DOI: 10.1002/masy.201100115

In Situ Direct Mechanistic Transformation from $FeCl_3$-Catalyzed Living Cationic to Radical Polymerizations

*Hiroshi Aoshima, Kotaro Satoh, Masami Kamigaito**

Summary: A trivalent iron chloride ($FeCl_3$) catalyst induced both living cationic and radical polymerizations of various monomers in the presence of an appropriate additive or ligand to yield polymers with controlled molecular weights and narrow molecular-weight distributions. The in-situ mechanistic transformation from a living cationic to a radical growing species during the styrene polymerization was achieved in a $FeCl_3$-based system with the simple addition of phosphine followed by an elevation of the reaction temperature. The growing cationic species was effectively converted into the radical species to produce a series of block copolymers that consist of styrene and various acrylic monomers.

Keywords: block copolymer; iron chloride; living cationic polymerization; living radical polymerization; mechanistic transformation

Introduction

Since the discovery of living cationic polymerization,[1–5] reversible activation of dormant species has become a common method for controlled/living polymerizations, and reversible activation is now widely applicable for almost all chain-growth polymerizations.[6–9] Most living cationic polymerizations have been developed via the two-electron reversible activation of a covalent or dormant species, such as carbon–halogen and carbon–oxygen bonds. These dormant species are then transformed into the growing carbocationic species by various metal salts, including Sn(IV),[10] Ti(IV),[11] Zn(II),[12] Fe(III),[13] etc., which are usually in a higher oxidation state and thus possess considerable Lewis acidity. As an analogy to living cationic polymerization, metal-catalyzed living radical polymerization or atom-transfer radical polymerization (ATRP) was discovered via the evolution of Kharasch or atom-transfer radical addition into radical polymerization, in which the dormant carbon–halogen bond is activated by a one-electron redox reaction of the metal center.[6,7] Effective transition-metal catalysts for this system include Ru(II),[14] Cu(I),[15–17] Fe(II)[18,19] etc., which are in a low oxidation state and thus able to release one electron to activate the dormant covalent bond. Therefore, depending on the nature of the metal catalyst, a carbon–halogen bond can generate both the growing cationic and the radical species to induce cationic and radical polymerization, respectively.

Mechanistic transformation of the propagating species can expand the scope of polymerizable monomers during the polymerization. This technique is especially effective for the synthesis of block copolymers from different types of monomers via different active species.[20,21] Recently, dormant carbon–halogen bonds have been used for the preparation of block copolymers by a mechanistic transformation between living cationic and radical polymerizations via heterolytic and homolytic cleavage, respectively. For example, Lewis-acid-catalyzed

---

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
E-mail: kamigait@apchem.nagoya-u.ac.jp

living cationic polymerizations of cationically polymerizable monomers, such as β-pinene, isobutylene, and styrene, have been converted into living/controlled radical polymerizations of methyl acrylate (MA), methyl methacrylate (MMA), and styrene by a switching of the catalysts to transition-metal complexes to yield block copolymers and vice versa.[22–25] However, most of the mechanistic transformations have been performed after the isolation of the halogen-capped polymer as the macroinitiator for the second-stage polymerization. For this technique, residues of the first metal catalysts must be rigorously removed because the metal catalysts for these two polymerizations are generally different.

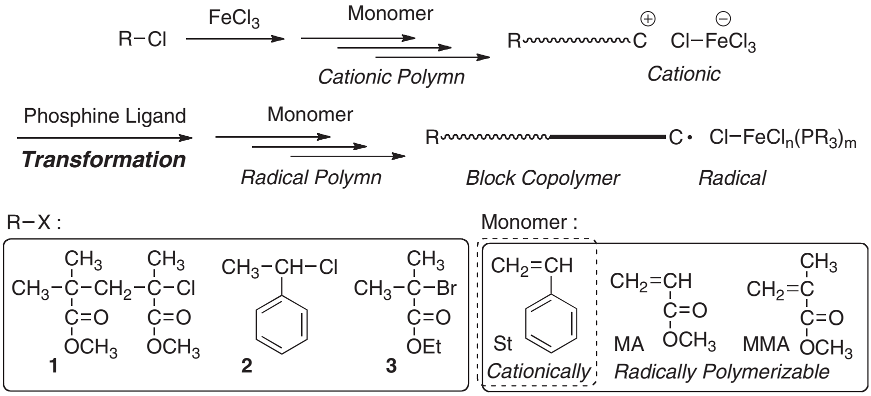
Among the various metal catalysts for living polymerizations, iron complexes are highly promising because they are non-toxic, environmentally benign, abundant, and cost-effective. Iron(III) chloride ($FeCl_3$), a higher-oxidation-state species, has been employed as the Lewis acid to catalyze living cationic polymerizations of vinyl ether in combination with halide initiators.[13] In addition, we have recently found that $FeCl_3$ also induces the living radical polymerization of styrene in conjunction with a halide initiator and an appropriate ligand such as tributylphosphine, contrary to the belief that the higher-oxidation-state iron(III) species would not be able to induce any radical polymerization without the intentional addition of reducing agents or radical initiators.[26] Although similar systems and their postulated mechanisms have been reported, discussions concerning the possible catalytic pathways still continue.[27–29]

This study is thus directed toward the in-situ mechanistic transformation of $FeCl_3$-catalyzed living cationic and radical polymerizations, both of which proceed by the reversible activation of C–Cl bonds by the same iron catalyst, for the synthesis of a series of block copolymers that comprise cationically and radically polymerizable monomers. The facile in-situ mechanistic transformation from cationic to radical polymerization was examined with the simple addition of phosphine or amine ligands to form the block copolymers in the same pot with the $FeCl_3$-based system (Scheme 1).

