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In-Situ Direct Mechanistic Transformation from RAFT to Living Cationic Polymerization for (Meth)acrylate−Vinyl Ether Block Copolymers

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ABSTRACT: In-situ direct mechanistic transformation from living radical to cationic polymerization was investigated using a trithiocarbonate-type reversible addition−fragmentation chain-transfer (RAFT) agent and an azo-initiator for RAFT polymerization of (meth)acrylates followed by the addition of a Lewis acid catalyst for the sequential living cationic block polymerization of vinyl ethers. Prior to the mechanistic transformation reaction, the possibility of living cationic polymerization was examined via activation of the thioester bond by Lewis acids, such as $SnCl_4$, $EtAlCl_2$, and $ZnCl_2$. The $CH_3CH(O\mathit{i}Bu)SC(S)SEt/SnCl_4$-initiating system induced living cationic polymerization of isobutyl vinyl ether (IBVE) in the presence of ethyl acetate (EtOAc) as an additive in toluene at 20 °C to give polymers with controlled molecular weights and narrow molecular weight distributions (MWDs) ($M_w/M_n = 1.18$). The RAFT copolymerization of methyl acrylate (MA) or methacrylate (MMA) and IBVE was then first carried out using $(CH_3)_2C(CN)SC(S)SEt$ in the presence of a low-temperature radical initiator [2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile); V-70] in toluene at 20 °C to result in controlled copolymers with a high incorporation of (meth)acrylate units along with unreacted IBVE monomer due to its radically non-homopolymerizable nature. On the addition of $SnCl_4$ in EtOAc to the reaction mixture, a fast and quantitative consumption of the residual IBVE occurred to give unimodal block copolymers with controlled molecular weights ($M_w/M_n = 1.3-1.4$) consisting of the (meth)acrylate-rich copolymer and vinyl ether homopolymer segments. A more definite acrylate−vinyl ether block copolymer was also obtained by RAFT homopolymerization of MA followed by the addition of IBVE and then $SnCl_4$ in EtOAc after an interval. ^1H NMR analysis of the model reaction for the living cationic polymerization revealed that the thioester terminal is reversibly activated in the presence of Lewis acid to form a cationic species, whereas partial substitution of the trithiocarbonate moiety with the chloride in $SnCl_4$ occurred.

Introduction

Living polymerization is one of the most efficient methods for the synthesis of well-defined block copolymers by sequential addition of a second monomer into the living polymer of the first monomer.[1] Although recent progress in living or controlled radical polymerization via a variety of mechanisms including anionic, cationic, coordination, radical, and condensation polymerizations has enabled the synthesis of various block copolymers in each system,[2−6] there are always limitations of polymerizable monomers that are inherent in the mechanisms. To overcome such limitations of comonomers for block copolymers, mechanistic transformation of a propagating chain end has been applied to the synthesis of various block copolymers since the first example of the mechanistic transformation from living anionic polymerization of styrene (St) to living cationic ring-opening polymerization of tetrahydrofuran (THF),[7] both of which were discovered more than 50 and 40 years ago, respectively.[8,9] Recently, mushroomed living or controlled polymerization systems have multiplied the accessible block copolymers via a number of combinations of those living polymerizations thorough transformation as summarized in recent reviews.[10,11]

Among various living polymerizations, living or controlled radical polymerizations have most recently been developed and can now be widely applicable to the majority of vinyl monomers, i.e., not only (meth)acrylic and styrenic monomers but also vinyl esters and amides.[5] However, certain families of vinyl monomers, such as nonpolar olefins and vinyl ethers, cannot be inherently homopolymerized via the radical mechanism, indicating that the use of mechanistic transformation reactions or other methods using dual initiators is required for the synthesis of their block copolymers.[10,11] In contrast, vinyl ethers can be homopolymerized into high molecular weight products only by cationic polymerizations.[3] Thus, efficient and versatile mechanistic transformation reactions from living radical to living cationic polymerizations or vice versa should be required for the well-defined synthesis of block copolymers between (meth)acrylates and vinyl ethers.

The mechanistic transformation reaction from radical to cationic polymerizations for block copolymer synthesis was first reported by Yagci et al. in the conventional radical polymerization of styrene, which was transformed into cationic polymerization of *n*-butyl vinyl ether by the addition of an iodonium or silver salt with a less nucleophilic counteranion (PF_6^- or BF_4^-) as an oxidant of the radical species.[12] A similar strategy was also employed for the simultaneous copolymerization of methyl methacrylate and *n*-butyl vinyl ether in the presence of both AIBN and $Ph_2I^+PF_6^-$.[13] Kamachi et al. also used the $Ph_2I^+PF_6^-$-induced in-situ transformation for the simultaneous polymerization of *p*-methoxystyrene or *N*-vinylcarbazole and cyclohexene oxide (CHO), in which the oxidation of the electron-rich radical species derived from the electron-donating vinyl monomer by the salt was confirmed by

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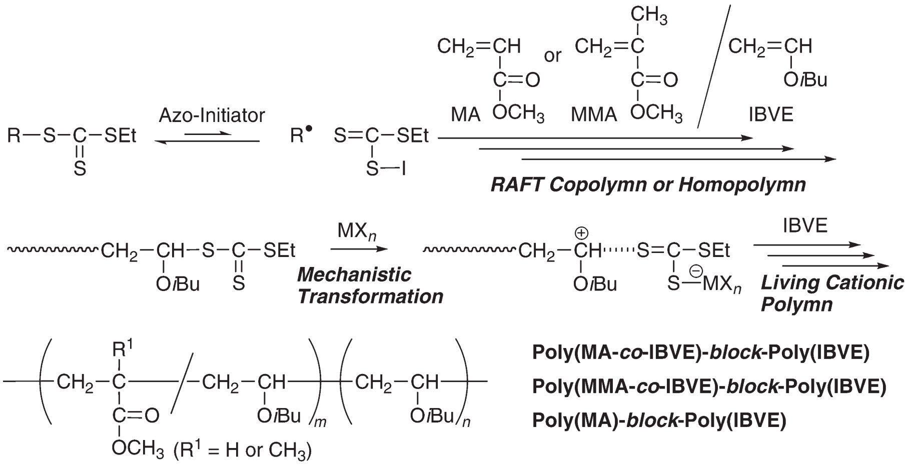
Scheme 1. Mechanistic Transformation of RAFT Living Radical Polymerization into Living Cationic Polymerization



