

Direct through Anionic, Cationic, and Radical Active Species: Terminal Carbon-Halogen Bond for "Controlled"/Living Polymerizations of Styrene

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ABSTRACT

In this work, we examined the synthesis of novel block (co)polymers by mechanistic transformation through anionic, cationic, and radical living polymerizations using terminal carbon-halogen bond as the dormant species. First, the direct halogenation of growing species in the living anionic polymerization of styrene was examined with CCl_4 to form a carbon-halogen terminal, which can be employed as the dormant species for either living cationic or radical polymerization. The mechanistic transformation was then performed from living anionic polymerization into living cationic or radical polymerization using the obtained polymers as the macroinitiator with the $\text{SnCl}_4/n\text{Bu}_4\text{NCl}$ or $\text{RuCp}^*\text{Cl}(\text{PPh}_3)/\text{Et}_3\text{N}$ initiating system, respectively. Finally, the combination of all the polymerizations allowed the synthesis block copolymers including unprecedented gradient block copolymers composed of styrene and *p*-methylstyrene.

KEYWORDS: living anionic polymerization / living cationic polymerization / living radical polymerization / carbon-halogen bond / mechanistic transformation / styrene

INTRODUCTION

Living polymerization has been achieved using various active species since the first discovery in the anionic polymerization of hydrocarbon monomers, such as styrene and dienes, owing to their stable active species.¹ Unlike anionic polymerization, it had been difficult to accomplish living polymerization in cationic and radical polymerizations for several decades.

In the 1980's, living cationic polymerization of vinyl monomers was finally realized. Because halide anion is one of good leaving groups, the carbon-halogen bond is generally regarded as the synthon of carbocationic species in organic chemistry. Sawamoto, Higashimura, and their co-workers first introduced an equilibrium between the unstable active species and stable covalent bond at the growing terminal in the cationic polymerization of vinyl ether with the HI/I_2 system.² Thereafter, the covalent bond is so-called dormant species and can be used for

expanding the scope of living cationic polymerization, in which the dormant species is reversibly activated by a judiciously-chosen Lewis acid catalyst into the carbocationic species to suppress side reactions, like chain transfer reactions.³⁻⁶ For example, the initiating system consisting of SnCl_4 as the Lewis acid in conjunction with ammonium salt ($n\text{-Bu}_4\text{NCl}$) allowed the living cationic polymerization of various monomers, including styrene derivatives and alkyl vinyl ethers, when coupled with carbon-chlorine bond as the dormant species.⁷⁻¹⁰

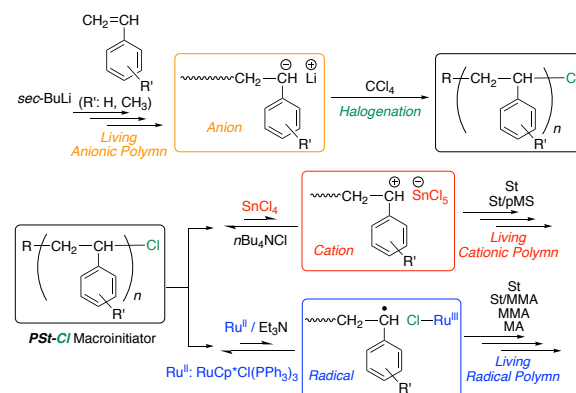
In addition, the carbon-halogen bond was also applied for controlling radical polymerization with transition metal-catalyzed redox activation first reported by Sawamoto and Matyjaszewski independently in the mid 1990s,^{11,12} which is based on the atom transfer radical addition in organic chemistry.¹³ In terms of versatility of applicable monomers, Sawamoto et al. found that $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$ ($\text{Cp}^* =$

pentamethylcyclopentadienyl) is one of the most promising catalysts for the living radical polymerization that is applicable to methyl methacrylate (MMA), methyl acrylate (MA), and styrene under the same condition in the combination with carbon–chlorine bond as the dormant species.¹⁴ Now, the concept for controlling the polymerizations by the dormant species has been established in various polymerizations systems especially for radical polymerization,^{15–20} which the IUPAC recently recommended to refer as reversible-deactivation polymerization.²¹

