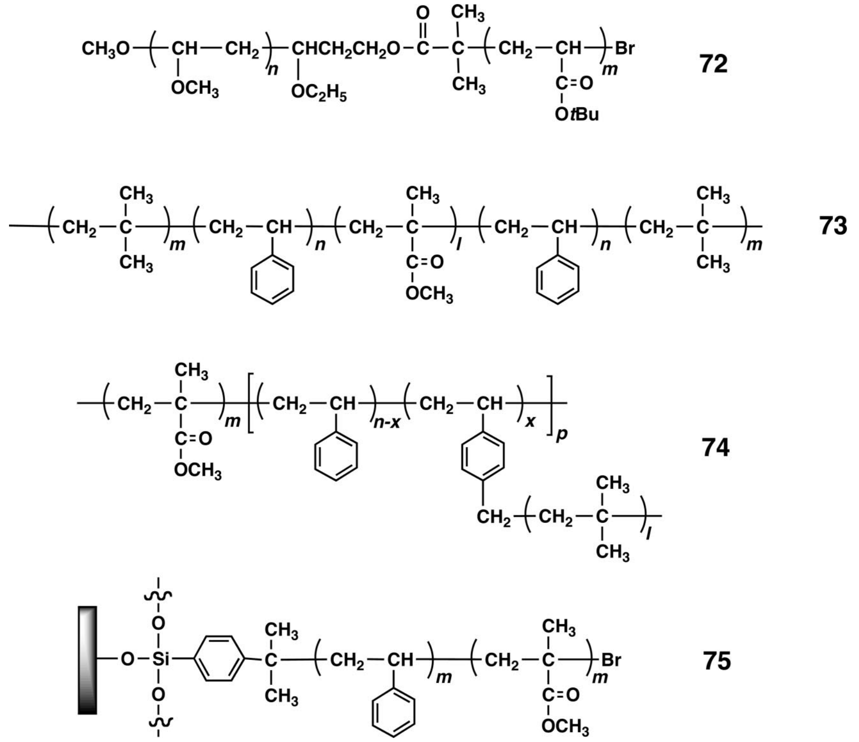


Figure 26. Other block or graft copolymers obtained via combination of cationic and radical polymerizations.

additional reactions (**68**).[399] Some carbon−halogen bonds, such as chlorine-capped PIB, prepared by living cationic polymerization cannot be used as initiating sites for ATRP, because of their lower activity toward redox reactions. A few units of St were then added to the living PIB, and the isolated PIBs could act as macroinitiators for the copper-catalyzed ATRP of St, acrylates, and methacrylates (**69**, **70**) as in Figure 25.[400] A similar strategy was used for the synthesis of PIB-*b*-poly(pAcOSt).[401] Jankova et al.[402] and Kennedy et al.[403] prepared di- and triblock copolymers of PIB and styrene or methacrylic acids (**69**, **70**) by use of PIBs having bromo ester groups.[403] The bromopropionyl or bromoisobutyryl groups were obtained by the quantitative modification of hydroxy functional PIBs. For example, radical polymerization of *tert*-butyl MA (tBMA) followed by hydrolysis gave the characteristic amphiphilic block copolymers.[404] Using similar combinations, several graft copolymers such as PIB-*g*-PMMA and PIB-*g*-PSt, could also be prepared by using partially brominated PIB-*co*-PMeSt as a macroinitiator for ATRP.[405] PIB with allyl halide end groups was also investigated as a new macroinitiator in ATRP.[406] The macroinitiator was prepared by the addition of 1,3-butadiene (BD) to living PIB in the presence of $Me_{1.5}AlBr_{1.5}$ or $TiCl_4$ catalyst (see section 7.2 for the details). Starting from the PIB-allyl-Br macroinitiator, block copolymers, PIB-*b*-PSt and PIB-*b*-P(MMA-*co*-St) (**71**), were obtained, whereas precision synthesis of PIB-*b*-PMMA without St was not achieved.

Block copolymers having Poly(VE) segments via combination of living cationic and radical polymerization were prepared by the use of a dual initiator having an acetal end group and a bromoisobutyrate group.[361] Poly(MVE)-Br was obtained by living cationic polymerization of MVE, while poly(BA)-acetal was synthesized by ATRP polymerization of BA. In the next step, these macroinitiators induced ATRP of several monomers and living cationic polymerization of MVE to give block copolymers (**72**, Figure 26). As other examples, transformations of ATRP, NMP, and RAFT by living cationic polymerization have been achieved to give many block copolymers[361,407−409] such as PIB-*b*-PSt-*b*-PMMA-*b*-PSt-*b*-PIB (**73**),[407,408] and graft copolymers such as PMMA-*b*-PSt-*g*-PIB (**74**).[409]

Surface-immobilized PSt-*b*-poly(meth)acrylate brushes (**75**) have been synthesized on silicate substrate.[410−412] Chlorine-terminated PSt brushes were first prepared by living cationic polymerization using $TiCl_4$ with DTBP in CH_2Cl_2 at −78 °C on flat silicate substrates via a "grafting from" approach, followed by ATRP of MMA, MA, DMAEMA, to give tethered diblock copolymer brushes.

6.2.2. Anionic Polymerization and Group Transfer Polymerization

The synthesis of thermoplastic elastomer triblock copolymers, PMMA-*b*-PIB-*b*-PMMA, has been first reported by living anionic polymerization of MMA using an α,ω-dilithiated PIBs macroinitiator (**76**, **77**; Figure 27).[413−415] As a novel site-transformation reaction, living PIB chains were quantitatively captured with DPE, to give DPE-capped PIB having methoxy or olefin groups, and then the quantitative metalation of DPE-capped PIB was carried out.[416,417] The stable macroanions (**78**, Figure 27) were used to initiate living anionic polymerization of butyl methacrylate (BMA) to give PBMA-*b*-PIB-*b*-PBMA block copolymers. Amphiphilic block copolymers by hydrolysis and various linear and star copolymers were also prepared. The end-capping process was improved by using thiophene instead of DPE; that is, the living PIB was quantitatively functionalized with thiophene and the thiophene end groups were subsequently metalated with BuLi.[418] The resulting stable macrocarbanion (**79**, Figure 27) could initiate living anionic polymerization. DDPE end-functionalized PIB was also prepared from the reaction of living PIB and DDPE.[419,420] The PIB-DDPE was quantitatively metalated with BuLi in THF at room temperature, and

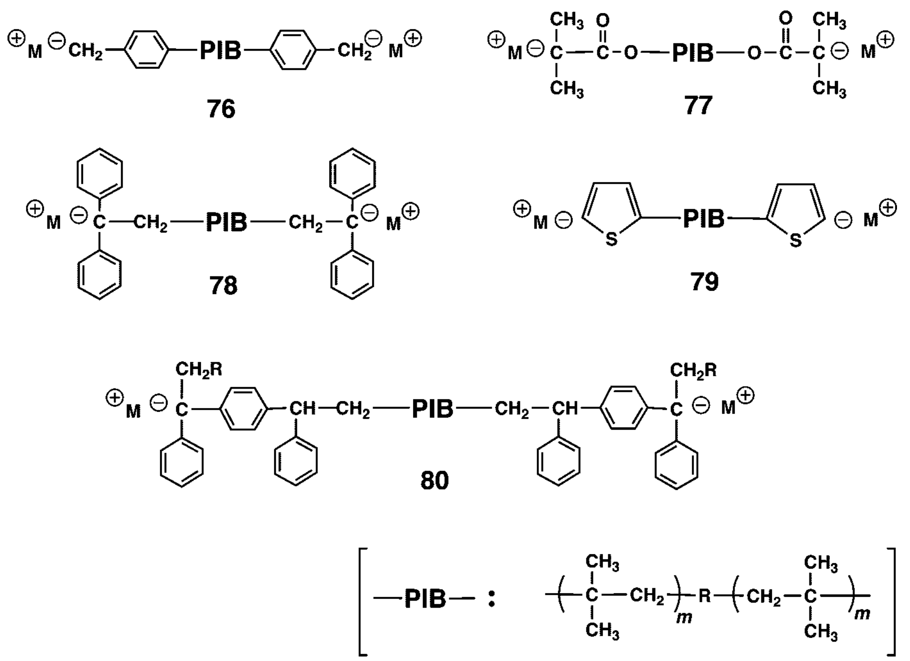
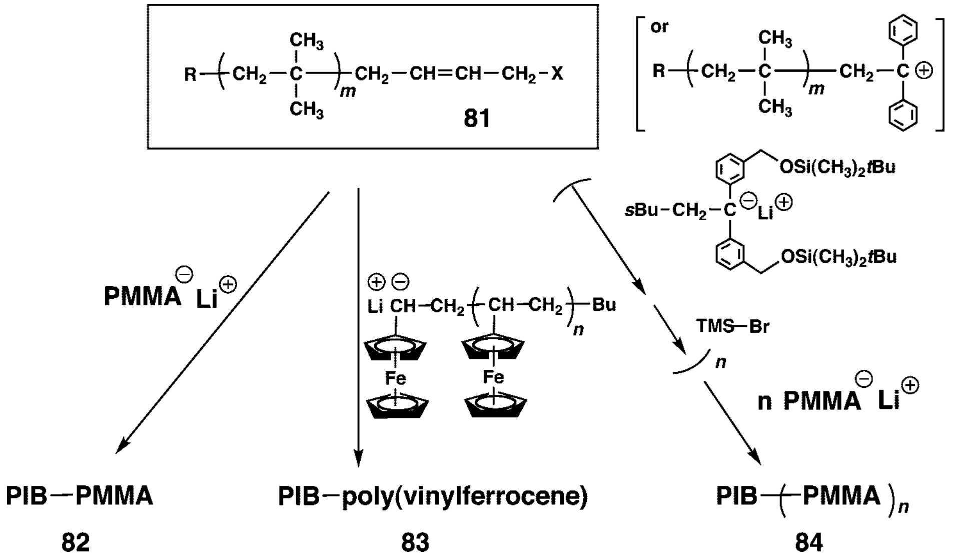