ESR study.[14−17] However, the well-defined synthesis of the block copolymers was difficult by these methods principally because they were based on the conventional radical polymerization that cannot control the chain length of the polymer. The transformation reaction based on such salts was recently applied for living or controlled radical polymerization of styrenes and methyl methacrylate (MMA) followed by living cationic ring-opening polymerization of CHO and THF, in which the dormant carbon−halogen terminal or the resulting radical species was irreversibly oxidized into the carbocationic species for the ring-opening polymerization.[18−20] The covalent or dormant carbon−halogen terminal obtained by the transition-metal-catalyzed living radical polymerization or atom transfer radical polymerization (ATRP) of MMA was further transformed into another dormant carbon−halogen terminal, which can be activated by a Lewis acid, by the addition of styrenic monomers,[21−23] and was changed into the living cationic polymerization of isobutene (IB) to give multiblock copolymers consisting of MMA−St−IB segments.[21,22]

Another route to the block copolymers via radical and cationic polymerizations is based on transformation from cationic to radical polymerization, where the chain end of the living cationic ring-opening polymerization of THF or living cationic polymerization of IB has been indirectly converted into another chain end effective for living radical polymerization.[15−31] The dormant carbon−halogen terminal obtained by living cationic polymerization of St or β-pinene was also directly used for the ATRP of St, methyl acrylate (MA), or MMA to result in their block copolymers.[32,33] Irrespective of various block copolymers via radical/cationic or cationic/radical transformations, almost no well-defined synthesis of block copolymers of vinyl ether and (meth)acrylic monomers has been reported so far except for an indirect method.[34]

In this study, we investigated in-situ direct mechanistic transformation of the living radical polymerization of MA or MMA into living cationic polymerization of vinyl ether using thioester groups as the dormant species (Scheme 1). The reversible addition−fragmentation chain-transfer (RAFT) polymerization is one of the most versatile living or controlled radical polymerizations for various monomers.[5] In the RAFT polymerization, the thioester terminal is activated by radical species originating from a radical initiator to reversibly result in the growing radical species and to induce the controlled radical polymerization. Although thioester groups (~C−SC(S)−Z) have not been employed as the initiating site or the dormant species for living cationic polymerization, there have been many examples of living cationic polymerization of vinyl ethers using oxygen−ester bonds in conjunction with metal halides as Lewis acid activators, where the carbocationic species is reversibly formed via activation with the Lewis acid.[3] This suggests the possibilities of living cationic polymerization from the thioester groups using appropriate Lewis acids as well as transformation from RAFT polymerization of (meth)acrylates into living cationic polymerization of vinyl ether for the block copolymer synthesis.

Results and Discussion

Living Cationic Polymerization of Vinyl Ether with a Trithiocarbonate/Lewis Acid Initiating System. Prior to the transformation of living radical to cationic polymerization, we first investigated living cationic polymerization of isobutyl vinyl ether (IBVE), which is a typical alkyl vinyl ether monomer often employed in living cationic polymerization study,[3] via activation of the thioester bond [C−SC(S)] of a trithiocarbonate group, which can be derived from the RAFT agent. Among various thioester groups for RAFT polymerizations, a trithiocarbonate-type compound was chosen because it seems relatively stable even in the presence of a Lewis acid.[35] For this, we synthesized a novel trithiocarbonate ester (**1**), which would generate the vinyl ether-derived carbocationic species via the Lewis acid-mediated activation in a similar way to the oxygen−ester version, as an initiator or the model compound for the RAFT polymer terminal generated by the radical addition of IBVE. This compound was obtained from the substitution of the chlorine of an HCl−IBVE adduct with sodium ethyl trithiocarbonate in high yield (see Experimental Section).

Living cationic polymerization of IBVE was then examined using **1** in conjunction with several Lewis acids ($EtAlCl_2$, $SnCl_4$, $ZnCl_2$), which are often employed for living cationic polymerization for the activation of carbon−halogen or carbon−oxygen bonds,[3] in toluene at 20 °C. A very fast polymerization occurred with $EtAlCl_2$ or $SnCl_4$ and was completed within 10 s, while a relatively weak Lewis acid, such as $ZnCl_2$, induced a slower and quantitative polymerization.[36,37] The number-average molecular weights (M_n) of the polymers were close to the calculated values assuming that one molecule of **1** generates one living polymer chain. However, the molecular weight distributions (MWDs) depended on the Lewis acids as indicated by size-exclusion chromatography (SEC) (Figure 1).

To tame the very fast uncontrolled polymerizations with $SnCl_4$ and $EtAlCl_2$, we then added ethyl acetate (EtOAc), which would mediate living cationic polymerization via interaction with the carbocationic species and/or strong Lewis acids in a similar way to the other reported systems.[38−40] Under the conditions with 1.0 M EtOAc, the polymerizations became slower. Especially for $SnCl_4$, the MWDs became narrower in

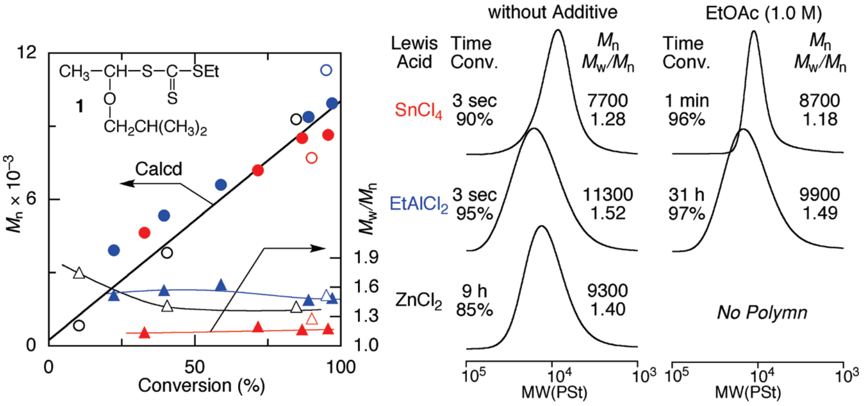


Figure 1. Living cationic polymerization of IBVE with isobutoxyethyl ethyl trithiocarbonate (**1**) and various Lewis acids in toluene at 20 °C: $[\mathrm{IBVE}]_0 = 0.5$ M; $[\mathbf{1}]_0 = 5.0$ mM; $[\text{Lewis acid}]_0 = 5.0$ mM; $[\text{ethyl acetate}]_0 = 0$ or 1.0 M. Lewis acid: $\mathrm{SnCl_4}$ (red ○, red △) with ethyl acetate (red ●, red ▲), $\mathrm{EtAlCl_2}$ (blue ○, blue △) with ethyl acetate (blue ●, blue ▲), $\mathrm{ZnCl_2}$ (○, △). The diagonal bold line indicates the calculated M_n assuming the formation of one living polymer per **1** molecule.