Meanwhile, the mechanistic transformation among the various growing active species during living polymerizations can overcome the limitation of polymerizable monomers to form block copolymers composed of different type of monomers.^{22–26} As mentioned above, the carbon–halogen bond can be applicable both for living cationic and radical polymerizations as the dormant species, in which only the nature of the catalysts was different. The direct mechanistic transformation was reported through carbon–halogen bond as the common dormant species from cationic polymerization into radical polymerizations, and vice versa.^{27–33} **More recently, similar transformations between cationic and radical species had also been reported using thiocarbonylthio-based RAFT terminal as the dormant species.**^{34–40} As for anionic polymerization, the introduction of carbon–halogen bond into the growing terminal would be useful for the such a transformation into cationic or radical species. Actually, it has also been attempted to transform the anionic polymerization of styrene into ring-opening cationic polymerization of THF through the stable carbon–halogen bond using molecular bromine since the 1970s by Burgess et al.^{41–43} The direct terminal halogenation during the anionic polymerization, however, rarely proceeded in quantitative yields, because the transformation was somehow suffered by Wurtz-type coupling reaction. Quite recently, we also reported the quantitative halogenation of the stereospecific living anionic polymerization of MMA using CX₄ (X = Cl or Br) as a halogen source to generate stereoregular PMMA with a terminal carbon–halogen bond.^{44,45} Therefore,

the mechanistic transformation was accomplished from the anionic polymerization into the subsequent transition metal-catalyzed living radical polymerization.

In this paper, the direct halogenation of living anionic polymerization of styrene was examined with CCl₄ to form a carbon–halogen terminal, which can subsequently be employed as the dormant species for either living cationic or radical polymerization to accomplish the direct mechanistic transformation on the same carbon atom (Scheme 1). Since styrene is a monomer that can be polymerized by any of the anionic, cationic, and radical species, the styrene polymerization through the career of various active species was also examined as well as the synthesis of novel gradient block copolymers.



SCHEME 1 Terminal Halogenation during Living Anionic Polymerization of Styrene for Mechanistic Transformation into Living Cationic and Radical Polymerizations

EXPERIMENTAL

Materials

Styrene (St; TCI, >99.0%), 1,1-diphenylethylene (DPE; TCI, >98.0%), 4-methylstyrene (pMS; TCI, >99.0%), methyl methacrylate (MMA; TCI, >99.8%), methyl acrylate (MA; TCI, >99.8%), CCl₄ (Kanto, >99.9%), and triethylamine (TEA; TCI, >99.0%) were distilled over calcium hydride before use. Toluene (Kanto, >99.5%; H₂O <10 ppm), tetrahydrofuran (THF; Kanto, >99.5%; H₂O <0.001%), and dichloromethane (KANTO, >99.5%; H₂O <0.005%) were dried and deoxygenized by passage through columns of

Glass Contour Solvent Systems before use. Tin tetrachloride (SnCl_4 ; Aldrich, >99.995%) and *sec*-butyllithium (*sec*-BuLi; Kanto, 1.08 mol/L in cyclohexane) was used as received. $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$ (provided from Wako) and tetrabutylammonium chloride (TCI, >98.0%) was used as received and handled in a glove box (MBRAUN LABMASTER SP) under a moisture and oxygen-free argon atmosphere (O_2 , <1 ppm).

Anionic Polymerization of Styrene and Subsequent Halogenation

The reactions were carried out by syringe techniques under dry argon atmosphere in baked glassware equipped with a three-way stopcock. A typical example for living anionic polymerization of styrene and subsequent halogenation is given below. In a 200 mL round-bottomed flask, the anionic polymerization was initiated by adding styrene (4.89 mL, 42.5 mmol) slowly via dry syringe into a prechilled initiator solution (45 mL) containing *sec*-BuLi (1.7 mmol) in methylcyclohexane (43 mL) and THF (0.7 mL) at -10°C . After stirring for 0.5 h, the solution was cooled to -78°C and diluted with THF (50 mL), which was in advance treated with a small amount of diphenylhexyllithium. And then, CCl_4 (68 mmol, 6.75 mL) was added dropwise to the reaction mixture. After 1 h, into the reaction mixture was then added 1 mL of degassed methanol to quench the reaction. The quenched solution was diluted with 100 mL of methylcyclohexane and washed with dilute hydrochloric acid and water, evaporated to dryness under reduced pressure. The obtained polymer was further purified by precipitation into methanol at -10°C twice and dried to afford the product polymers (PSt-Cl: $M_n = 2600$, $M_w/M_n = 1.07$, 4.13 g, 93%).