Figure 27. Initiators for synthesis of triblock copolymers containing PIB segments.

Scheme 7. PIB-Based Block Copolymer Synthesis via Coupling Reaction



the macroinitiators could initiate the various living anionic polymerizations of methacrylate monomers, yielding diblock copolymers with high block efficiency. Synthesis of triblock copolymer poly(MMA-*co*-HEMA)-PIB-poly(MMA-*co*-HEMA) can be investigated by use of metalated DDPE-PIB-DDPE (**80**).[421]

To prepare well-defined block copolymers, coupling of two homopolymers prepared by different mechanisms is a convenient and efficient method.[422−431] For example, the diblock copolymers PIB-*b*-PMMA (**82**) and PIB-*b*-poly(vinylferrocene) (**83**) were prepared by coupling reactions of PIB-allyl-X (**81**, see section 7.2 for the details) or DPE-capped PIB (mentioned before) with a corresponding living homopolymer obtained by living anionic or group transfer polymerization[422,424] (Scheme 7). The new A_2B, A_4B, and A_8B asymmetric star polymers (**84**) (A = PMMA, B = PIB) as well as A_2BA_2, A_4BA_4, and A_8BA_8 pompom polymers were synthesized via the coupling reaction of living PMMA with multifunctional PIBs in THF at −40 °C.[422] The starting multifunctional PIBs with 2, 4, and 8 benzyl bromide moieties were prepared by an iterative divergent methodology using PIB-allyl-X or X-allyl-PIB-allyl-X. Di- and triblock copolymers, poly(MVE)-*b*-PSt and poly(MVE)-*b*-PSt-*b*-poly(isoprene), were prepared by the methodology involving the synthesis of an end-chlorinated poly(MVE) obtained by living cationic polymerization and its coupling reaction with the living anionic PSt or PSt-*b*-poly(isoprene).[429,430]

6.2.3. Ring-Opening Polymerization

Grubbs et al. reported the transformation reactions for block copolymer synthesis, which involved changing the mechanism from living ring-opening olefin metathesis polymerization (ROMP) to acid-catalyzed aldol-type group transfer polymerization (aldol-GTP).[432,433] Polynorbornene and poly(dicyclopentadiene) with one aldehyde end group were prepared by ROMP and the successive reaction with terephthalaldehyde. The aldehyde end group induced aldol-GTP of *tert*-butyldimethylsilyl VE in the presence of $ZnCl_2$, followed by the cleavage of the silyl groups to give

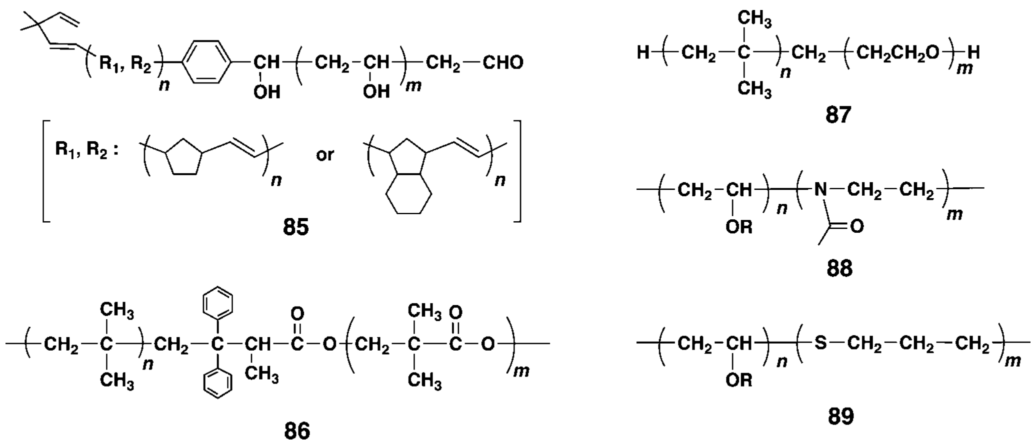
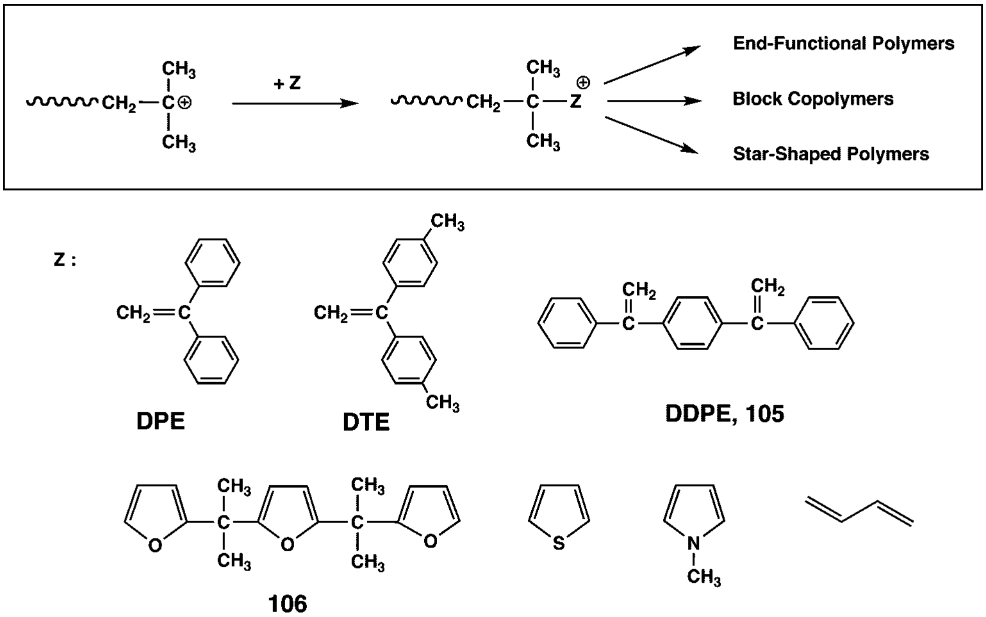


Figure 28. Block copolymers obtained via combination of cationic and ring-opening polymerizations.