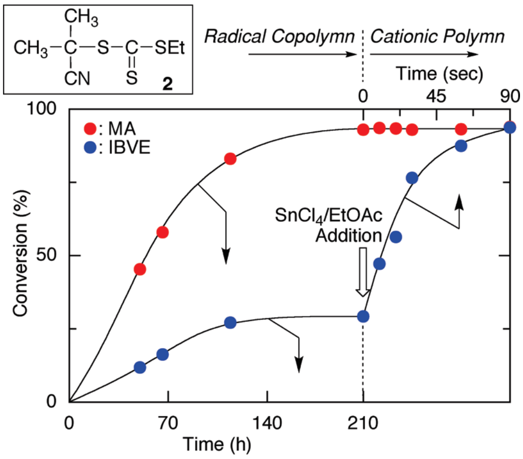


Figure 2. Time–conversion curve for the mechanistic transformation polymerization of MA (red ●) and IBVE (blue ●) in toluene at 20 °C from RAFT copolymerization with 2-cyanoisopropyl ethyl trithiocarbonate (**2**) and 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) to living cationic polymerization with $\mathrm{SnCl_4}$/ethyl acetate: $[\mathrm{MA}]_0 = [\mathrm{IBVE}]_0 = 1.0$ M; $[\mathbf{2}]_0 = 20$ mM; $[\text{V-70}]_0 = 5.0$ mM; $[\mathrm{SnCl_4}]_{\mathrm{add}} = 5.0$ mM; $[\text{ethyl acetate}]_{\mathrm{add}} = 1.0$ M.

the presence of EtOAc than in its absence. Furthermore, the M_n increased in direct proportion to monomer conversion and agreed well with the calculated values in each case with $\mathrm{SnCl_4}$ and $\mathrm{EtAlCl_2}$ in the presence of EtOAc and with $\mathrm{ZnCl_2}$ in the absence of EtOAc. Thus, living cationic polymerization of IBVE proceeded most probably via activation of the C–SC(S) bond with Lewis acids under appropriate conditions.

Transformation of RAFT Radical Copolymerization of (Meth)acrylate and Vinyl Ether into Living Cationic Homopolymerization of Vinyl Ether. Although vinyl ether cannot be homopolymerized via a radical mechanism, the radical copolymerization with (meth)acrylates proceeds to give copolymers containing vinyl ether, where no vinyl ether–vinyl ether sequences form. Here, we investigated the RAFT copolymerization of an equimolar mixture of MA and IBVE in the presence of a trithiocarbonate-type RAFT agent (**2**) with 2-cyanoisopropyl and ethyl moiety coupled with a low-temperature radical initiator such as 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70), in toluene at 20 °C, and $\mathrm{SnCl_4}$ in EtOAc was added to transform the growing species from radical to cation at the same temperature when most of the MA was polymerized.

As shown in Figure 2, under the RAFT copolymerization conditions, both the monomers were consumed simultaneously, while the consumption of MA was much faster than that of IBVE. On the addition of the Lewis acid in EtOAc, fast consumption of IBVE occurred without any changes in the MA conversion. This suggests that radical copolymerization of MA and IBVE proceeded in the first stage to result in the MA-rich copolymers and that $\mathrm{SnCl_4}$ induced fast cationic homopolymerization of IBVE during the second stage.

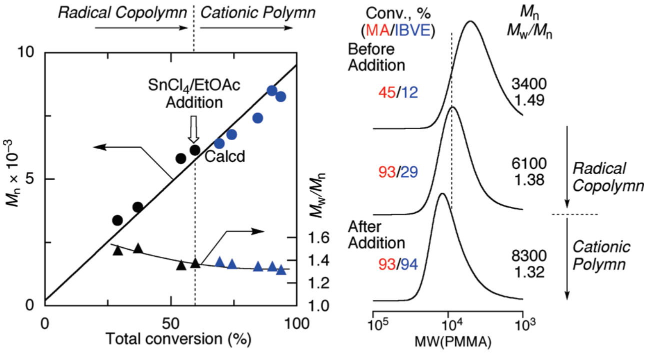


Figure 3. M_n, M_w/M_n, and SEC curves of MA–IBVE copolymers obtained in the same experiments as for Figure 2. The diagonal bold line indicates the calculated M_n assuming the formation of one copolymer chain per **2** molecule.

Before the addition of the Lewis acid, the SEC curves of the obtained copolymers showed narrow MWDs and shifted to high molecular weight along with the consumption of the both monomers (Figure 3). This shows the first example of a successful controlled RAFT copolymerization of acrylate and vinyl ether although a similar controlled/living radical polymerization was reported in the metal-catalyzed system. On the addition of $\mathrm{SnCl_4}$, the SEC curve further shifted to higher molecular weight with retaining narrow unimodal MWDs. Furthermore, the M_n increased in direct proportion to total monomer weight–conversion and agreed well with the calculated values assuming that one polymer molecule is generated from one molecule of **2** throughout the first and second stages of the polymerizations. These results indicate that living radical copolymerization of MA and IBVE was followed by living cationic polymerization of IBVE via the radical/cation transformation of the growing chain end derived from **2**.

The ^{1}H NMR analysis of the obtained products also supported these results. The copolymers obtained during the RAFT copolymerization showed both characteristic peaks of MA (*b* and *c*) and IBVE (*e*, *f*, and *h*) units (Figure 4A), whereas the