Experimental Part

Materials

Styrene (KISHIDA, 99.5%), methyl methacrylate (MMA; Tokyo Kasei; >99.8%), and methyl acrylate (MA; Tokyo Kasei; >99%) were distilled over calcium hydride under reduced pressure before use. $FeCl_3$ (Aldrich, >99.99%), $FeBr_3$ (Aldrich, 98%), and PPh_3 (Aldrich, 99%) were used as received and handled in a glove-box (VAC Nexus) under a moisture- and oxygen-free argon



Scheme 1.
Mechanistic Transformation from $FeCl_3$-catalyzed Living Cationic to Radical Polymerization.

atmosphere ($O_2 < 1$ ppm). PnBu$_3$ (KANTO, >98%) and PtBu$_3$ (Aldrich, 98%) were used as received. NnBu$_3$ (Wako, >98%), 1-chloroethylbenzene [MeCH(Ph)Cl (**2**)] (Tokyo Kasei, >97%), ethyl 2-bromoisobutyrate [$Me_2C(CO_2Et)Br$ (**3**)] (Tokyo Kasei, >98%), and chlorobenzene (Wako, >97%) were distilled from calcium hydride before use. $(MMA)_2$–Cl [$Me_2C(CO_2Me)CH_2C(CO_2Me)(Me)Cl$ (**1**)] was prepared according to the literature.[30] Toluene (Kanto, >99.5%; $H_2O < 10$ ppm), CH_2Cl_2 (Kanto, >99.5%; $H_2O < 10$ ppm), diethyl ether (Et_2O; Kanto, >99.5%; $H_2O < 10$ ppm), and methylcyclohexane (MCHx; Kanto, >98%; H_2O <0.1%) were dried and deoxygenized by passage through columns of Glass Contour Solvent Systems before use.

In Situ Mechanistic Transformation from Living Cationic to Radical Polymerization

A typical example for the in-situ mechanistic transformation from the living cationic polymerization of styrene into the living radical polymerization of MA is given below. The cationic polymerization was initiated by addition of the CH_2Cl_2 solution (1.0 mL) of $FeCl_3$ (0.25 mmol; 0.041 g) and MA (5.0 mmol; 0.45 ml) into a monomer solution (4.0 mL), containing styrene (2.5 mmol; 0.29 mL), **2** (0.1 mmol; 0.17 mL of 0.59 M in CH_2Cl_2), and chlorobenzene (0.13 mL), in CH_2Cl_2/MCHx mixture (1.37/2.05 mL) at –40 °C. The total volume of the reaction mixture was thus 5.0 mL. When the conversion of styrene reached 92% (120 h, $M_n = 2000$, $M_w/M_n = 1.21$), the CH_2Cl_2/MCHx solution (1/1 v/v; 1.25 mL) of PPh_3 (2.5 mmol; 0.66 g) was directly added to the polymerization solution and maintained this at –40 °C of 12 h. The solution was then evenly charged in seven glass tubes, and the tubes were sealed by flame under a nitrogen atmosphere. The tubes were immersed in thermostatic oil bath at 80 °C. After an additional 200 h, the polymerization was terminated by cooling the reaction mixtures to –78 °C. The monomer conversions were determined from the concentration of the residual monomer measured by gas chromatography (>99% for styrene) with chlorobenzene and ^{1}H NMR (37% for MA) with MCHx as the internal standard respectively. The quenched reaction mixture was diluted with toluene (ca. 30 ml), washed with dilute hydrochloric acid and water to remove complex residues, evaporated to dryness under reduced pressure, and vacuum-dried to give poly(styrene-*b*-MA) copolymer ($M_n = 2700$, $M_w/M_n = 1.30$).

Measurements

^{1}H NMR spectra were recorded on a JEOL ESC-400 spectrometer, operating at 400 MHz. The number-average molecular weight (M_n) and molecular weight distribution (MWD; M_w/M_n) of the polymers were measured by size-exclusion chromatography (SEC) using THF at a flow rate 1.0 mL/min at 40 °C on two polystyrene gel columns [Shodex KF-805L (pore size: 20–1000 Å; 8.0 mm i.d. × 30 cm)] that were connected to a JASCO PU-2080 precision pump and a JASCO RI-2031 detector. The columns were calibrated against 10 standard polystyrene samples (Varian; $M_p = 575$–2783000, $M_w/M_n = 1.02$–1.23) for polystyrene and styrene-MA copolymers or 11 standard poly(MMA) samples (Varian; $M_p = 202$–1677000, $M_w/M_n = 1.02$–1.23) for poly(MMA).