Scheme 8. Capping Agents for Various Functionalized PIBs



amphiphilic diblock copolymers with a narrow MWD containing a PVA block segment (**85**).[432,433]

The synthesis of block copolymers containing rubbery PIB and crystalline poly(pivalolactone) [poly(PVL)] segments, PIB-*b*-poly(PVL) (**86**, Figure 28), was achieved by site transformation of living cationic to anionic ring-opening polymerization. As a macroinitiator, PIB, having ω-carboxylate potassium salt was prepared by living polymerization of IB with $TiCl_4$ in the presence of DTBP, followed by capping with DTE (Scheme 8), quenching with 1-methoxy-1-trimethylsilyloxypropene, and hydrolysis.[434] The successive polymerization of poly(PVL) was carried out with 18-crown-6 in THF. The synthesis of ABC triblock copolymer with glassy [poly(αMSt)], rubbery (PIB), and crystalline [poly(PVL)] segments was achieved selectively.[435] PIB-*b*-PEO (**87**) was prepared by using the similar method involving synthesis of HO-functionalized PIB and ring-opening polymerization of ethylene oxide from the PIB macroinitiator with a phosphazene base.[436,437] On the other hand, as site transformations of living cationic to cationic ring-opening polymerization, synthesis of block copolymers **88** and **89** has been investigated using VEs with imino ethers[438−440] and a cyclic sulfide.[441] For example, Kobayashi et al. have prepared various amphiphilic diblock copolymers **88** exhibiting good surface activities in a one-pot procedure.[438]

6.3. Control of MWD and Sequence in Block Copolymer Synthesis

6.3.1. Control of MWD in Block Copolymer Synthesis

Polydispersity is an important factor for determining polymer properties and, hence, has been studied for a long time in various fields, from basic solution studies to functional properties. Hatada and Kitayama et al. have prepared polymers without polydispersity ($M_w/M_n = 1.00$) by a combination of living polymerization and supercritical fluid chromatography techniques, and they demonstrated that the uniform polymers exhibited different properties from those of polydisperse polymers.[442,443] Matsushita et al.[444] and Hillmyer et al.[445] have investigated the effects of polydispersity on the morphology of diblock copolymers in the bulk state, and Eisenberg et al.[446] have examined the self-assembling behavior in solution. Although these advantages of polydispersity have been reported, only a few attempts have been made to prepare polymers with targeted polydispersity. In general, polydispersity can be adjusted by mixing

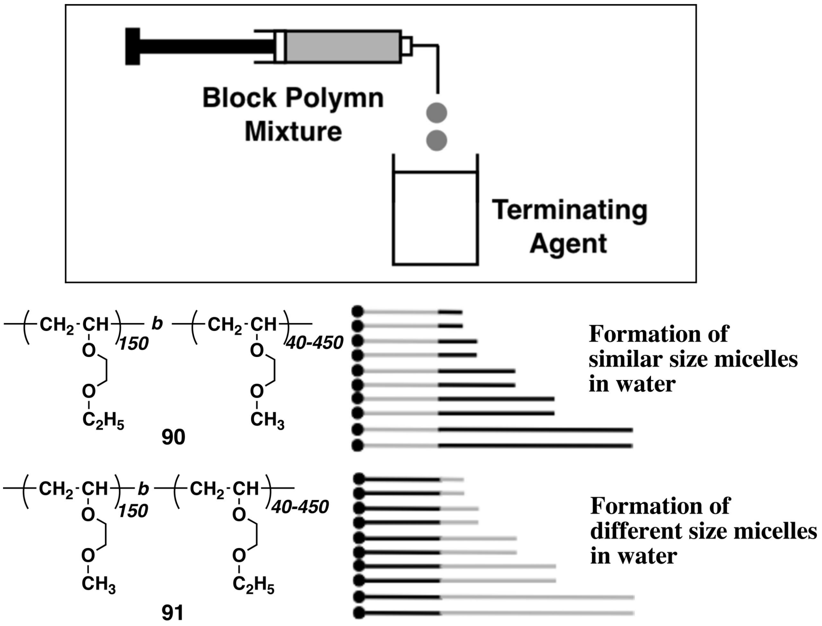


Figure 29. Concept for control of MWD in block copolymer synthesis.

polymers with various molecular weights. Therefore, a novel synthetic strategy is required to synthesize MWD-designed block copolymers with well-controlled structures, as shown in Figure 29.

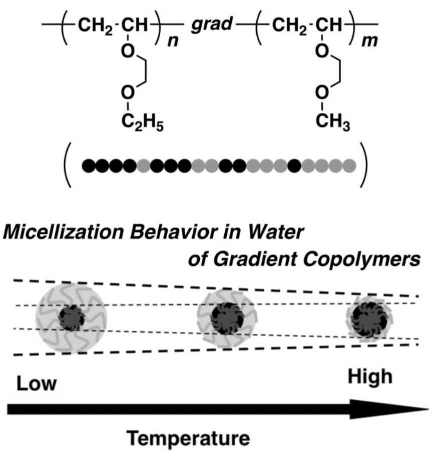
We have synthesized diblock copolymers with designed MWDs by using a continuous living cationic polymerization system, which includes gradually feeding a polymerization reaction mixture into a terminating agent.[447] For example, we have prepared thermosensitive diblock copolymers of MOVE and EOVE, poly(EOVE)-*b*-poly(MOVE), containing a thermosensitive EOVE segment with oxyethylene side chains and a hydrophilic MOVE segment (hydrophilic below 63 °C). For the synthesis of EOVE_{150}-*b*-MOVE_{40-450} **90** in Figure 29, base-assisting living cationic polymerization of the first monomer, EOVE, was carried out in a test tube at 30 °C to give a living polymer with very low polydispersity ($M_n = 1.7 \times 10^4$, $M_w/M_n = 1.07$). To this polymerization mixture were added 450 equiv of the second monomer, MOVE, and then the mixture was transferred to a gastight microsyringe. During the second stage of polymerization, the reaction mixture was added continuously using a syringe pump to methanol, in which the feed rate was calculated from time−conversion curves, to yield a MWD-designed block copolymer ($M_n = 3.1 \times 10^4$, $M_w/M_n = 1.38$, EOVE/MOVE = 1.0/1.7). This polymer had an almost monodisperse thermosensitive MOVE segment and a broadly distributed hydrophilic MOVE counterpart. With the same feeding rate, but opposite polymerization sequence, another polymer, MOVE_{150}-*b*-EOVE_{40-450} **91**, having an almost monodisperse hydrophilic MOVE segment and a broadly distributed EOVE counterpart ($M_n = 3.1 \times 10^4$, $M_w/M_n = 1.41$, EOVE/MOVE = 1.2/1.0) was obtained.

The thermosensitive behavior of these polymers in water was as follows. The diblock copolymer EOVE_{150}-*b*-MOVE_{40-450} formed micelles with narrow size distributions in water at 35 °C ($D_H = 86$ nm, $D_w/D_n = 1.05$), similar to conventional diblock copolymers with a narrow MWD ($D_H = 59$ nm, $D_w/D_n = 1.01$) for EOVE_{150}-*b*-MOVE_{150} ($M_w/M_n = 1.05$). On the other hand, MOVE_{150}-*b*-EOVE_{40-450} with various lengths of thermosensitive segment formed micelles with a broader size distribution ($D_H = 114$ nm; $D_w/D_n = 1.11$). The length distribution of the thermosensitive EOVE segment played an important role in the formation of aggregates with a narrow size distribution in water.

6.3.2. Control of Sequence in Block Copolymer Synthesis: Gradient Copolymers

Sequence distribution controlled polymers, such as block and graft copolymers, could be synthesized by living polymerization, and these polymers exhibit different behavior from homopolymer blend systems and random copolymers. For the synthesis of tapered or gradient copolymers, pioneering research using living anionic polymerization has been reported by Cunningham et al.[448] and Hashimoto et al.,[449] and from semibatch living radical polymerization by Matyjaszewski et al.[450] Furthermore, various gradient copolymers have recently been prepared by radical polymerization[451−454] and ring-opening metathesis polymerization,[455] which are rather robust polymerization systems. However, semibatch copolymerization has not been examined from the point of view of living ionic polymerization. In a gradient copolymer, the monomer composition changes continuously along the polymer chain. These polymers are thus expected to show different properties compared to block and random copolymers. Many of the characteristics of gradient copolymers have been determined,[456] including T_g, morphology, compatibilizing ability, surface activity, and theoretical simulation of phase segregation in bulk conditions. For the solution properties, LCST-type phase separation behavior in water[452,457] and micellization behavior in an organic solvent[458] have been examined.

Encouraged by the excellent living nature of base-assisting living polymerization in a half-open system, we decided to examine the design and synthesis of a variety of gradient copolymers.[459−462] The gradient synthesis was conducted by continuously feeding MOVE into a living cationic polymerization reaction mixture of EOVE in the presence of an added base. The polymerization proceeded smoothly and the monomer conversion agreed with the calculated values, affording a narrowly distributed polymer **92** in Figure 30 ($M_n = 4.5 \times 10^4$, $M_w/M_n = 1.15$, EOVE/MOVE = 260/



92

Figure 30. Thermoresponsive gradient poly(VE) and its micellization behavior in water.

340). A linear relationship between M_n and conversion as well as the clear shift and invariable narrowness of the MWD curves were observed. The longer the reaction time (the higher the molecular weight), the larger was the ratio of MOVE to EOVE, which was confirmed by ^{1}H NMR measurements, indicating the formation of a gradient copolymer.