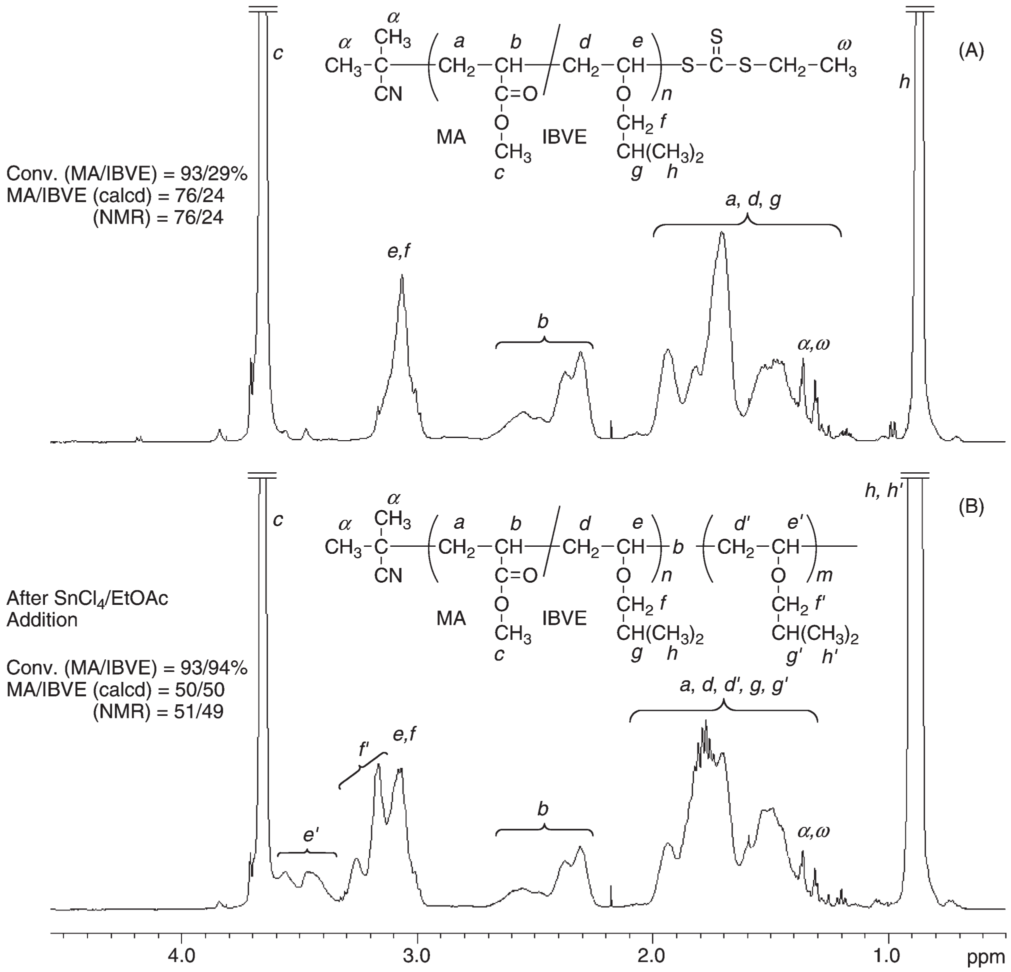


Figure 4. ^{1}H NMR spectra ($CDCl_3$, 55 °C) of MA-*r*-IBVE copolymer obtained in the RAFT copolymerization with **2**/V-70 in toluene at 20 °C (A) and (MA-*r*-IBVE)-*b*-IBVE copolymer obtained after mechanistic transformation on addition of $SnCl_4$/ethyl acetate (B).

shapes of some peaks (*b*, *e*, and *f*) were different from those of the homopolymers, suggesting formation of the copolymers. More specifically, the main-chain peaks (*e* and *f*) of the IBVE units were quite different from those of the homopolymer because MA units were located at both sides of the IBVE unit obtained in the radical copolymerization. In addition to these large peaks, small signals assignable to the cyanopropyl unit (α) at the α-end and the ethyl trithiocarbonate group (*ω*) at the *ω*-end were observed though the functionality of these groups could not be properly calculated due to large overlapping signals of the repeating units. The incorporated ratio of MA and IBVE units in the copolymers obtained by the ^{1}H NMR analysis (MA/IBVE = 76/24) agreed well with the calculated value (MA/IBVE = 76/24) from the monomer conversion and feed ratio.

The products obtained after addition of $SnCl_4$ showed additional signals (*e*′ and *f*′), which were distinguished from those of the previous signals (*e* and *f*), assignable to the homopolymer segments of the IBVE units (Figure 4B). Furthermore, the α- and *ω*-chain end groups were similarly observed. The incorporated ratio of the two monomer units (MA/IBVE = 51/49) measured by ^{1}H NMR also agreed well with the calculated value (MA/IBVE = 50/50).

A similar transformation from living radical into cationic polymerizations was examined using a methacrylic monomer, such as MMA, coupled with IBVE in toluene at 20 °C. As shown in Figure 5, the conversion of IBVE was lower than that in the copolymerization with MA due to the lower radical copolymerizability of vinyl ether with methacrylate than with acrylate. However, the polymers obtained in the RAFT copolymerization showed relatively narrow MWDs. On the addition of $SnCl_4$ in EtOAc, IBVE was consumed rapidly and almost quantitatively while the consumption of MMA did not occur after the addition of the Lewis acid. The SEC curves of the products further shifted to high molecular weight with slightly narrowed MWDs, indicating that the living cationic block polymerization of IBVE smoothly proceeded from the thioester chain end of the copolymers obtained by the RAFT copolymerization of MMA and IBVE.

These results showed for the first time that controlled RAFT copolymerization of (meth)acrylate and vinyl ether as well as successful in-situ direct transformation from RAFT into living cationic polymerization was achieved via activation of the thioester-terminal by a Lewis acid to generate block copolymers consisting of (meth)acrylate/vinyl ether copolymer and vinyl ether homopolymer segments.

Transformation of RAFT Radical Homopolymerization of Acrylate into Living Cationic Homopolymerization of Vinyl Ether. To further synthesize well-defined block copolymers with homopolymer segments of acrylate and vinyl ether, we first investigated RAFT homopolymerization of MA, then added IBVE to change the acrylate-terminal unit into the vinyl ether predominantly, and finally added $SnCl_4$ in EtOAc to induce living cationic block polymerization of IBVE.

For this, we first polymerized MA with **2** and V-70 in toluene at 20 °C to obtain the homopolymer of MA with controlled molecular weight and narrow MWDs (M_n = 4000, M_w/M_n = 1.16) in 98 h as shown in Figure 6. We then

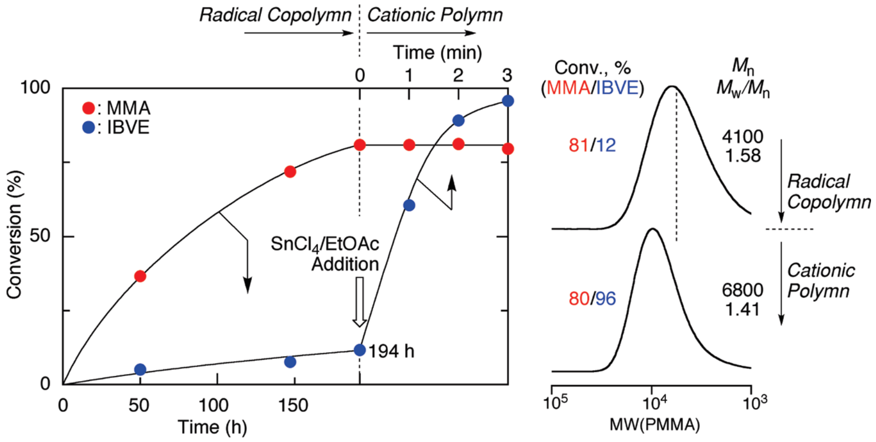


Figure 5. Time−conversion and SEC curves for the mechanistic transformation polymerization of MMA (red ●) and IBVE (blue ●) in toluene at 20 °C from RAFT copolymerization with **2**/V-70 to living cationic polymerization with SnCl$_4$/ethyl acetate: [MMA]$_0$ = [IBVE]$_0$ = 1.0 M; [**2**]$_0$ = 20 mM; [V-70]$_0$ = 5.0 mM; [SnCl$_4$]$_{add}$ = 5.0 mM; [ethyl acetate]$_{add}$ = 1.0 M.