Results and Discussion

Living Cationic and Radical Polymerizations Catalyzed by $FeCl_3$

Prior to the study of the mechanistic transformations during the polymerizations, each living cationic and radical polymerization of styrene was investigated using $FeCl_3$ as the catalyst (Figure 1). The cationic polymerization of styrene was first examined using $FeCl_3$ in conjunction with a chloride initiator [MeCH(Ph)Cl (**2**)] in a mixture of solvents (CH_2Cl_2/MCHx) at –40 °C. The polymerization proceeded smoothly and reached a nearly quantitative conversion in 85 h. As the polymerization proceeded, the SEC curves shifted to a higher-molecular-weight region but main-

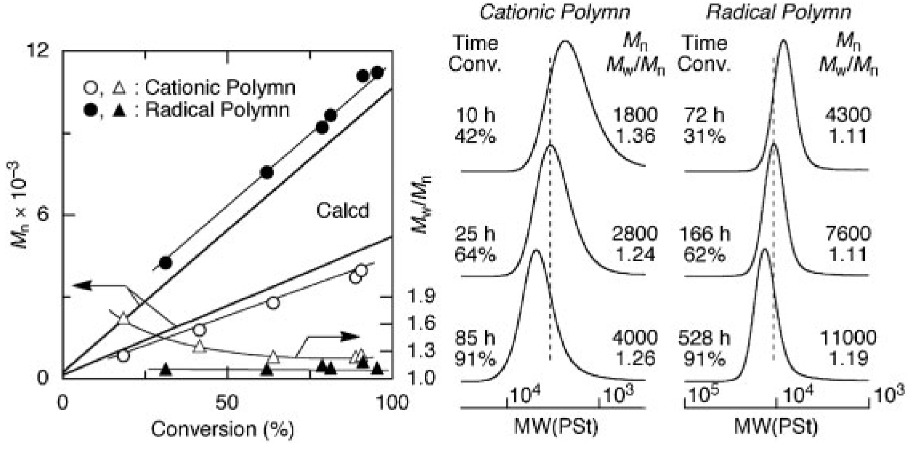


Figure 1.

$FeCl_3$-catalyzed living radical and cationic polymerization of styrene in the presence (radical) or absence (cationic) of P*n*Bu$_3$: [styrene]$_0$ = 4.0 M, [**1**]$_0$ = 40 mM, [$FeCl_3$]$_0$ = 10 mM, [P*n*Bu$_3$]$_0$ = 20 mM in toluene at 100 °C (for radical polymerization), [styrene]$_0$ = 0.5 M, [**2**]$_0$ = 10 mM, [$FeCl_3$]$_0$ = 50 mM, [Et_2O]$_0$ = 300 mM in CH_2Cl_2/MCHx (1:1 v/v) at −40 °C (for cationic polymerization).

tained their narrow MWDs (Figure 1). The M_n of the cationically obtained polystyrene increased in direct proportion to the monomer conversion. In addition, this value agreed well with the calculated value if one chloride initiator molecule was assumed to generate one living polymer chain (open symbols), although the cationic polymerization was well controllable below 5,000 molecular weights as in the reported systems for styrene.[1–5] Thus, the Lewis-acidic $FeCl_3$ induces living cationic polymerization of styrene via the heterolytic cleavage of the C–Cl terminal.

As reported in our previous paper, trivalent $FeCl_3$ also catalyzes living radical polymerization of styrene in the presence of a phosphine ligand, which is contrary to a general belief that a higher-oxidation-state metal species should inhibit or retard this polymerization.[26] Coupled with tributylphosphine (P*n*Bu$_3$) as the ligand, $FeCl_3$ was used as a catalyst for the polymerization of styrene in conjunction with another chloride initiator, $Me_2C(CO_2Me)CH_2C(CO_2Me)(Me)Cl$ (**1**), in toluene at 100°C. The polymerization proceeded in a living fashion to produce polymers with controlled M_n and narrow MWDs ($M_w/M_n \sim 1.2$) (filled symbols in Figure 1).

The radical polymerization in the presence of P*n*Bu$_3$ was significantly slower (91% conversion in 528 h) than the cationic polymerization that occurred in its absence (91% conversion in 85 h), even when this system was at a higher temperature. These results indicate that $FeCl_3$ effectively induces both the living radical and cationic polymerizations of styrene via activation of the C–Cl bonds in a reaction that is dependent on the various conditions and additives used. We also investigated the radical polymerizations of (meth)acrylic monomers, such as MMA and MA. Each radical polymerization of MMA and MA using $FeCl_3$ also proceeded with a range of ligands and halide initiators in toluene at 100 °C (Table 1). For the MMA polymerization, the use of **1** as the initiator gave controlled molecular weights irrespective of the phosphine or amine ligands used (entries 1–4), whereas **2** resulted in uncontrolled molecular weights because of slower initiation from the secondary C–Cl bond as compared to the tertiary bond of the producing PMMA (entry 5). Among the tested conditions, when **1** was coupled with the use of tri-*t*-butyl phosphine (P*t*Bu$_3$) or tributylamine (N*n*Bu$_3$) as the ligand, $FeCl_3$ afforded PMMA with the narrowest

Table 1.
Living Radical Polymerization of MMA and MA with FeX_3/Ligand[a]

Run	Monomer	R–X	FeX_3	Ligand	Time (h)	Conv.[b] (%)	M_n[c]	M_n(calcd)[d]	M_w/M_n[d]
1	MMA	1	$FeCl_3$	$PnBu_3$	36	90	7500	9300	1.36
2	MMA	1	$FeCl_3$	$PtBu_3$	24	90	9200	9300	1.24
3	MMA	1	$FeCl_3$	PPh_3	130	92	7600	9500	1.47
4	MMA	1	$FeCl_3$	$NnBu_3$	720	93	9500	9600	1.18
5	MMA	2	$FeCl_3$	$PtBu_3$	150	84	14000	8600	1.35
6	MA	1	$FeCl_3$	PPh_3	52	92	8700	8200	1.68
7	MA	2	$FeCl_3$	PPh_3	140	97	9400	8500	1.68
8	MA	3	$FeBr_3$	PPh_3	145	86	8500	7600	1.15

[a]Polymerization conditions: $[MMA]_0 = 2.0$ M, $[R–X]_0 = 20$ mM, $[FeCl_3]_0 = [ligand]_0 = 10$ mM in toluene at 100 °C (for MMA). $[MA]_0/[R–X]_0 = 100$, $[FeX_3]_0 = [ligand]_0 = 40$ mM in toluene at 100 °C (for MA).[b]Determined by gas chromatography.[c]$M_n(calcd) = MW(Monomer) \times [Monomer]_0/[R–X]_0 \times Conv. + MW(R–X)$.[d]Determined by size-exclusion chromatography in THF (PMMA standard).