Transformation into Cationic Polymerization from PSt-Cl macroinitiator

The transformation into cationic polymerization was also carried out by syringe techniques under dry argon in baked glassware equipped with three-way stopcock. A typical example for cationic polymerization is given below. In a 100

mL round-bottomed flask were placed anionically-prepared polystyrene with chlorine terminal as the macroinitiator ($M_n = 2600$, $M_w/M_n = 1.07$, $F_n = 0.98$, 1.59 g, 0.60 mmol), styrene (3.45 mL, 30.0 mmol), *o*-dichlorobenzene (1.70 mL) as the internal standard, and CH_2Cl_2 (17.3 mL). Into the solution, the CH_2Cl_2 solution (6 mL) containing SnCl_4 (3.0 mmol) and *n*-Bu₄NCl (1.20 mmol) was added under stirring at -15°C to initiate the polymerization. In predetermined intervals, the polymerization was terminated by quenching the reaction by methanol. The monomer conversion was determined from the concentration of the residual monomer measured by ^1H NMR with *o*-dichlorobenzene as the internal standard (for 45 min, 55% conversion). The quenched solution was diluted with 100 mL of toluene and washed with dilute hydrochloric acid and water three times, evaporated to dryness under reduced pressure, and further purified by precipitation from THF solution into methanol at -10°C twice and dried to afford the product polymers (PSt-Cl: $M_n = 5000$, $M_w/M_n = 1.09$, 2.78 g, 84%).

Transformation into Radical Copolymerization from PSt-Cl macroinitiator

The block copolymerization by transformation into radical polymerization was also carried out by syringe techniques under dry argon. A typical example for transformation to the radical copolymerization of styrene and MMA is given below. In a 50 mL round-bottomed flask was placed the anionically-prepared PSt-Cl ($M_n = 2600$, $M_w/M_n = 1.07$, $F_n = 0.98$, 0.34 g, 0.13 mmol), $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$ (20.4 mg, 0.026 mmol), triethylamine (0.024 mL, 0.26 mmol), toluene (4.17 mL), tetralin (0.44 mL), styrene (0.74 mL, 6.5 mmol), and MMA (0.69 mL, 6.5 mmol) at room temperature. Immediately after mixing, seven aliquots (1.0 mL each) of the solutions were injected into backed glass tubes. The reaction vials were sealed and placed in an oil bath kept at 80°C . In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to -78°C . The monomer conversions were determined by ^1H NMR with tetralin as an internal standard. The quenched solution was diluted with 100 mL of toluene and washed with dilute hydrochloric acid and water

three times, and evaporated to dryness to give the product (PSt-Cl: $M_n = 5000$, $M_w/M_n = 1.09$, 2.78 g, 84%).

Measurements

Monomer conversions were determined from the concentration of residual monomer by the ^1H NMR spectroscopy. The ^1H NMR spectra were recorded on a JEOL ECS-400 spectrometer, operating at 400 MHz in CDCl_3 . The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of the product were measured by size-exclusion chromatography (SEC) operated at 40 °C in THF as the eluent (flow rate 1.0 ml/min) on two polystyrene gel columns [TSKgel MultiporeH_{XL}-M (7.8 mm i.d. x 30 cm)] connected to a JASCO PU-2080 precision pump and JASCO RI-2031 detector. The columns were calibrated against 10 standard polystyrene samples (Varian; $M_p = 575\text{--}2783000$, $M_w/M_n = 1.02\text{--}1.23$).

RESULTS AND DISCUSSION

Terminal Halogenation during Living Anionic Polymerization of Styrene

First, the halogenation was investigated for the growing terminal in the living anionic polymerization of styrene, which was initiated with *sec*-butyllithium (*sec*-BuLi) as the initiator in methylcyclohexane as a hydrocarbon solvent in the presence of a small amount of THF as the accelerator at -10 °C. After quantitative consumption of the styrene monomer, the reaction was terminated by adding CCl_4 as the halogenating agent. Whereas a unimodal SEC chromatogram with narrow molecular weight distributions (MWDs) was obtained by quenching with methanol (Figure 1A), the SEC curves became bimodal upon the CCl_4 addition due to the coupling reaction as reported in the literatures (Figure 1B).⁴¹ In general, the carbanionic species of hydrocarbon monomer, such as styrene, is so highly reactive that Wurtz-type coupling reaction occurs by $\text{S}_\text{N}2$ between the newly-formed halogenated terminal and another growing active chain end.⁴⁶ To avoid the bimolecular coupling reaction, the following