The thermosensitive behavior of aqueous solutions of the gradient copolymers was examined by turbidity measurements, DLS, and SANS. The gradient copolymers in this study were expected to undergo continuous phase transition from one chain end to another with increasing temperature. The resulting gradient copolymers of EOVE and MOVE underwent thermally induced association in water, forming micelles with a hydrophobic core derived from EOVE-rich segments. Interestingly, the size of the micelles obtained from gradient copolymers decreased monotonously with increasing solution temperature (Figure 30).[461,462] The thermosensitive self-association behavior was different from those of the corresponding conventional block copolymers, whose micelles were unchanged in size. In the gradient copolymers, with increasing temperature, the contribution of the hydrophobic interaction dominates the hydrophilicity of the MOVE gradually, resulting in the formation of smaller micelles with larger cores than micelles at lower temperatures. Various stimuli-responsive forced gradient copolymers were also prepared by continuously feeding a monomer into a polymerization mixture.[460] The gradient composition of the polymers obtained experimentally was consistent with those obtained by calculation, even when the monomers employed had quite different relative reactivity ratios. Each gradient copolymer clearly differed from the corresponding block and random copolymers in their thermally or selective solvent-induced self-association behaviors in solution.[460]

7. End-Functionalized Polymers

End-functionalized polymers such as macromonomers and telechelic polymers are of great interest due to their potential applications in many important areas, and a variety of end-functionalized polymers have been successfully prepared by use of various living/controlled polymerizations. In the living cationic polymerizations reported thus far, three major methods for the synthesis of end-functionalized polymers are as follows: (i) initiation from functional initiators, (ii) end-capping by functional terminators, and (iii) a combination of (i) and (ii), i.e., telechelic polymer synthesis.

7.1. Initiation from Functional Initiators

The functional initiator method was first demonstrated by use of an HI adduct of VE with a pendant functional group Y (**93**, Figure 31). The initiator was prepared in situ by treatment of a corresponding VE with an equimolar amount of HI. These functional initiators were able to initiate living polymerization of not only another VE[365,463] but also pMOSt[160] in the presence of a Lewis acid such as I_2 or ZnI_2, to lead to a living polymer that carries the terminal function Y derived from **93**. By the use of this method, various end-functionalized polymers including COOH, OH, and NH_2 groups have been prepared quantitatively. The first examples of VE macromonomers having a methacrylate,[464] an allyl,[463] or an epoxy group (by the chemical modification of an allyl group)[463] were also synthesized by use of **94** or **95** (Figure 31). For example, macromonomer containing a methacrylate group, which is unreactive under cationic polymerization conditions, was prepared using initiator **94**. The polymerization proceeded in living fashion, to give living polymers with narrow MWDs and perfect functionalities ($F_n \sim 1$). The corresponding water-soluble macromonomers having hydroxy groups were also prepared by using silyloxyethyl VEs followed by desilylation.[369] As other initiators, (i) combinations of (cyclic) acetal (or aldehyde) and trimethylsilyl iodide (**96**, **97**)[360,465−468] and (ii) HI adducts of various monomers (St, MMA, tBMA, and vinyl acetate) (**98**)[469] were able to initiate living polymerization in the presence of a Lewis acid. By use of these techniques, several end-functionalized poly(VE)s such as hydroxy- and ester-terminated poly(VE)s were obtained.[463]

A series of end-functionalized poly(VE),[470] PSt[182] and its derivatives,[163,193,215,471] were also prepared using HCl or RCOOH adducts of VEs (**93**)[381] through living processes in the presence of either added bases or added salts. For example, the living cationic polymerizations of αMSt,[193] St,[182] and pClSt[215] were initiated by the HCl adduct of CEVE and Lewis acids such as $SnBr_4$ and $SnCl_4$ in the presence of $n$$Bu_4NCl$. PolySt,[182] poly(pMSt),[182] and poly(α-MeSt) macromonomers[471] having terminal methacrylate could be prepared by the use of the corresponding VE-Cl (**93**, X = Cl). Furthermore, end-functionalized poly(β-pinene) was obtained by living cationic polymerization using the same VE-Cl initiators [CEVE-Cl, AcOVE-Cl, and VEM-Cl (Y = $CH_2{=}C(CH_3)COO$; X = Cl)] and $TiCl_3(OiPr)$ catalyst in the presence of $n$$Bu_4NCl$ in CH_2Cl_2 at −40 °C.[472]

Several end-functionalized PIBs have been obtained from functional initiators (**99**−**101**, Figure 32). For example, the PIB-methacrylate macromonomer was obtained by living cationic polymerization of IB using 3,3,5-trimethyl-5-chloro-1-hexyl methacrylate (**99**).[473,474] The well-defined macromonomers were further copolymerized with MMA using group transfer polymerization, whereas homopolymerization of the macromonomers resulted in oligomers. A series of novel chlorosilyl-functional initiators (**100**) were prepared, because the chlorosilyl group is unreactive toward Lewis acids or carbocations.[475] The living cationic polymerization of IB with **100**/$TiCl_4$ in hexane/CH_3Cl at −80 °C gave well-defined PIBs having mono-, di-, and trichlorosilyl headgroups. They were used for the synthesis of PIB brushes on silicon wafers by the "grafting from" technique. Puskas et al. have employed a class of unique epoxide initiators (**101**) in the living cationic polymerization of IB using $TiCl_4$ with

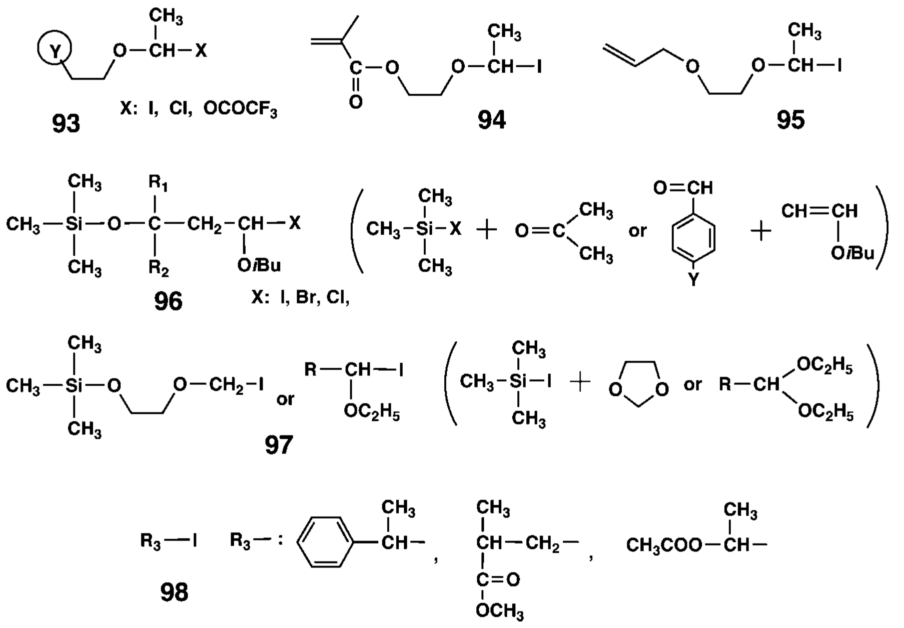


Figure 31. Functional initiators for end-functional poly(VE)s or PSts.

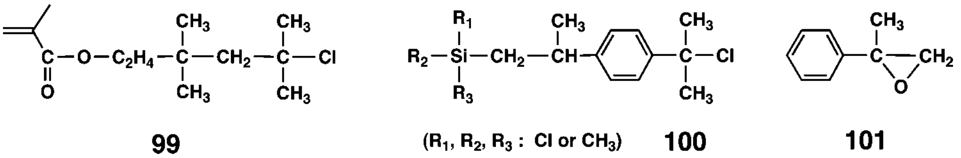


Figure 32. Functional initiators for end-functional PIBs.

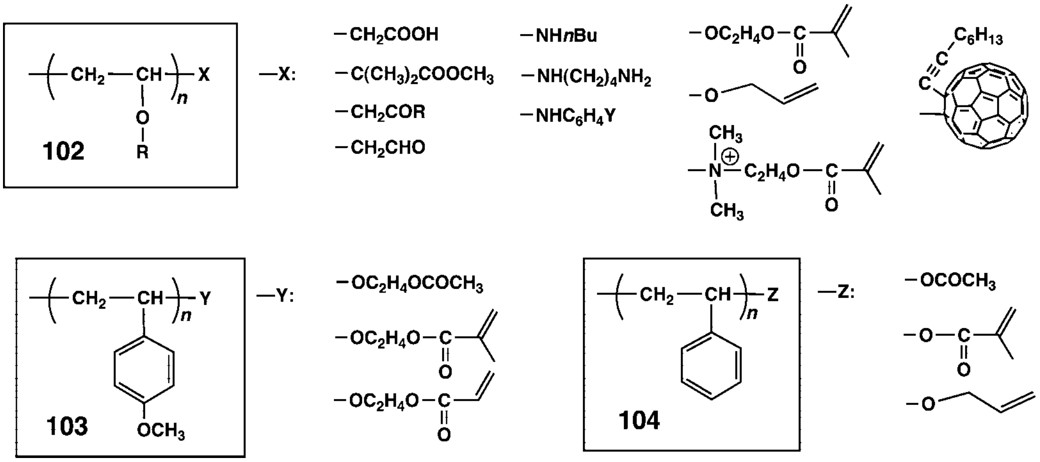


Figure 33. Functional terminators for end-functional poly(VE)s or PSts.