MWDs ($M_w/M_n \sim 1.2$). In contrast, in the MA polymerization, both **1** and **2** gave polymers with similarly controlled M_n values, which were similar to the calculated values, in conjunction with $FeCl_3$ and triphenylphosphine (PPh_3) (entries 6 and 7), whereas the MWDs were slightly broad. The combination of a bromide initiator (**3**) and $FeBr_3$ further improved the control of the MA polymerization to afford polymers with narrow MWDs ($M_w/M_n = 1.15$) (entry 8). Thus, the R–X/$FeCl_3$/PR'_3 or NR'_3 system proved effective for living radical polymerizations of not only styrene, but also of MMA and MA with an appropriate choice of the ligand and initiator.

In Situ Direct Mechanistic Transformation during Styrene Polymerization

We subsequently examined the in-situ mechanistic transformation of the cationic to the radical growing species during the styrene polymerization. The living cationic polymerization of styrene was first investigated with $FeCl_3$ in CH_2Cl_2/MCHx at –40 °C. This experiment was then followed by the addition of $PnBu_3$ and the elevation of the reaction temperature to 100 °C to continue the second polymerization via the radical intermediate in a single pot. When the cationic polymerization reached a nearly quantitative conversion (90% in 60 h), a fresh feed of styrene and $PnBu_3$ was added to the polymerization mixture, which was kept at –40 °C for an additional 12 h and was then heated to 100 °C. Upon heating, the second-stage styrene polymerization resumed, likely via formation of the radical growing species.

Figure 2 shows the M_n values and SEC curves of the obtained polymer during the styrene polymerization. After the addition of the monomer and the phosphine ligand, the SEC curves further shifted to higher molecular weights while maintaining unimodal distributions, and the M_n increased with monomer conversion. The M_n slightly deviated from the calculated line in the later stages of the polymerization, which was likely because of a chain-transfer reaction, such as β-proton elimination at the C–Cl terminus of polystyrene, induced by the Lewis-acidic $FeCl_3$ in a polar solvent (CH_2Cl_2) at a high temperature. Similar results were reported in living radical polymerizations of styrene derivatives with the Fe(II) or Cu(II) complex coupled with an iodine or bromide initiator. Thus, the mechanistic transformation of the $FeCl_3$-catalyzed living cationic to radical polymerization of a single monomer, styrene, was achieved by the simple addition of the phosphine ligand and an elevation of the reaction temperature.

Synthesis of Styrene-MA Block Copolymers via Mechanistic Transformation

The synthesis of block copolymers consisting of styrene and MA was then examined via an in-situ mechanistic transformation with an R–Cl/$FeCl_3$/ligand system

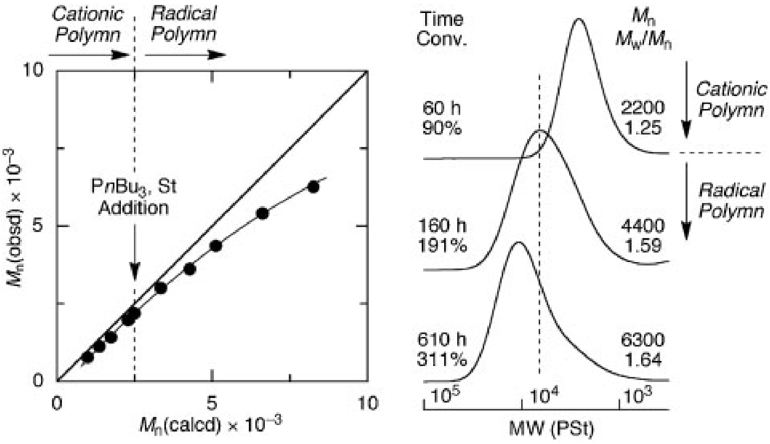


Figure 2.

M_n, M_w/M_n and SEC curves of polystyrene obtained by the mechanistic transformation from living cationic to radical polymerization of styrene: $[\text{styrene}]_0 = 0.5$ M, $[\text{styrene}]_{\text{add}} = 2.0$ M, $[\mathbf{2}]_0 = 20$ mM, $[FeCl_3]_0 = 50$ mM, $[PnBu_3]_{\text{add}} = 500$ mM, $[Et_2O]_0 = 300$ mM in CH_2Cl_2/MCHx (1:1 v/v) at –40 °C to 100 °C.

(Figure 3). The cationic polymerization of styrene was first performed with **2**/$FeCl_3$ in the absence or presence of MA (A and B, respectively).