strategies were attempted; (1) after the polymerization of styrene was completed, the reaction solution was diluted with THF and then CCl_4 was added at -78 °C, and (2) before the addition of CCl_4 , non-homopolymerizable 1,1-diphenylethylene (DPE) was added in order to convert the growing end to a bulkier carboanionic species with a single monomer insertion.⁴⁷ Note that THF solvent for the dilution was treated with a small amount of diphenylhexyllithium (DPHLi), which is the adduct of *sec*-BuLi and DPE, to avoid the deactivation of the growing terminal by adventitious impurities like water and oxygen during the diluting process. Both of the methods worked well to result in unimodal SEC curves with narrow MWDs (Figure 1C and D), and the number-average molecular weight (M_n) of the obtained polymer well agreed with the calculated value assuming that all polymer chains were generated from the *sec*-BuLi initiator.

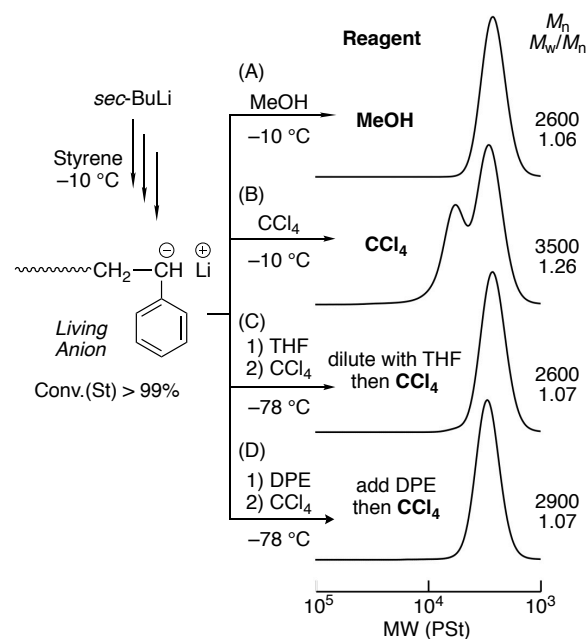


FIGURE 1 SEC curves of polystyrene obtained by quenching the anionic polymerization with MeOH (A), with CCl_4 (B), with CCl_4 after dilution with THF (C), and with CCl_4 after DPE-capping (D): $[\text{styrene}]_0/[\text{sec-BuLi}]_0 = 850/34$ mM in methylcyclohexane including THF (170 mM) at -10 °C, and $[\text{sec-BuLi}]_0/[\text{DPE}]_{\text{add}}/[\text{CCl}_4]_{\text{add}} = 1/5/40$.

The terminal structure of the obtained polystyrenes was then analyzed by ^1H NMR

spectroscopy. Figure 2 shows the ^1H NMR spectra of the product polymers with hydrogen terminal obtained by quenching with methanol (A) and those with chlorine terminal by using CCl_4 after dilution with THF (B) or addition of DPE (C). The polymers gave characteristic signals of repeating units, i.e., aromatic (c), methylene (a), and methine (b) protons, along with the initiating methyl groups (d and e) derived from *sec*-BuLi at 0.8 ppm. In addition to these peaks, the polymers obtained using CCl_4 showed new absorptions at 4.4 (for B) and 2.6 ppm (for C), which could be ascribed to the methine proton ($-\text{CH}-\text{Cl}$) adjacent to a chlorine atom at styrene terminal and the methylene protons ($-\text{CH}_2-\text{CPh}_2-\text{Cl}$) of a chlorine-terminated DPE unit, respectively. In both cases, the functionality of the chlorine group could be estimated to almost unity (*f*: 0.98 and *g*: 0.95, respectively) by comparing their peak intensity with the initiating methyl groups (d and e), which suggests that the growing terminal in living anionic polymerization was quantitatively capped with chlorine atom.