DTBP.[476] On quenching with methanol, PIB with a primary hydroxy headgroup and a *tert*-alkyl chloride end group was obtained.

7.2. End-Capping by Functional Terminators

In end-capping techniques, living poly(VE)s were quenched with certain nucleophiles having a functional group.[315] Using the appropriate nucleophiles under suitable reaction conditions, the reaction simply involved an addition of a nucleophile to the living ends, to give an end-capped polymer, where side reactions such as β-proton abstraction by the nucleophile did not occur. As one of the oldest examples, hexamethylenediamine was allowed to react with HI/I_2-induced living polymers, to give end-functionalized poly(VE)s.[315] After that, malonate anions,[477] silyl ketene acetals,[431] silyl enol ethers,[478] amines,[315] anilines,[479] alcohols,[480] and partially hydrolyzed poly(vinyl acetate)[481] have all been used as nucleophiles to synthesize various end-functionalized (or graft) poly(VE)s **102** in Figure 33. For example, the sodium salt of malonate carboanions reacts quantitatively with the living ends of poly(VE)s, initiated with HI/I_2 or HI/ZnI_2, to functionalize them with carboxyl groups connected by a stable C−C bond.[477] A functional compound having hydroxy groups such as 2-hydroxyethyl methacrylate (HEMA) was also able to react quantitatively with the living ends, to give macromonomers having a methacrylate end.[396,482] Well-defined macromonomers having a methacrylate or allylic terminal were obtained by reacting the living polymer ends, initiated by CF_3SO_3H in CH_2Cl_2 at −30 °C in the presence of thiolane (added base), with HEMA or allyl alcohol.[396] Water-soluble C_{60} having poly(VE) segments was also prepared by these methods.[483,484]

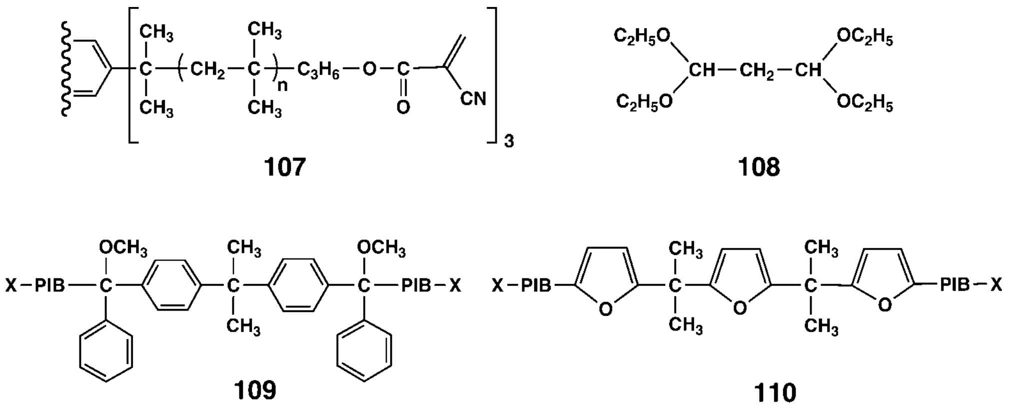


Figure 34. Bi- or multifunctional PIBs and an example of a bifunctional initiator.

For pMeOSt, secondary or primary alcohols such as 2-hydroxymethacrylate or acrylate could be introduced to the living polymers initiated by HI/ZnI_2 in CH_2Cl_2 at −15 °C, to give a series of end-functionalized polymers of pMeOSt (**103**), whereas sodiomalonic esters and tertiary alcohols hardly reacted with the living end of poly(pMOSt).[160] In contrast to the success for VE and pMOSt, in the living polymerization of St initiated with $SnCl_4$ in the presence of $n\mathrm{Bu_4NCl}$ in CH_2Cl_2 at −15 °C, the usual bases such as methanol, benzylamine, dimethyl sodiomalonate, and sodium methoxide were apparently incapable of reacting with the living end. Quenching by trimethylsilyl compounds with methacryloxy, acetoxy, and allyl groups gave ω-end-functionalized poly(St) **104**, with the corresponding terminal groups for which the F_n values were close to unity.[485] Living poly(αMSt) chains, prepared by living cationic polymerization with CEVE-Cl/$SnBr_4$ in CH_2Cl_2 at −78 °C, were allowed to react with multifunctional silyl enol ethers to synthesize multiarmed poly(αMeSt).[486]

For IB, direct end-capping on a PIB living end with allyltrimethylsilane, which was based on an earlier report by Kennedy et al.,[487] was found to give an allyl-capped polymer.[487] This allyl-end-macromonomer can be converted into an epoxide- or hydroxy-capped PIB. In a similar manner, quantitative addition of 2-phenylallyltrimethylsilane to the living PIB end yielded α-methylstyryl functional macromonomer.[488] However, the macromonomer exhibited low reactivity in cationic copolymerization with IB, because of its steric hindrance. In the chain-end modifications, the synthesis of *exo*-olefin-terminated PIB[489] and halogen-free PIB[490] was quantitatively accomplished in one pot by β-proton abstraction with a hindered base and in situ hydride transfer from tributylsilane.

In the capping reaction of living PIB with DPE (or DTE), it was confirmed that the quantitative capping of DPE (or DTE) occurred and all dormant chain ends were converted to active ionic species.[491,492] The stable and fully ionized diarylcarbocation was used for the synthesis of various end-functionalized PIBs[493] and block copolymers[19] [Scheme 8; see also section 6.1]. Furthermore, DDPE (**105**) has been investigated as a potential coupling agent for a facile route to PIB-DPE macromonomers.[494] For 2-substituted furans,[495] bis-furan **106**,[496] thiophene,[418] and *N*-methylpyrrole,[497] the rapid and quantitative monoadditions of π-nucleophiles have been observed under the appropriate conditions. Recently, Faust et al. reported on the synthesis of haloallyl-end-functional PIBs (PIB-allyl-X, X = Cl or Br) using the capping reaction of living PIB with BD.[498] Under certain conditions in hexane/CH_3Cl solvent mixtures at −80 °C in conjunction with $TiCl_4$ or $Me_{1.5}AlBr_{1.5}$ as Lewis acids at [BD]/[chain end] $\leq$ 12, monoaddition of BD followed by instantaneous halide transfer from the counteranion and selective formation of the *trans*-1,4-adduct was observed quantitatively.[498] A new general methodology for S_N2 reactions on PIB-allyl-X has also been developed for the efficient preparation of end-functional PIBs including hydroxy, amino, carboxy, azide, propargyl, methoxy, and thymine end groups.[499] The quantitative functionalization was determined by ^1H and ^{13}C NMR, FT-IR, and MALDI-TOF MS spectroscopies. The methodology was extended to the synthesis of hydroxy telechelic PIBs (HO-allyl-PIB-allyl-OH) and PIB block copolymers [PIB-*b*-PEO], where the latter was synthesized by the substitution reaction of PIB-allyl-Cl with polymeric nucleophiles PEO-O^-Na^+.[495]