Even in the presence of MA, the cationic styrene polymerization proceeded in a living fashion, although the rate of this reaction was slower compared with the rate of the reaction in which MA was absent, to afford polystyrenes with slightly narrower MWDs. This result shows that MA serves as a Lewis base to retard the cationic polymerization and to yield narrower MWDs. Immediately before the styrene was consumed, PPh_3, with or without MA, was added to the reaction mixture (Figure 3A and 3B, respectively). The mixture was maintained at –40 °C for an additional 12 h and heated to 80 °C. In both cases, the radical polymerization of MA took place smoothly after the addition and subsequent heating of the reaction mixture to produce the block copolymers. The SEC curves further shifted to high molecular weights, although the MWDs became slightly broader. More importantly, a narrower MWD was attained with procedure (B) in which only the addition of the ligand induced the in-situ mechanistic transformation from cationic to radical polymerization.

This in-situ mechanistic transformation was further utilized for the synthesis of block copolymers that consisted of polystyrene and random copolymers of styrene and MA blocks. In this synthesis, transformation by the ligand addition was conducted during the course of the cationic homopolymerization of styrene in the presence of MA to switch the reaction mechanism to a radical copolymerization of the residual styrene and MA. The living cationic polymerization of styrene was thus performed in the presence of MA at –40 °C, followed by the addition of PPh_3 at 61% styrene conversion in 22 h. After the addition of the phosphine ligand, the temperature was elevated to 80 °C, and the MA and the residual styrene were smoothly and simultaneously copolymerized. As shown in Figure 4, the SEC curves shifted to high molecular weights while retaining relatively narrow and unimodal MWDs ($M_w/M_n \sim 1.3$).

Thus, the $FeCl_3$-catalyzed living cationic polymerization of styrene can also be transformed into the radical (co)polymerization of MA, both of which proceed via activation of the dormant carbon–chlorine bond by the same metal catalyst, $FeCl_3$. The block copolymerization via this transformation not only proceeded well, but also

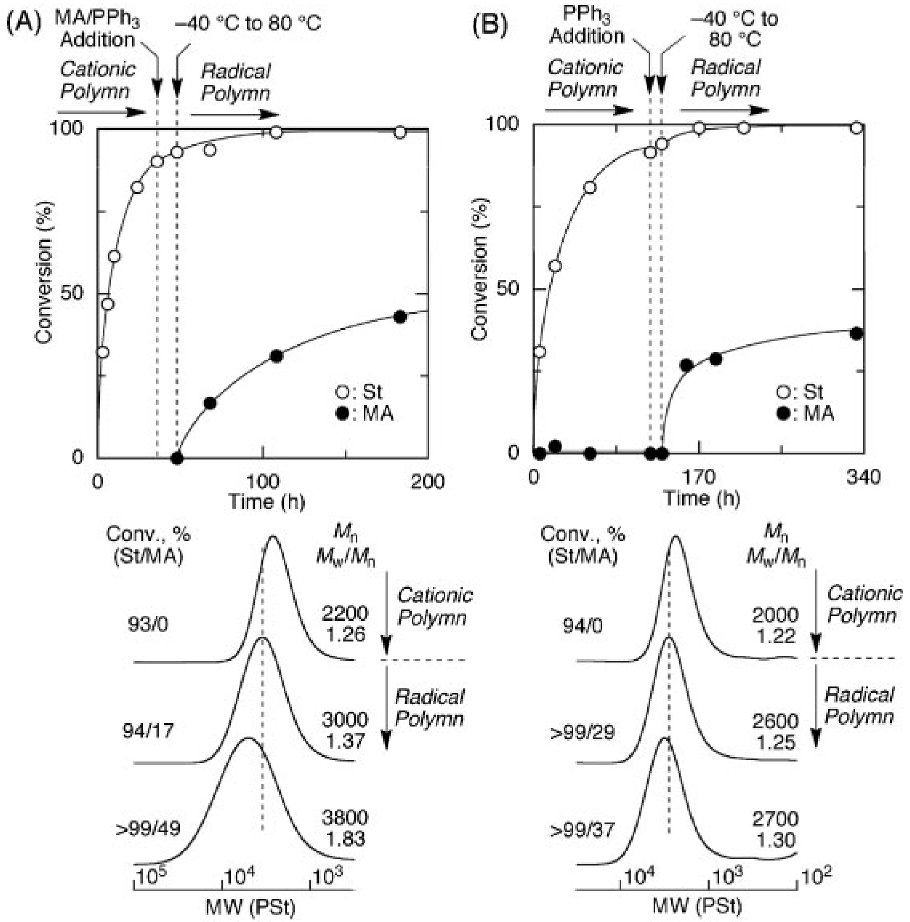


Figure 3.
Time-conversion and SEC curves of poly(styrene-*b*-MA) obtained by the transformation from living cationic polymerization of styrene to living radical polymerization of MA in CH_2Cl_2/MCHx (1:1 v/v) at −40 °C to 80 °C: (A); $[\text{styrene}]_0 = 0.5$ M, $[\text{MA}]_{\text{add}} = 2.0$ M, $[\mathbf{2}]_0 = 20$ mM, $[\text{FeCl}_3]_0 = 50$ mM, $[\text{PPh}_3]_{\text{add}} = 500$ mM, $[\text{Et}_2\text{O}]_0 = 300$ mM, (B); $[\text{styrene}]_0 = 0.5$ M, $[\text{MA}] = 1.0$ M, $[\mathbf{2}]_0 = 20$ mM, $[\text{FeCl}_3]_0 = 50$ mM, $[\text{PPh}_3]_{\text{add}} = 500$ mM.

gave tunable compositions of styrene and MA in the resulting block copolymer when a proper time was chosen for the addition of the ligands.