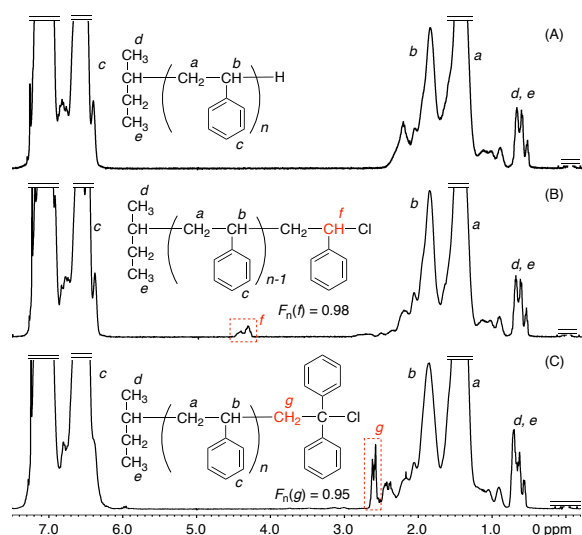


FIGURE 2 ^1H NMR spectra (400 MHz, CDCl_3 , 55 $^\circ\text{C}$) of polystyrene obtained by quenching the anionic polymerization with MeOH (A), with CCl_4 after dilution with THF (B), and with CCl_4 after DPE-capping (C): $[\text{sec-BuLi}]_0/[\text{DPE}]_{\text{add}}/[\text{CCl}_4]_{\text{add}} = 1/5/40$.

Direct Mechanistic Transformation into "Controlled"/Living Cationic and Radical Polymerizations

The terminal-halogenated polystyrenes (PSt-Cl) thus obtained by the halogenation of living anionic polymerization possess exactly the same structure as those prepared by living cationic or metal-catalyzed radical polymerizations, in which the terminal C-Cl bond was employed as the dormant species. Therefore, the direct mechanistic transformation of the terminal into cationic and radical polymerizations was then examined employing the obtained PSt-Cl as the macroinitiator, of which the terminal carbon atom was originally the growing anionic species, after purification by reprecipitation.

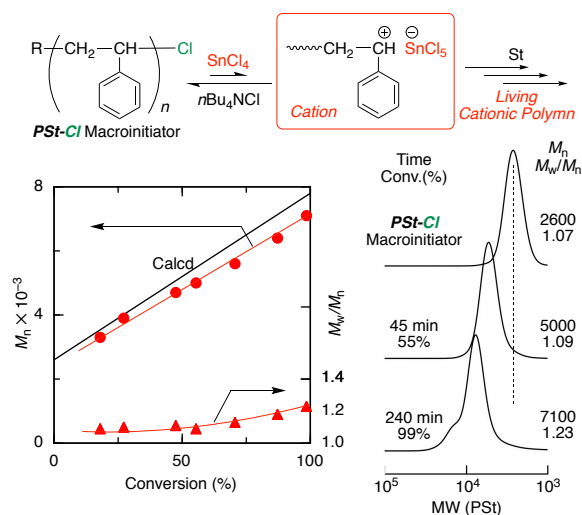


FIGURE 3 Living cationic polymerization of styrene using chlorine-terminated polystyrene (PSt-Cl) prepared by anionic polymerization as the macroinitiator with $\text{SnCl}_4/n\text{-Bu}_4\text{NCl}$ in CH_2Cl_2 at $-15\text{ }^\circ\text{C}$: $[\text{styrene}]_0 = 1.0\text{ M}$, $[\text{PSt-Cl}]_0 = 20\text{ mM}$, $[\text{SnCl}_4]_0 = 100\text{ mM}$, $[n\text{-Bu}_4\text{NCl}]_0 = 40\text{ mM}$.

The transformation from PSt-Cl macroinitiator into cationic polymerization was investigated by using a Lewis acid catalyst. The cationic polymerization of styrene was carried out in CH_2Cl_2 at $-15\text{ }^\circ\text{C}$ by the conventional initiating system for living cationic polymerization of styrene, in which the dormant C-Cl bond was reversibly activated by SnCl_4 in the presence of $n\text{-Bu}_4\text{NCl}$ (Figure 3).^{7,8} The M_n of the obtained polymer further increased along with the monomer conversion agreeing with the calculated value. The SEC curve shifted to the higher molecular weight region while maintaining relatively narrow MWDs, although a small shoulder peak was observed in the high molecular weight region at the latter stage of

polymerization most probably due to intermolecular Friedel-Crafts reaction as seen in the literature.⁷ The polymer obtained after the cationic polymerization was further analyzed by ¹H NMR spectroscopy to show exactly the same terminal structure as in the macroinitiator with increasing the degree of polymerization of styrene (Figure S1). Thus, the anionic polymerization could directly be converted into living cationic polymerization via terminal C–Cl bond.