7.3. Combination of Sections 7.1 and 7.2 for Telechelic Polymer Synthesis

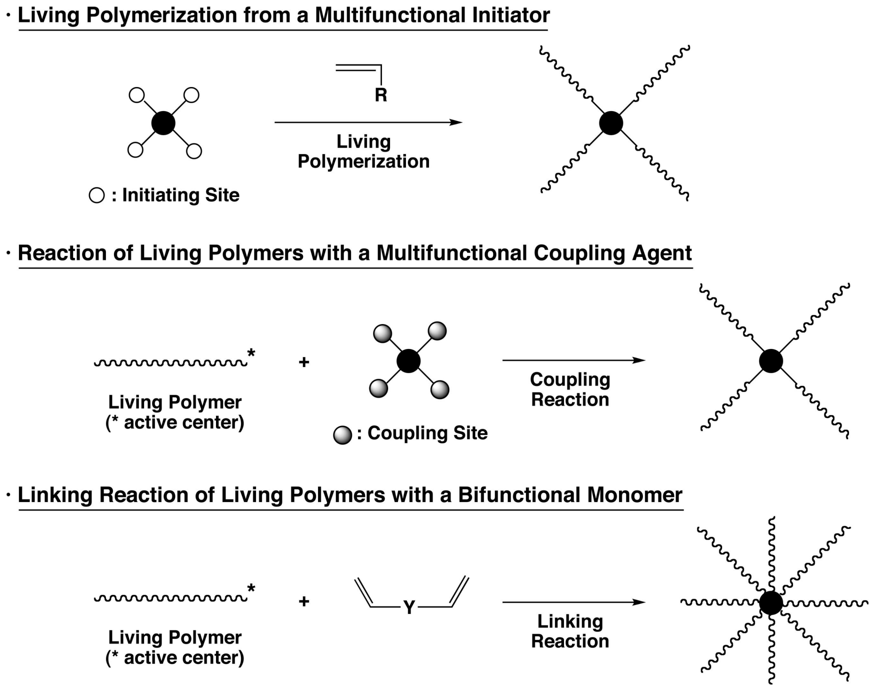
α,ω-Bi- (telechelic) and multifunctional polymers with functional groups at each end such as **107**[500−502] in Figure 34 were prepared (i) by using bi- or multifunctional initiators such as **108** followed by end-capping with functional terminators,[350,500−504] (ii) by coupling of α-end-functional (X) living polymers with coupling agents, to give telechelics such as **109** or **110**,[504,505] and (iii) by combination of the functional initiators and terminators.[477] Figure 34 shows typical examples of α,ω-bi- and multifunctional polymers and a bifunctional initiator.

8. Functionalized Star-Shaped Polymers

8.1. Background

Functionalized nanoparticles with uniform size, such as dendrimers, have been of great interest in a variety of fields over a couple of decades.[506,507] Star polymers can also be nanoparticles with functional groups. In general, the spherical shape and dense structure of this polymer form provide properties and functions different from those of corresponding linear polymers.[508−511] The synthesis of star polymers is achieved by living polymerization with a multifunctional initiator, coupling of a linear living polymer with a multifunctional coupling agent, or linking of linear polymers with a divinyl compound (Scheme 9).[508,512,513] These methods of star polymer synthesis were established after the discovery of living anionic polymerization. Since then, various star-shaped polymers have been synthesized via living anionic processes.[509,514,515] However, no star polymers with pendant polar functional groups had been synthesized, especially

Scheme 9. Methodologies for Star Polymer Synthesis



before 1990. Although star polymers of methacrylates had already been reported,[516−518] those polymers were not regarded as functionalized materials in a practical sense.

Amphiphilic starlike polymers were prepared by free radical polymerization in 1990.[519,520] A mixture of a monomer (acrylic or methacrylic acid) with a microgel with vinyl groups, obtained from divinylbenzene and styrene, was treated with a radical initiator. The simultaneous polymerization and grafting onto reaction yielded the starlike polymers that varied in size and arm length. Well-defined functionalized star polymers were first reported in living cationic polymerization.[508,521] Amphiphilic star block copolymers of VEs with hydroxy[521] or carboxy[522] groups were prepared via polymer-linking reaction of living polymers with a bifunctional monomer (Figure 35). The solubility characteristics of the product polymers altered drastically depending on the segment arrangement in the arm chain.[521,522] Following these polymers, heteroarm[523] and core-functionalized[524] star polymers were synthesized using similar "arm-first" methods. Carboxy-containing amphiphilic star polymers of norbornene derivatives were also prepared via ring-opening metathesis polymerization[525] shortly after the first report on hydroxy-containing amphiphilic star polymers by cationic polymerization. Despite these progresses, not so many functionalized star polymers were reported at that time. Constructing complex architectures was a major trend, especially in living anionic polymerization.[509,514,515,526,527]

The synthesis of functionalized star polymers has drawn renewed attention from polymer chemists because of the advent and further development of controlled/living radical polymerization.[273,528−541] Various star polymers of low polydispersity have been synthesized mostly using the first two methods. For example, multifunctional initiators[540,542−545] or chain transfer agents[540,546,547] with dendritic scaffolds were employed for the star polymer synthesis. However, a drawback of the two methods is that arduous synthesis of initiators, terminators, and transfer agents is indispensable.

The "arm-first" linking reaction is a ready and effective means of preparing star polymers with many arms.[273,528−538,541,548,549] Moreover, polar functional groups can be placed at arms' pendants and/or a cross-linked core by radical and cationic polymerization. Thus, this section focused on recently

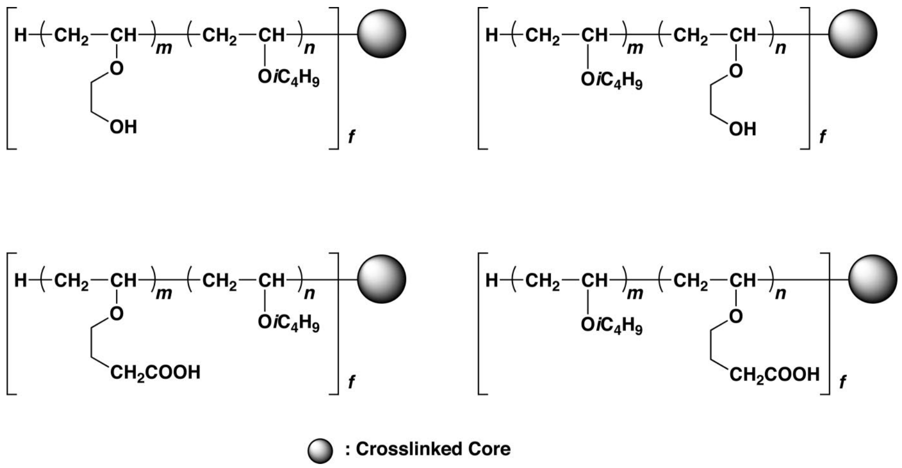


Figure 35. Amphiphilic star block copolymers.

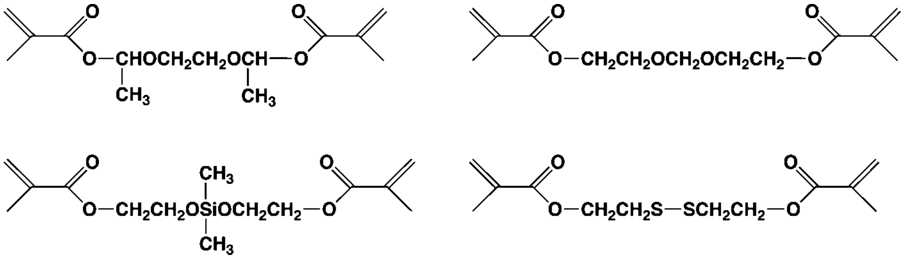


Figure 36. Degradable cross-linkers for star polymer synthesis.

reported functionalized star polymers via polymer-linking reaction of living polymers with a divinyl compound.

8.2. Star Polymers as Nanocarriers

Typical polymers studied for drug delivery systems (DDS) are dendrimers, polymeric micelles of well-defined block copolymers, and star polymers. Numerous examples were reported on dendrimers and micelles. However, time-consuming synthesis for relatively large dendrimers and concentration dependence of size for micelles are obstacles for application. Star polymers can be spherical in shape with various sizes and their synthetic methods are easier than those of dendrimers. The density of arm chains is, of course, constant at any concentration due to their covalently bonded core-arm structures. Thus, star polymers have drawn attention as nanocarriers for drugs, genes, and proteins.[550]

Among star polymers, core cross-linked star versions have some advantages for encapsulation of small compounds. For example, the space of a microgel core, the size of which is tunable, is good for storing small materials. One drawback of this type of star polymers is the difficulty in releasing compounds at once, since the microgel core has a network structure. Recently, star polymers with a degradable core were synthesized via controlled/radical polymerization.[551] Bifunctional monomers with a readily degradable spacer, such as esters,[552−554] silyloxy,[555] acetal,[556] or disulfide[557] bonds (Figure 36), were used in polymer-linking reactions. Furthermore, star polymers consisting of ε-caprolactone and lactide arm chains and a degradable core were reported, which can be totally degradable nanocarriers.[558−560] A degradable polymer with a sensing moiety for DDS was prepared using ring-opening polymerization with a metal-containing multifunctional initiator.[561] An iron tris(bipyridine)-centered initiator produced six-arm poly(ethylene glycol)−poly(lactic acid) star block copolymers. This type of star polymers would be fragmented with their solution colors changed under acidic conditions.