Figure 5 shows the ^{1}H NMR spectra of the polystyrene and block copolymers that were obtained with the $FeCl_3$-based system. The polymer obtained by the cationic polymerization of styrene in the presence of MA (Figure 5A) showed the characteristic signals of polystyrene without any concomitant MA units. In addition to the large absorptions that correspond to phenyl (*c*) and main-chain aliphatic (*a* and *b*) protons, small signals due to the end groups appeared, including a $–CH_3$ group (a', 0.8–1.1 ppm) at the α-end and a CH(Ph)–Cl group (b', 4.4 ppm) at the ω-end. The appearance of these signals was attributed to the chlorine atom at the growing terminal. Both of these groups are derived from the use of **2** as an initiator. The M_n value obtained from the peak intensity ratio of b' to c [M_n(NMR, ω-end) = 1900] was similar to that obtained by SEC [M_n(SEC) = 2100]. The functionality of the ω-end (b': Fn = 0.91) was almost unity, which indicates that one polymer was

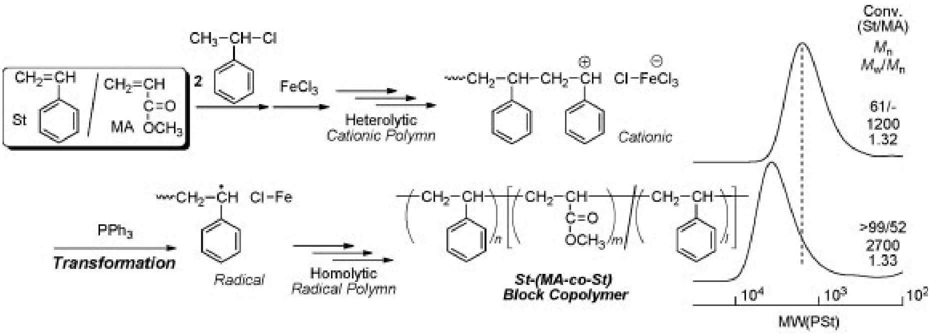


Figure 4.

SEC curves of polystyrene and poly(styrene-*b*-MA) obtained by the transformation from living cationic polymerization of St to living radical copolymerization of MA: $[\text{styrene}]_0 = 0.5$ M, $[\text{MA}]_0 = 1.0$ M, $[\mathbf{2}]_0 = 20$ mM, $[\text{FeCl}_3]_0 = 50$ mM, $[\text{PPh}_3]_{\text{add}} = 500$ mM, in CH_2Cl_2/MCHx (1:1 v/v) at −40 °C to 80 °C.

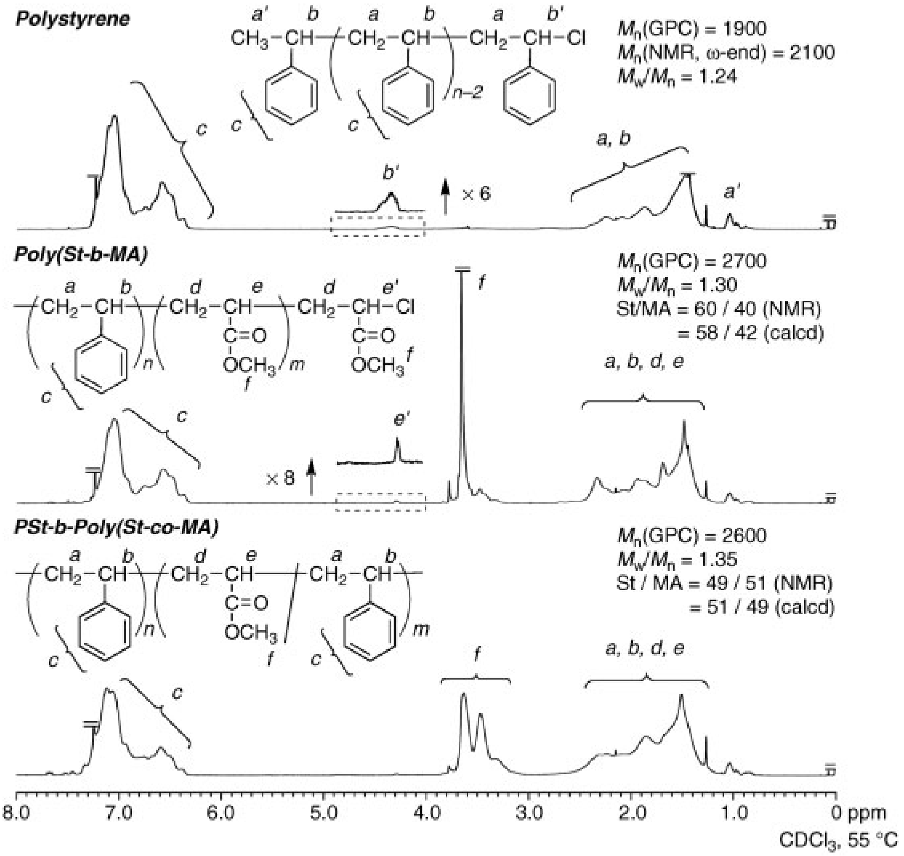


Figure 5.