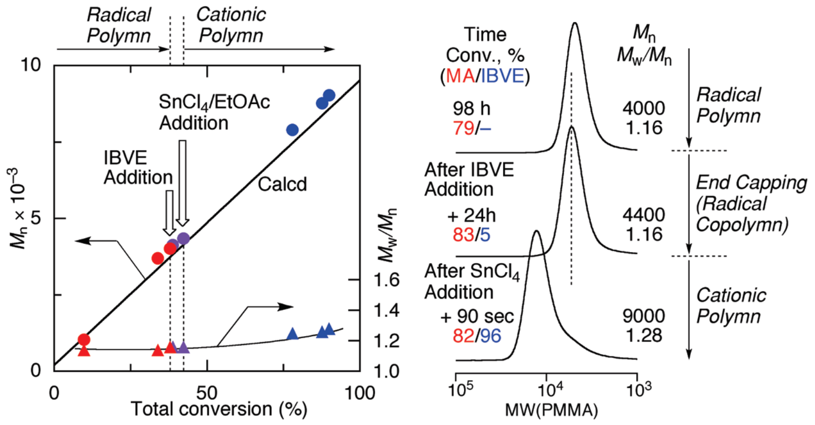


Figure 6. M_n, M_w/M_n, and SEC curves for the block copolymerization of MA and IBVE in toluene at 20 °C via the mechanistic transformation from RAFT polymerization with **2**/V-70 to living cationic polymerization with SnCl$_4$/ethyl acetate: [MA]$_0$ = 1.0 M; [**2**]$_0$ = 20 mM; [V-70]$_0$ = 5.0 mM; [IBVE]$_{add}$ = 1.0 M; [SnCl$_4$]$_{add}$ = 5.0 mM; [ethyl acetate]$_{add}$ = 1.0 M.

added an equimolar amount of IBVE to the initial feed of MA into the polymerization mixture and maintained this for 24 h at the same temperature. During this interval, the conversion of MA slightly increased from 79 to 83% and a small amount of IBVE was also consumed (5%). Along with the slight monomer consumptions, the M_n values slightly increased while retaining narrow MWDs (M_n = 4400, M_w/M_n = 1.16).

The ^{1}H NMR analysis of the products also showed small signals (*e*, *f*, and *h*) of the IBVE units (Figure 7B) in addition to the large absorptions of MA units (*a*, *b*, and *c*) (Figure 7A). The peak intensity ratio of the IBVE units in the products was very low (MA/IBVE = 97/3) and was almost consistent with the calculated value (MA/IBVE = 95/5). These results indicate that the MA terminal reacts with IBVE to result in short blocks consisting of MA and IBVE units and/or the IBVE-trithiocarbonate terminal groups predominantly.

Finally, on the addition of SnCl$_4$ in EtOAc, a fast consumption of IBVE occurred and was almost completed in 1.5 min. The SEC curves more clearly shifted to high molecular weight while retaining narrow MWDs (M_n = 9000, M_w/M_n = 1.28 in Figure 6). Furthermore, the M_n increased in direct proportion to monomer conversion and agreed well with the calculated values during all stages of the polymerizations. The obtained polymers showed characteristic signals of both homopolymer segments (Figure 7C), where the whole spectrum was quite different from that of copolymers with MA/IBVE copolymer and IBVE homopolymer segments (Figure 4B). The incorporated ratio of MA and IBVE (MA/IBVE = 47/53) was also in good agreement with the calculated value (MA/IBVE = 46/54). These results indicate that almost ideal block copolymers of acrylate and vinyl ether can be obtained by in-situ one-pot transformation of RAFT homopolymerization of acrylate followed by the sequential addition of vinyl ether and Lewis acid. However, the products obtained by shortening the interval period for the sequential additions from 24 into 1 h showed bimodal MWDs most probably due to formation of the block copolymers and remaining homopolymer of MA, which cannot initiate the living cationic polymerization of IBVE without being end-capped with IBVE units.

Model Reaction between Thioester Terminal of Vinyl Ether and Lewis Acid. As suggested by the successful results on the transformation from living radical to cationic polymerization, the trithiocarbonate terminal group is most probably activated by the Lewis acid to generate the cationic propagating species, whereas the anion exchange reaction between trithiocarbonate at the chain end and chloride on the Lewis acid activator is also possible. To clarify the dormant and/or the propagating species in the living cationic polymerization, the model reaction between **1**, i.e., the model terminal or the initiator for the living cationic

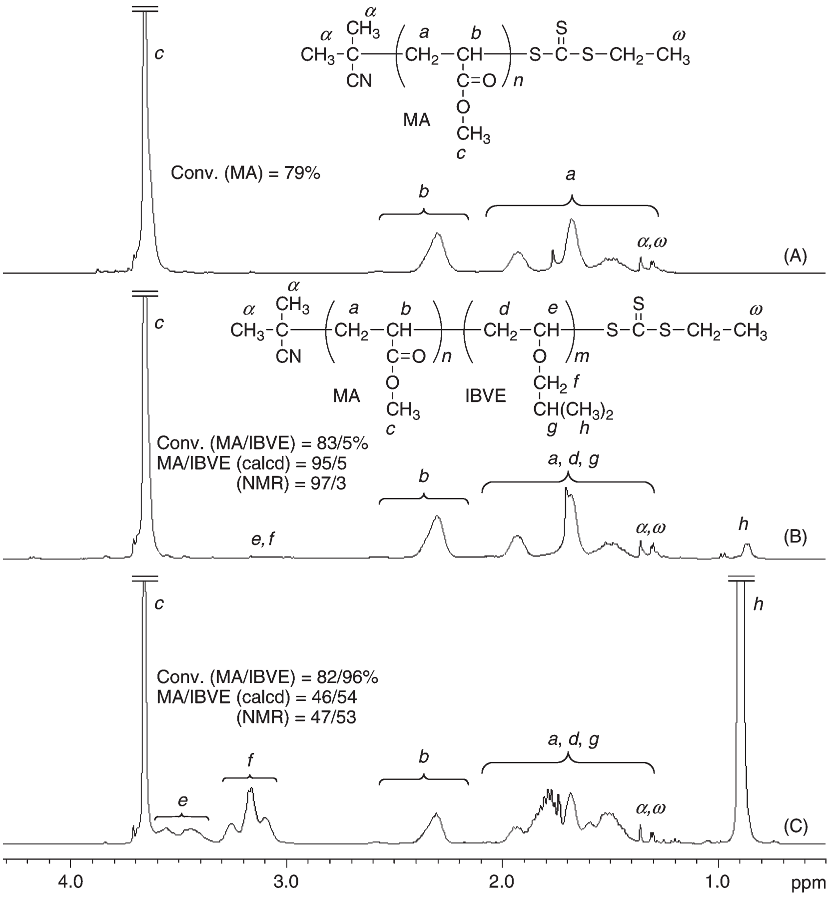


Figure 7. ^{1}H NMR spectra ($CDCl_3$, 55 °C) of MA homopolymer obtained in the RAFT copolymerization with **2**/V-70 in toluene at 20 °C (A), the polymer capped with short blocks consisting of MA and IBVE units (B), and MA-*b*-IBVE copolymer obtained after mechanistic transformation on addition of $SnCl_4$/ethyl acetate (C).

polymerization, and $SnCl_4$ was analyzed by ^{1}H NMR in toluene-d_8.