8.3. Selective Synthesis of Star-Shaped Polymers with Narrow MWDs

In any systems of the "arm-first" polymer-linking reaction for star polymer synthesis, some amount of starting polymers inevitably remain unreacted,[273,512,513,528−538,548,549] especially when longer linear polymers were employed. Under the conditions that induce high yield reaction, MWDs of product polymers would become broader. Therefore, fractionation has to be conducted to obtain a star polymer with a narrow MWD. Since the first example in anionic polymerization was reported, this problem has been persistent.

Quantitative and well-controlled reactions have recently been reported in cationic polymerization. Well-defined star polymers were obtained *via* living polymerization of IBVE using the IBEA/$EtAlCl_2$ initiating system in hexane in the presence of ethyl acetate at 0 °C.[562] The treatment of linear living polymers ($M_n = 1.54 \times 10^4$, $M_w/M_n = 1.05$) with 1,4-cyclohexanedimethanol divinyl ether (CHDVE, $r = [\mathrm{CHDVE}]_0/[\text{living ends}] = 10$) in hexane at 0 °C produced soluble star polymers in quantitative yield in 7 h (reaction conditions: $[\mathrm{IBVE}]_0 = 1.5$ M, $[\mathrm{IBEA}]_0 = 10.0$ mM, $[\mathrm{EtAlCl_2}]_0 = 20.0$ mM, $[\text{ethyl acetate}]_0 = 1.0$ M).[562] The product polymers exhibited extremely narrow MWDs ($M_w/M_n = 1.1-1.2$) for a star polymer. This is the first example of the selective preparation of nearly monodisperse star-shaped polymers in quantitative yield *via* a polymer-linking reaction by any polymerization mechanism. Narrow MWDs were also attained with star-shaped poly(IBVE) obtained from living polymers with $DP_n = 50-300$.[562] The M_w of the product polymers ranged from 6×10^4 to 30×10^4, corresponding to arm numbers ranging from 9 and 44. The more stable growing ends obtained by base-assisting living cationic process, relative to other living cationic systems, and association of the growing chain ends driven by solvation with the added base likely facilitated the polymer linking reaction.

Well-controlled synthesis was also achieved in radical polymerization. A macromonomer of an acrylate and a bifunctional vinyl compound were treated with an ATRP initiating system.[563] This reaction yielded a star polymer with a narrow MWD ($M_w/M_n \sim 1.2$). In this case, low radical concentration throughout the reaction suppressed star−star coupling reaction; hence, well-defined star polymers were obtained. Another successful case was the synthesis of star polystyrene by living anionic polymerization.[564] Incremental addition of divinylbenzene into a THF solution of polystyryl lithium at 25 °C produced star polymers in yield, whereas 20−30% of starting linear polystyrene remained unreacted using a conventional one-dose addition method.

Thermoresponsive star-shaped polymers that have arms containing oxyethylene side chains were also prepared in quantitative yield.[562] The resulting star polymers exhibited highly sensitive LCST-type phase separation in water. Their clouding points were similar to those of the linear polymers corresponding to the arm chains. Star block copolymers showed characteristic transition behavior in phase separation. A two-step transition was observed with the star polymer (**111**, in Figure 37) with a segment with the lower clouding point in the outer layer. The transition temperatures correspond to two segments. In contrast, one sharp transition was observed with the counterpart (**112**, in Figure 37) with the opposite arrangement at near the higher clouding point. This star polymer apparently behaves as a star polymer with homopolymer arm chains with different properties concealed. Another interesting feature was observed with the star block copolymers in reversible physical gelation at higher concentration.[562] A 10% aqueous solution of the star block

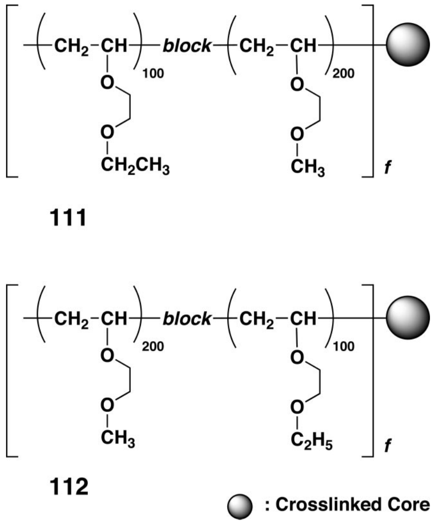


Figure 37. Thermosensitive star block copolymers.

copolymer **111** underwent rapid physical gelation upon heating. Intermolecular aggregation caused by dehydration of the outer segments upon heating resulted in physical three-dimensional networks of the star polymers. A 15 wt % aqueous solution of the opposite arrangement (**112**) of the block arm underwent a sol−gel transition upon cooling. This apparently unexpected transition is attributed to changes in the diameter of the star molecules, driven by the hydration or dehydration of poly(EOVE) segments.

8.4. New Strategies for Selective Star Polymer Synthesis

Base-assisting living systems produced star polymers with very narrow MWD selectively in high yield. The assembly of the growing ends of the starting polymers is an important factor for such selective syntheses. Inspired by these results, star polymer synthesis was examined under conditions where the assembly of the starting living polymers is promoted.[565] To construct a micelle-like structure in a reaction mixture, a polymer-linking reaction was examined using living block copolymers under conditions conducive to aggregation of block copolymers. The diblock copolymer used had a thermosensitive segment that undergoes UCST-type phase separation in alkane solution. The poly(EOVE) segment undergoes phase separation in octane at 26 °C. The block copolymerization was performed at 30 °C. When second-stage polymerization was almost complete, the reaction mixture was cooled to 0 °C, and divinyl compound CHDVE ($r = 10$) was added. The resulting star polymer product [M_n(GPC) = 4.71×10^5] has higher molecular weights than star polymers [M_n(GPC) = 3.82×10^5] prepared using conventional conditions.[565] On the other hand, the opposite polymerization sequence yielded lower molecular weight products [M_n(GPC) = 1.80×10^5]. Thus, the importance of assembly of linear living polymers for selective star polymer synthesis was demonstrated.

A drawback of the above-mentioned method, however, is that the use of a diblock copolymer is unavoidable. Therefore, another method for selective synthesis was devised: linking reactions of homopolymers in a mixture of good and poor solvents.[565] Poly(MOVE) is soluble in toluene but insoluble in hexane. The reaction of a living polymer [M_n(GPC) = 1.67×10^4] with CHDVE in a mixture of toluene and hexane (1:1 v/v) yielded star polymers with relatively narrow MWD in almost quantitative yield. In addition, the number of arms increased with increasing amount of poor solvent. Star polymer formation was likely promoted by living polymer aggregation enhanced by the presence of poor solvent. The use of octane, an even poorer solvent, produced higher molecular weight star polymers.

8.5. Metal Nanoparticles Stabilized by Star-Shaped Polymers

Gold nanoparticles (Au NPs) were shown to have catalytic ability for organic reactions, and they have been studied widely over the world.[566] However, Au NPs in solution readily aggregate; hence, the particles should be covered with a polymer or organic compound. The finely dispersed Au NPs in solution were prepared by Tsukuda and Sakurai, and the size dependence of catalytic reactivity was studied in detail with several reations.[567−572] However, a persistent problem in their practical use is aggregation of Au NPs, especially during reactions and/or workup procedures. This problem was solved by using star polymers with hydrophilic arms and a hydrophobic core.[573] Star poly(EOEOVE) was prepared by the reaction of living EOEOVE polymers with CHDVE using $Et_{1.5}AlCl_{1.5}$ and 1,4-dioxane in toluene at 0 °C. Under these conditions, a star polymer was obtained in quantitative yield within 8 h [DP(arm) = 200, M_w(GPC-MALLS) = 9.4×10^5, $M_w/M_n = 1.36$, 28 arms].[573] The resulting star polymer was soluble in water at room temperature.

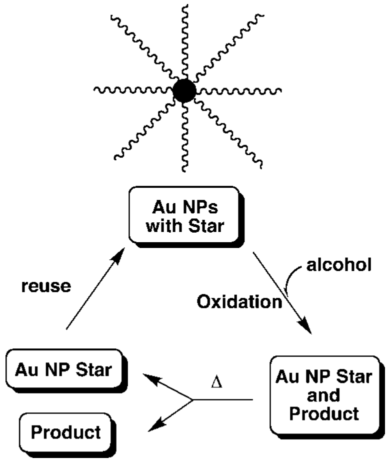
Au NPs were prepared by the reduction of $HAuCl_4$ using $NaBH_4$ in an aqueous solution of the star polymer.[567−572] The resulting clear brownish solution showed a very small absorbance at 520 nm, the surface plasmon resonance of the metallic gold clusters and indicative of the formation of very small NPs.[567−572] TEM analysis revealed that most of the resulting particles are less than 4 nm in diameter. Surprisingly, the Au NPs never underwent negative aggregation on repeated phase transitions.[573]

These unique particles were proven to catalyze the oxidation of several alcohols in water under aerobic and mild conditions. For example, benzyl alcohol was completely consumed in 1 h ([benzyl alcohol] = 16.7 mM, [Au] = 0.33 mM, [KOH] = 50 mM, at 27 °C, in water) to yield benzoic acid in almost quantitative yield.[573] In addition, the star-protected particles did not undergo negative aggregation at any point during the reaction or even during workup procedures.[573] Such a high level of stability and durability as that obtained by the reduction of $HAuCl_4$ has not been previously reported for any type of polymer-stabilized Au NP catalyst.