^{1}H NMR spectra of polystyrene, poly(styrene-*b*-MA), and poylystyrene-*b*-poly (styrene-*co*-MA) obtained by the mechanistic transformation. See Figure 3B and 4 for synthesis conditions.

generated from one initiator during the cationic polymerization. As shown in Figure 5B and 5C, the polymers obtained after the mechanistic transformation showed the signals of the MA units, which are the methoxy (*f*) and main-chain aliphatic (*d* and *e*) protons, in addition to those of the styrene units. When styrene and MA were randomly copolymerized in the second stage of polymerization, the peak *f* became broader and split due to the comonomer sequences and cotacticity (Figure 5C). The signal of the methine proton (b') at the chloride ω-terminal of polystyrene completely disappeared after the transformation, and, alternatively, a small signal (e') appeared at 4.3 ppm, which was assigned to the methine proton [$CH(CO_2Me)–Cl$] at the terminal of the poly(MA) segment. In both spectra, the unit ratios of styrene to MA calculated from the peak areas of *c* and *f* (60/40 and 49/51) agreed well with the calculated values from the monomer conversion and feed ratio (58/42 and 51/49, respectively).

Mechanistic Transformation for MMA-Containing Block Copolymer

A similar transformation from the cationic polymerization of styrene to the radical polymerization of MMA was also investigated. The transformation that occurred after the nearly complete consumption of styrene resulted in bimodal MWDs in the second-stage MMA radical polymerization. This result was attributed to a slower initiation of the MMA polymerization from the CH(Ph)–Cl terminal of polystyrene, as observed in the MMA homopolymerization with initiator **2** (see entry 5 in Table 1). In contrast, the addition of MMA and P*t*Bu$_3$ during the course of the cationic polymerization of styrene resulted in unimodal SEC curves that shifted to higher molecular weights in the second-stage radical copolymerization of styrene and MMA to form polystyrene-*b*-poly(styrene-*co*-MMA) copolymers (Figure 6). This result suggests that radical cross-propagation between MMA and residual styrene yielded a more equal opportunity for propagation to almost all the polymer chains during the second-stage radical polymerizations because styrene can smoothly be polymerized both from the secondary CH(Ph)–Cl and tertiary $C(CH_3)(CO_2Me)–Cl$ terminals.

The ^1H NMR spectrum of the polystyrene-*b*-poly(styrene-*co*-MMA) showed the characteristic signals of PMMA, i.e., the main-chain aliphatic (*d*), α-methyl (*e*), and methoxy (*f*) protons, in addition to the

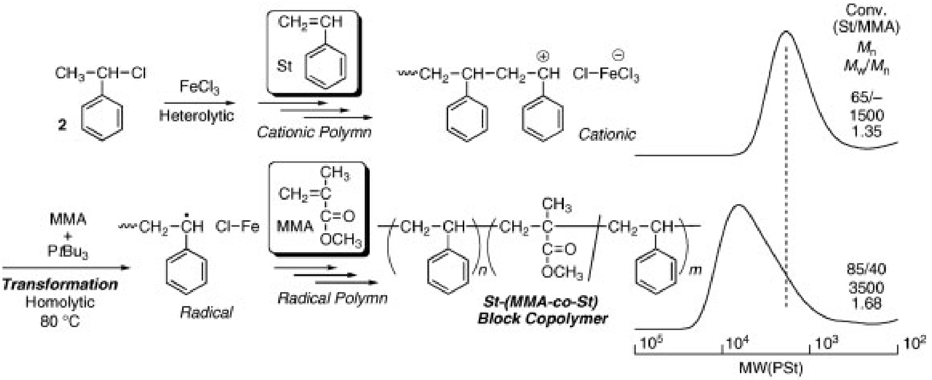


Figure 6.

SEC curves of polystyrene and poly(styrene-*b*-MMA) obtained by the transformation from living cationic polymerization of styrene to living radical polymerization of MMA: $[styrene]_0 = 0.5$ M, $[MMA]_{add} = 2.0$ M, $[\mathbf{2}]_0 = 20$ mM, $[FeCl_3]_0 = 50$ mM, $[PtBu_3]_{add} = 50$ mM, $[Et_2O]_0 = 300$ mM in CH_2Cl_2/MCHx (1:1 v/v) at −40 °C to 80 °C.

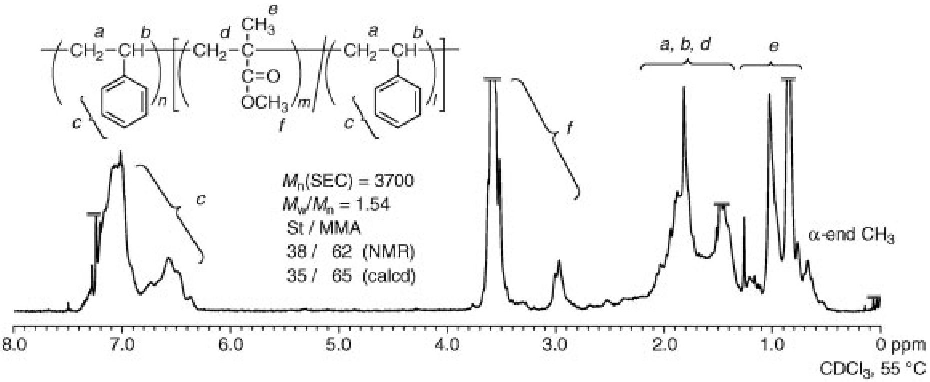


Figure 7.