As shown in Figure 8A, **1** showed the characteristic methine proton (*b*) adjacent to the trithiocarbonate moiety and two diastereotopic geminal methylene protons (c_1 and c_2) due to the effect of the asymmetric center carbon (*b*) in the molecule similar to the other adducts between protic acid and IBVE.[36,37,42] In addition, the methylene protons (d_1 and d_2) of the ethyl thioester in the trithiocarbonate moiety were split into two peaks due to the similar effects of the asymmetric center.

On the addition of $SnCl_4$ in EtOAc at 0 °C, these peaks in the methine and methylene proton regions broadened in addition to the appearance of a new broad peak (b') (Figure 8B). On decreasing the temperature of the mixture stepwise to −80 °C, almost all the peaks became sharp, which enabled these peak assignments and clarified what happened in the reaction mixture. Especially at −80 °C (Figure 8E), an additional pair of peaks (c_1' and c_2') was clearly observed, where these new peaks (b', c_1', and c_2') were assigned to the methine and methylene protons of the HCl−IBVE adduct[36,37] generated by the anion exchange reaction between **1** and $SnCl_4$. The ratio of the trithiocarbonate and chloride adducts can be calculated from the peak intensity ratios of *b* and b'. The values (b/b') were dependent on the temperature and varied between ~1/1 and ~2/1, indicating that a partial trithiocarbonate group was reversibly changed by the chloride anion originating from $SnCl_4$. However, more than half of the trithiocarbonate moiety remained at the carbon terminal irrespective of the presence of an equimolar amount of chlorine atom to the trithiocarbonate group in the reaction mixture ($[\mathbf{1}]_0/[SnCl_4]_0 = 4/1$; i.e., $[-SC(S)SEt]/[-Cl] = 1/1$) under the conditions with the same feed ratio as that for the polymerizations. This indicates that the trithiocarbonate moiety still remained at the dormant polymer terminal even during the living cationic polymerization.

The formation of the cationic species from both the adducts was confirmed by the broadening methylene peaks (c_1 and c_2 for **1** and c_1' and c_2' for the chloride) at higher temperatures, indicating that a fast exchange of the diastereotopic protons occurred through the formation of the sp^2-like carbocationic species.[36,37,42] In addition, the methylene protons of the chloride adduct became much broader than those of **1** even at a low temperature (−60 °C) and finally coalesced into a broad peak at −20 and 0 °C. This suggests that a relatively fast activation/deactivation process occurred for the chloride adduct via reversible activation of the C−Cl bond by the Lewis acid. Furthermore, the peaks of both the methine protons (*b* and b') of **1** and the chloride adduct broadened at higher temperatures, indicating that an interchange reaction occurred between **1** and the chloride adduct via the cationic intermediate. Thus, the C−SC(S)SEt bond in **1** can be activated by the Lewis acid to form the carbocationic intermediate and generate the concurrent HCl−IBVE adduct reversibly (Scheme 2). Furthermore, another possible mechanism for activation of the trithiocarbonate, other than the direct Lewis-acid-mediated activation of the C−SC(S)SEt bond, might be a cationic RAFT process where the C=S bond of the thioester terminal is attacked by

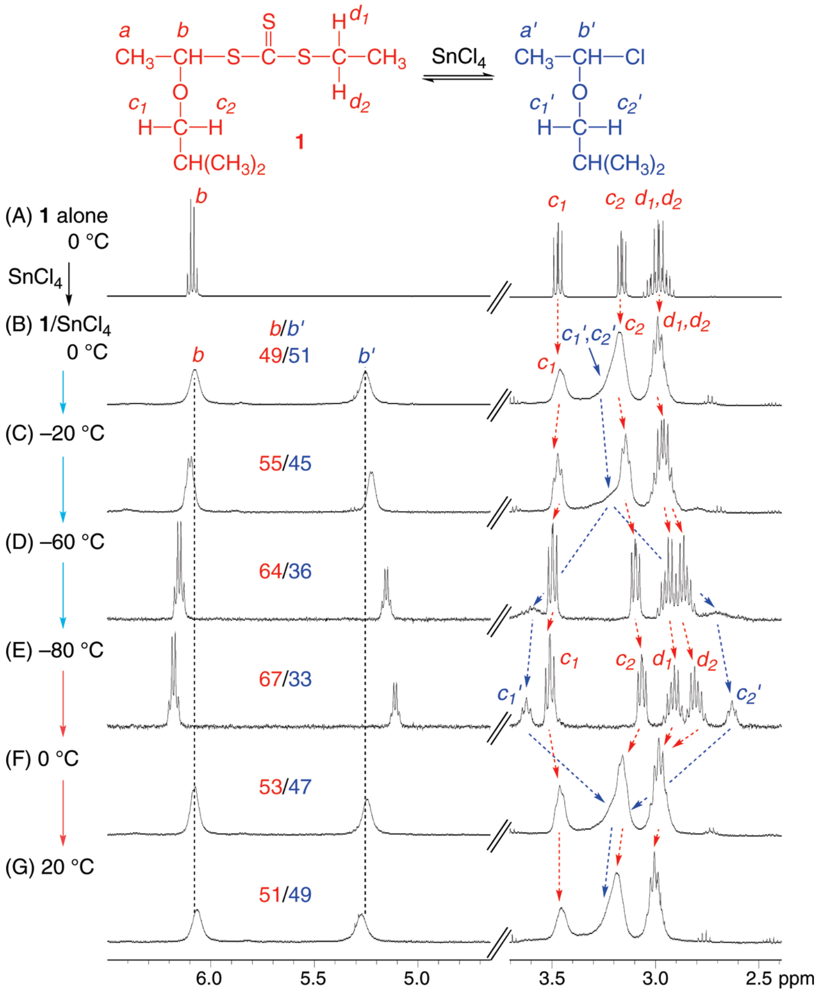
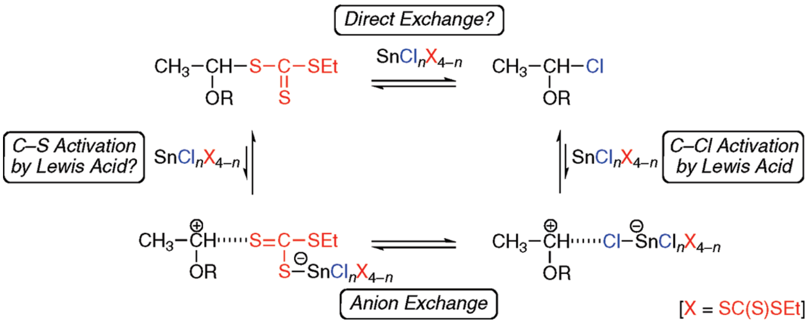