The durability and thermosensitivity of the Au NPs allowed facile catalyst reuse. After the reaction, the catalyst was precipitated by raising the solution temperature above the clouding point, such as 60 °C, and then was separated by filtration (Scheme 10). The catalyst maintained its activity, catalyzing alcohol oxidation reactions at least six times, the rates of which were very comparable.[573]

Fine stabilization of Au NPs in organic solvent was attained using five-arm star polymers with PEO-*b*-PCL arms.[574] A template star block copolymer was prepared using a five-arm star-shaped PEO macroinitiator for controlled ring-opening polymerization of ε-caprolactone. Thus, a series of star-block copolymers with a PEO inner layer, constant in size, covered by a PCL layer of variable thicknesses was obtained. The PEO core absorbed $KAuCl_4$ in DMF, and gold

Scheme 10. Catalyst Reuse Cycle for an Au Nanoparticle Protected by a Thermosensitive Star Polymer



nanoparticles were subsequently obtained by reduction with $NaBH_4$. The average sizes of the resulting Au NPs were in the same range for all star block copolymers. This indicated that the reduction was well templated by the PEO core. On the other hand, clear dependences of the size distribution and long-term stability in DMF on the PCL block length were observed. PCL blocks serve as stabilizing blocks for these nanoparticles. The PEO-*b*-PCL stars were also utilized for the preparation of stable palladium (Pd) nanoparticles in DMF.[575] The particles (0.1 mol %) catalyzed the Heck reaction of styrene and 4-bromoacetophenone, which was completed in 24 h. Stable Pd nanoparticles, which induced the Heck coupling of iodobenzene and ethyl acrylate, were also prepared using thermosensitive vinyl ether star polymers.[576] With these systems, the use of expensive and toxic phosphine ligands becomes unnecessary, and a new view for the reaction mechanism would be obtained, since the system contains only zerovalent Pd.

9. Conclusions

In this report, we discuss advances in living polymerization initiators, including the design and synthesis of a variety of new polymers, with a focus on the most recent developments. Many innovative breakthroughs and developments have been seen, and the future of this field looks very promising. Various kinetic analyses have also been accomplished, which we are unfortunately not able to include in these discussions due to space limitations. A lot of very interesting research is also happening in the fascinating field of photoinduced or thermally induced cationic polymerization by latent initiators, cationic ring-opening polymerization of heterocyclic compounds, etc. Therefore, it is suggested that this review be read in combination with other review papers as well.

The fabrication of macromolecular aggregates that display various functions and properties will become increasingly important in the development of polymer synthesis. To accomplish this, it will be necessary to design and synthesize polymers in which the primary structure, including monomer sequences and stereoregularity, is precisely controlled. The synthesis of concept polymers of new forms completely unheard of in the past is another challenge that awaits. The development of new polymerization catalyst systems that will serve as the basis for this will be indispensable, and as is briefly touched on in the section on initiators, it appears that further coordination and merging of the fields of organic chemistry, inorganic/catalytic chemistry, and chemical engineering will become necessary in the future.

10. Abbreviations (see also Figure 5 for various initiators)

acac	acetylacetone
AIBN	azobisisobutyronitrile
ATRP	atom transfer radical polymerization
AuNP	gold nanoparticle
AzoVE	azo-containing vinyl ether
BMA	butyl methacrylate
BnVE	benzyl vinyl ether
*n*Bu	*n*-butyl
tBuVE	*tert*-butyl vinyl ether
CEVE	2-chroloethyl vinyl ether
CHDVE	1,4-cyclohexanedimethanol divinyl ether
Cp	cyclopentadienyl
CPD	cyclopentadiene
cryo-TEM	transmission electron microscope using cryo-preparation apparatus
CVE	cetyl vinyl ether ($CH_2{=}CH{-}O{-}C_{16}H_{33}$)
DDS	drug delivery system
D_H	hydrodynamic diameter
DLS	dynamic light scattering
DMA	*N*,*N*-dimethylacetamide
DMSO	dimethyl sulfoxide
DPE	1,1-diphenylethylene
DP_n	degree of polymerization
DTBP	2,6-di-*tert*-butylpyridine
D_w/D_n	size distribution
EOEOVE	2-(2-ethoxy)ethoxyethyl vinyl ether
EOVE	2-ethoxyethyl vinyl ether
ESR	electron-spin resonance
Et	ethyl
F_n	functionality
FTIR	Fourier-transform infrared spectroscopy
FTIR-ATR	attenuated total reflection FTIR
GTP	group transfer polymerization
HEMA	2-hydroxyethyl methacrylate
HOSt	*p*-hydroxystyrene
HOVE	2-hydroxyethyl vinyl ether
Hx	hexane
IB	isobutene
IBEA	1-(isobutoxy)ethyl acetate
IBVE	isobutyl vinyl ether
ID	indene
IP	isoprene
LCST	lower critical solution temperature
$Ln(OTf)_3$	lanthanide triflate
m	meta
MALDI-TOF-MS	matrix-assisted laser desorption-ionization time-of-flight mass spectrometer
MCH	methylcyclohexane
Me	methyl
MMA	methyl methacrylate
M_n	number-average molecular weight
MOVE	2-methoxyethyl vinyl ether
MSE	α-methylstyrene epoxide
*β*MSt	*β*-methylstyrene
MVE	methyl vinyl ether
M_w	weight-average molecular weight
MWD	molecular weight distribution
ND	norbornadiene
NIPAM	*N*-isopropylacrylamide
NMP	nitroxide-mediated polymerization
NVC	*N*-vinylcarbazole
o	ortho
OAc	acetate

ODVE	octadecyl vinyl ether
OEVE	vinyl ether with oxyethylene pendant
p	para
pAcOSt	*p*-acetoxystyrene
PBO	poly(butylene oxide)
PBS	phosphate buffered saline
PCL	poly(*ε*-caprolactone)
pClMSt	*p*-(chloromethyl)styrene
pClSt	*p*-chlorostyrene
PEO	poly(ethylene oxide)
PET	poly(ethylene terephthalate)
Ph	phenyl
PIB	polyisobutene
PIB-Allyl-X	haloallyl-end-functional polyisobutene
PLA	poly(lactic acid)
PMMA	poly(methyl methacrylate)
pMOSt	*p*-methoxystyrene
PMPC	poly(2-methacryloyloxyethyl phosphorylcholine)
pMSt	*p*-methylstyrene
poly(EO-EOVE)	poly[2-(2-ethoxy)ethoxyethyl vinyl ether]
poly(EOVE)	poly(2-ethoxyethyl vinyl ether)
poly(MOVE)	poly(2-methoxyethyl vinyl ether)
poly(MVE)	poly(methyl vinyl ether)
poly(NIPAM)	poly(*N*-isopropylacrylamide)
poly(OEVE)	poly(vinyl ether)s with oxyethylene pendant
poly(PVL)	poly(pivalolactone)
ptBOSt	*p-tert*-butoxystyrene
ptBSt	*p-tert*-butylstyrene
PVA	poly(vinyl alcohol)
RAFT	reversible addition−fragmentation transfer
ROMP	ring-opening olefin metathesis polymerization
SANS	small-angle neutron scattering
SET-LRP	single-electron-transfer living radical polymerization
St	styrene
TEGVE	methyl triethylene glycol vinyl ether
TEM	transmission electron microscope
TEMPO	2,2,6,6-tetramethylpiperazine-1-oxyl
T_g	glass transition temperature
THF	tetrahydrofuran
THI	tetrahydroindene (bicyclo[4.3.0]-2,9-nonadiene)
TMSt	2,4,6-trimethylstyrene
T_{ps}	phase separation temperature
UCST	upper critical solution temperature
UV	ultraviolet (spectroscopy)
VE	vinyl ether

11. Acknowledgments

We are grateful to Drs. Motomasa Yonezumi and Kenichi Seno for their assistance in preparing the manuscript.

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CR900225G