^{1}H NMR spectrum of poylystyrene-*b*-poly(styrene-*co*-MMA) obtained in the same experiments as for Figure 6.

polystyrene signals (*a*–*c*) (Figure 7). Similar to the polystyrene-*b*-poly(styrene-*co*-MA) copolymer, a broadened methoxy group (*f*) was observed in the spectrum, which indicates that the obtained polymer contained the random copolymer segment. The signals around 0.5–1.3 ppm, which can be attributed to α-methyl protons of MMA units and methyl groups at α-chain end, were also complicated due to cotacticity of the styrene-*co*-MMA segments. The styrene/MMA ratio, which was obtained from the peak areas of the phenyl (*c*) and methoxy (*f*) groups (38/62), was nearly identical to the calculated value from the monomer conversion and feed ratio (35/65). These results indicate that the mechanistic transformation of a radical copolymerization of MMA was achieved by addition of the appropriate ligand in the $FeCl_3$-based system.

Conclusion

In conclusion, both the living cationic and radical polymerizations were achieved using higher-oxidation-state $FeCl_3$ as the catalyst under appropriate reaction conditions. As a result, the in-situ mechanistic transformation from the $FeCl_3$-mediated living cationic polymerization to the radical polymerization successfully occurred via the activation of the C–Cl terminal of polystyrene after the simple addition of the phosphine ligand and subsequent heating. This method could be further utilized for the one-pot synthesis of various block copolymers between cationically and radically polymerizable monomers.

[1] M. Miyamoto, M. Sawamoto, T. Higashimura, *Macromolecules* **1984**, *17*, 265.
[2] R. Faust, J. P. Kennedy, *Polym. Bull.* **1986**, *15*, 317.
[3] M. Sawamoto, *Prog. Polym. Sci.* **1991**, *16*, 111.
[4] J. E. Puskas, G. Kaszas, *Prog. Polym. Sci.* **2000**, *25*, 403.
[5] S. Aoshima, S. Kanaoka, *Chem. Rev.* **2009**, *109*, 5245.
[6] M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev.* **2001**, *101*, 3689.
[7] K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921.
[8] C. J. Hawker, A. W. Bosman, E. Harth, *Chem. Rev.* **2001**, *101*, 3661.
[9] G. Moad, E. Rizzardo, S. H. Thang, *Aust. J. Chem.* **2005**, *58*, 379.
[10] Y. Ishihama, M. Sawamoto, T. Higashimura, *Polym. Bull.* **1990**, *24*, 201.
[11] G. Kaszas, J. E. Puskas, C. C. Chen, J. P. Kennedy, *Polym. Bull.* **1988**, *20*, 413.
[12] M. Sawamoto, C. Okamoto, T. Higashimura, *Macromolecules* **1987**, *20*, 2693.
[13] A. Kanazawa, Y. Hirabaru, S. Kanaoka, S. Aoshima, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5795.
[14] M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **1995**, *28*, 1271.
[15] J.-S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **1995**, *117*, 5614.
[16] V. Percec, B. Barboiu, *Macromolecules* **1995**, *28*, 7970.

[17] D. M. Haddleton, C. B. Jasieczek, M. J. Hannon, A. J. Shooer, *Macromolecules* **1997**, *30*, 2190.

[18] T. Ando, M. Kamigaito, M. Sawamoto, *Macromolecules* **1997**, *30*, 4507.

[19] K. Matyjaszewski, M. Wei, J. Xia, N. E. McDermott, *Macromolecules* **1997**, *30*, 8161.

[20] Y. Yagci, M. A. Tasdelen, *Prog. Polym. Sci.* **2006**, *31*, 1133.

[21] N. Hadjichristidis, M. Pitsikalis, H. Iatrou, *Adv. Polym. Sci.* **2005**, *189*, 1.

[22] a) S. Coca, K. Matyjaszewski, *Macromolecules* **1997**, *30*, 2808; b) S. Coca, K. Matyjaszewski, *J. Polym Sci. Part A: Polym. Chem.* **1997**, *35*, 3595.

[23] X. Chen, B. Ivan, J. Kops, W. Batsberg, *Macromol. Rapid. Commun.* **1998**, *19*, 585.

[24] J. Lu, H. Liang, A. Li, Q. Cheng, *Eur. Polym. J.* **2004**, *40*, 397.

[25] a) L. Toman, M. Janata, J. Spevacek, P. Vlcek, P. Latalova, B. Masar, A. Sikora, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 6096; b) L. Toman, M. Janata, J. Spevacek, P. Vlcek, P. Latalova, A. Sikora, B. Masar, *J. Polym Sci. Part A: Polym. Chem.*, **2005**, *43*, 3823.

[26] K. Satoh, H. Aoshima, M. Kamigaito, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6358.

[27] C. R. Becer, R. Hoogenboom, D. Fournier, U. S. Schubert, *Macromol. Rapid. Commun.* **2007**, *28*, 1161.

[28] a) Z. Xue, N. T. B. Linh, S. K. Noh, W. S. Lyoo, *Angew. Chem., Int. Ed.* **2008**, *47*, 6426; b) Z. Xue, D. He, S. K. Noh, W. S. Lyoo, *Macromolecules.* **2009**, *42*, 2949.

[29] Y. Kwak, K. Matyjaszewski, *Polym. Int.* **2009**, *58*, 242.

[30] T. Ando, M. Kamigaito, M. Sawamoto, *Macromolecules* **2000**, *33*, 2819.