Figure 8. ^{1}H NMR spectra of **1** (A) and the mixture of **1**/$SnCl_4$ in the presence of ethyl acetate (B–G) in toluene-d_8: $[\mathbf{1}]_0 = 100$ mM; $[SnCl_4]_0 = 25$ mM; $[\text{ethyl acetate}]_0 = 100$ mM.

Scheme 2



the carbocationic species generated from the C–Cl bond to form another cationic species via a cationic addition–fragmentation process. This point is now under investigation using Lewis-acid-free initiating systems.

The reversibility of the exchange reactions was further confirmed by the fact that a series of broad signals appeared on further increasing the temperature to 0 °C (Figure 8F), which are almost the same as those of the first spectrum at 0 °C (Figure 8B). Similar and slightly broader peaks were obtained even at 20 °C (Figure 8G), where the living cationic polymerization was achieved. Thus, the propagating cationic species is reversibly formed via activation of the thioester bond in the presence of Lewis acid.

Conclusion

In conclusion, this paper contributed to three major findings, i.e., (1) in-situ direct transformation from RAFT radical polymerization into living cationic polymerization, (2) controlled RAFT copolymerization of (meth)acrylates and vinyl ethers, and (3) living cationic polymerization via reversible activation of the thioester terminal. More specifically, we succeeded in an effective transformation using the trithiocarbonate-type RAFT agents in conjunction with an azo-initiator and appropriate Lewis acid in the presence of ester additives. This method would be highly effective for the synthesis of well-defined block copolymers between radically and cationically polymerizable monomers because of the broad versatility of the RAFT process among various living radical polymerization systems as well as the recent remarkable developments in living cationic polymerizations.

Experimental Section

Materials. Isobutyl vinyl ether (IBVE) (Tokyo Kasei, $>95\%$) and methyl acrylate (Tokyo Kasei, $>99\%$) were distilled from calcium hydride under reduced pressure before use. $\mathrm{SnCl_4}$ (Aldrich, 99.995%), $\mathrm{ZnCl_2}$ (Aldrich; 1.0 M solution in *n*-diethyl ether), $\mathrm{EtAlCl_2}$ (Kanto; 1.0 M solution in *n*-hexane), ethanethiol (Wako, $>98\%$), carbon disulfide ($\mathrm{CS_2}$) (Kishida, $>99\%$), and sodium hydride (Kishida, 60% in oil) were used as received. Toluene (Kanto, $>99.5\%$, $\mathrm{H_2O} < 10$ ppm) and diethyl ether ($\mathrm{Et_2O}$) (Kanto, $>99.5\%$, $\mathrm{H_2O} < 50$ ppm) were further dried and deoxygenized by passage through columns of Glasscontour solvent system before use. Ethyl acetate (EtOAc) (Kanto, $>99.5\%$) and 1,2,3,4-tetrahydronaphthalene (Kishida; 99.5%) were distilled from calcium hydride before use. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (Wako, $>95\%$) was purified by washing with acetone at −15 °C and was evaporated to dryness under reduced pressure. *S*-2-Cyano-2-propyl *S*′-ethyl trithiocarbonate (**2**) was synthesized according to the literature.[43]

Synthesis of *S*-1-Isobutoxyethyl *S*′-Ethyl Trithiocarbonate (1). **1** was synthesized by the reaction between the HCl adduct of IBVE (IBVE−HCl) and sodium ethyl trithiocarbonate, both of which were in situ prepared from IBVE and ethanethiol, respectively. According to the reported method,[37] the IBVE−HCl was prepared by adding IBVE (3.26 mL, 25 mmol) dropwise into 1.0 M $\mathrm{Et_2O}$ solution of hydrogen chloride (27.5 mL, 27.5 mmol) at 0 °C. In another vessel, $\mathrm{CS_2}$ (1.65 mL, 27.5 mmol) was added dropwise at 0 °C to the solution of sodium ethanesulfide, which was prepared from ethanethiol (1.85 mL, 25 mmol) and sodium hydride (1.0 g, 25 mmol) in dry $\mathrm{Et_2O}$ (10 mL), and the dispersion solution was stirred at room temperature for 2 h to form sodium ethyl trithiocarbonate. Into the suspension was added the IBVE−HCl solution (23.2 mmol) dropwise at 0 °C over a period of 30 min under stirring. After stirring at ambient temperature for an additional 1.5 h, the reaction was quenched by diluting with $\mathrm{Et_2O}$ and the solution was washed with brine and water. The solvent was removed by evaporation to give the crude product (4.61 g, 77% yield), and the product was purified by column chromatography on silica gel with *n*-hexane as an eluent. The trithiocarbonate **1** was obtained as yellow liquids (2.06 g, 8.6 mmol, 35% yield). ^{1}H NMR (toluene-d_8, 0 °C): δ 0.78 and 0.80 (d, 6H, $\mathrm{OCH_2CH(C\mathit{H}_3)_2}$, $J = 6.9$ Hz), 0.96 (t, 3H, $\mathrm{SCH_2C\mathit{H}_3}$, $J = 7.3$ Hz), 1.58 (d, 3H, $\mathrm{C\mathit{H}_3CH}$, $J = 6.0$ Hz), 1.73 (m, 1H, $\mathrm{OCH_2C\mathit{H}(CH_3)_2}$), 2.96 and 2.99 (dq, 2H, $\mathrm{SC\mathit{H}_2CH_3}$, $J_{\mathrm{vic}} = 7.3$ Hz, $J_{\mathrm{gem}} = -9.6$ Hz), 3.15 and 3.46 (dd, 2H, $\mathrm{OC\mathit{H}_2CH(CH_3)_2}$, $J_{\mathrm{vic}} = 6.4$ and 6.9 Hz, $J_{\mathrm{gem}} = -9.2$ Hz), 6.08 (q, 1H, $\mathrm{CH_3C\mathit{H}}$, $J = 6.0$ Hz). ^{13}C NMR ($\mathrm{CDCl_3}$, rt): δ 13.1, 19.4, 22.9 (all $\mathrm{\mathit{C}H_3}$), 28.4 ($\mathrm{OCH_2\mathit{C}H(CH_3)_2}$), 31.0 ($\mathrm{S\mathit{C}H_2CH_3}$), 76.4 ($\mathrm{O\mathit{C}H_2CH(CH_3)_2}$), 89.0 ($\mathrm{CH_3\mathit{C}H}$), 224.9 ($\mathrm{S\mathit{C}(S)S}$).

Living Cationic Polymerization of IBVE. The living cationic polymerization of IBVE with **1** was carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure is given below. The reaction was initiated by sequential addition of solutions of **1** (0.015 mmol; 0.6 mL of 25.0 mM in toluene) and mixture solutions (0.60 mL) of $\mathrm{SnCl_4}$ (0.015 mmol) and EtOAc (3.0 mol) via dry syringes into a monomer solution (1.8 mL) containing IBVE (1.5 mmol) and 1,2,3,4-tetrahydronaphthalene (0.040 mL) in toluene at 20 °C. The total volume of the reaction mixture was 3.0 mL. After stirring for 1 min, the polymerization was terminated with methanol (1.0 mL) containing a small amount of ammonia. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR with 1,2,3,4-tetrahydronaphthalene as an internal standard (96%). The polymer yield by gravimetry was in good agreement with the ^{1}H NMR conversion of the monomer. The quenched reaction mixture was washed with dilute hydrochloric acid, aqueous sodium hydroxide solution, and then water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymers ($M_n = 8700$, $M_w/M_n = 1.18$).

Transformation of RAFT Radical Copolymerization into Cationic Polymerization. A typical example for the mechanistic transformation from the RAFT copolymerization of MA and IBVE to the IBVE living cationic polymerization is given below. The RAFT radical copolymerization was initiated by addition of prechilled solution of V-70 (0.12 mL of 96 mM solution, 0.011 mmol) via dry syringe into a monomer solution (2.2 mL) containing MA (2.3 mmol), IBVE (2.3 mmol), 1,2,3,4-tetrahydronaphthalene (0.035 mL), and **2** (0.046 mmol) in toluene at 20 °C. The total volume of the reaction mixture was 2.3 mL. After 210 h, the MA−IBVE random copolymer ($M_n = 6100$, $M_w/M_n = 1.38$) was obtained, of which monomer conversions determined by ^{1}H NMR spectroscopy with 1,2,3,4-tetrahydronaphthalene as an internal standard reached 93% for MA and 29% for IBVE, respectively. And then, for the transformation into cationic polymerization, the toluene solution (0.3 mL) of $\mathrm{SnCl_4}$ (0.015 mmol) and EtOAc (0.30 mmol) was added to the copolymerization mixture via dry syringe at the same temperature. After stirring for an additional 1.5 min, the reaction was terminated with methanol (1.0 mL) containing a small amount of ammonia. The monomer conversions were also determined by ^{1}H NMR spectroscopy (93% for MA and 94% for IBVE, respectively). The product was recovered by the same work-up process as before to give (MA-*r*-IBVE)-*b*-IBVE copolymer ($M_n = 8300$, $M_w/M_n = 1.32$).

Transformation of RAFT Radical Homopolymerization into Cationic Polymerization. The RAFT radical polymerization of MA was initiated by addition of prechilled solution of V-70 (0.21 mL of 62 mM solution, 0.013 mmol) via dry syringe into a monomer solution (1.75 mL) containing MA (2.6 mmol), 1,2,3,4-tetrahydronaphthalene (0.027 mL), and **2** (0.052 mmol) in toluene at 20 °C. The total volume of the reaction mixture was 1.96 mL. When the conversion of MA reached 79% (98 h, $M_n = 4000$, $M_w/M_n = 1.16$), IBVE (0.34 mL, 2.6 mmol) was added to the reaction mixture via dry syringe in order to cap the polymer terminal with IBVE-trithiocarbonate groups. After an interval of 24 h at the same temperature, the conversions of MA and IBVE became 83% and 5%, respectively ($M_n = 4400$, $M_w/M_n = 1.16$). And then the mixture solution (0.3 mL) of $\mathrm{SnCl_4}$ (0.013 mmol) and EtOAc (2.6 mmol) in toluene was added to the reaction mixture in order to transform the growing species from radical to cation. After stirring for an additional 1.5 min, the polymerization was terminated with methanol (1.0 mL) containing a small amount of ammonia. The monomer conversions were also determined by ^{1}H NMR spectroscopy (82% for MA and 96% for IBVE). The product was recovered by the same work-up process as before to give the MA-*b*-IBVE copolymer ($M_n = 9000$, $M_w/M_n = 1.28$).

Model Reaction. ^{1}H NMR spectra were recorded on a JEOL ECS-400 spectrometer, operating at 399.78 MHz. The main parameters were as follows: spectral width = 7503.0 Hz (18.77 ppm), pulse width = 4.7 μs (45°), acquisition time + pulse delay = 30 s, data points = 16 384, number of transients = 8 (4 min for one spectrum). The probe temperature was regulated with a variable-temperature apparatus JEOL Air/VT unit (temperature fluctuation ≤1 deg). The model reaction was started by adding the prechilled solution of $\mathrm{SnCl_4}$ (0.1 mL of 250 mM solution, 25 mmol) and EtOAc (0.2 mL of 500 mM solution, 100 mmol) via dry syringes into a solution of **1** (0.2 mL of 500 mM solution, 100 mmol) in a septum-capped NMR tube under a dry nitrogen in toluene-d_8 at 0 °C. The total volume of the mixture was 1.0 mL. Immediately after mixing, the tube was then sealed by flame under a nitrogen atmosphere and was placed in the thermostated probe of NMR. The acquisition was started ca. 3 min after the sample tube reached the determined temperature. The chemical shifts were determined with reference to the methyl group of toluene-d_8 (2.09 ppm).

Measurements. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR spectroscopy with 1,2,3,4-tetrahydronaphthalene as an internal standard. ^{1}H NMR spectra were recorded on a JEOL ECS-400 spectrometer, operating at 400 MHz. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of the product polymers were determined by size-exclusion chromatography (SEC) in THF at 40 °C on two polystyrene gel columns [Shodex KF-805 L (pore size: 20−1000 Å; 8.0 mm i.d. × 30 cm) × 2; flow rate 1.0 mL/min] connected to a JASCO PU-2080 precision pump and a JASCO RI-2031 detector. The columns were calibrated against eight standard polystyrene samples (Shodex; $M_p = 520-900\,000$; $M_w/M_n = 1.01-1.14$) for IBVE homopolymer and eight standard poly(MMA) samples (Shodex; $M_p = 202-1\,950\,000$; $M_w/M_n = 1.02-1.09$) for MA homopolymer and MA−IBVE copolymers.

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