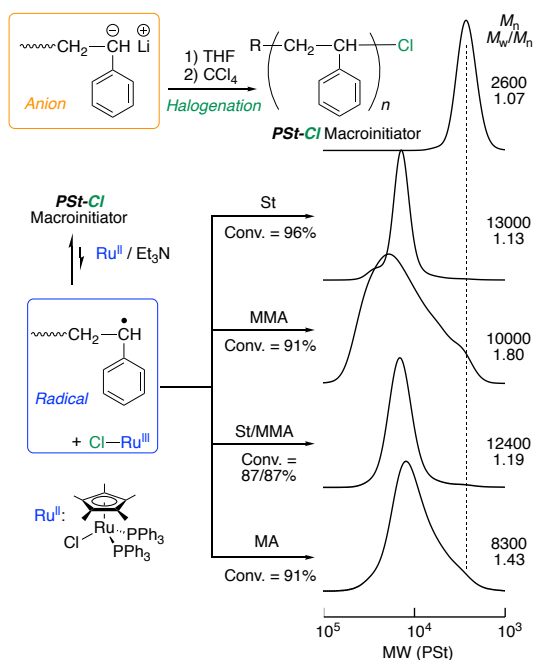


FIGURE 4 Living radical polymerizations using chlorine-terminated polystyrene (PSt-Cl) prepared by anionic polymerization as the macroinitiator with $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_3/\text{Et}_3\text{N}$ in toluene at 80 °C: $[\text{monomer}]_0 = 2.0$ M, $[\text{PSt-Cl}]_0 = 20$ mM, $[\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2]_0 = 4.0$ mM, $[\text{Et}_3\text{N}]_0 = 40$ mM.

Similarly, the PSt-Cl obtained by anionic polymerization was also employed as the macroinitiator for the Ru-catalyzed living radical polymerization of various monomers, including styrene, MMA, MA, and the 1:1 mixture of St and MMA. These monomers were polymerized in conjunction with PSt-Cl in toluene at 80 °C by $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$ as the catalyst in the presence of triethylamine as the co-activator (Figures 4 and S2–S5).¹⁴ The monomers were consumed quantitatively in all cases to generate the block copolymers. In the chromatogram of the MMA polymerization, the

original peak of PSt-Cl was clearly left in the original position during the reaction and the MWDs became broader as the polymerization proceeded (Figure S4). This indicates the slower initiation of MMA from the PSt-Cl terminal because the newly-formed chlorine-capped MMA terminal has higher reactivity. Meanwhile, in the case of styrene and the mixture with MMA, the SEC curves shifted to the high molecular weight region maintaining narrow MWDs and the original peak of macroinitiator almost disappeared.

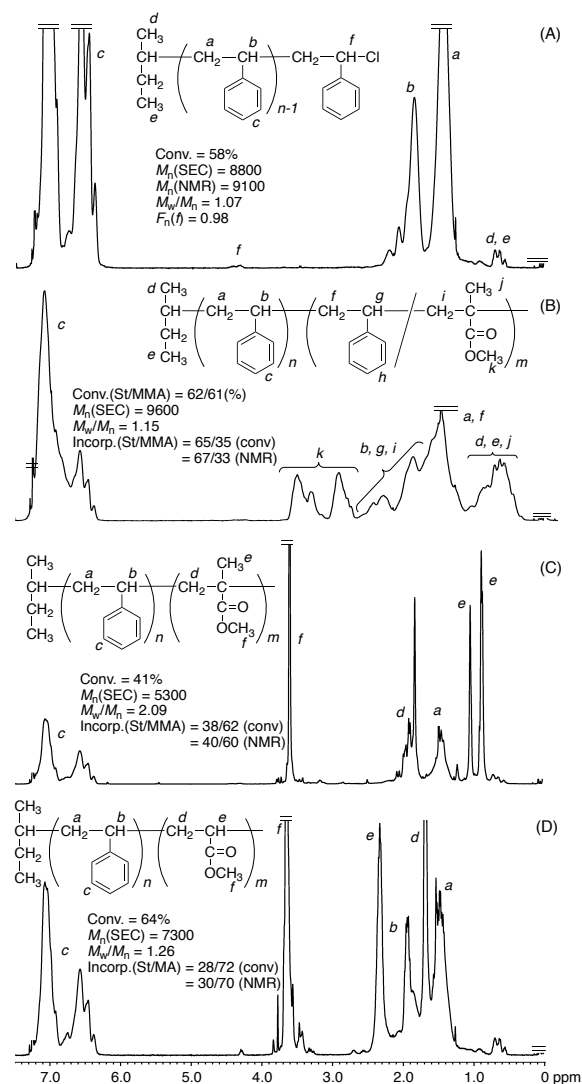


FIGURE 5 ¹H NMR spectra (400 MHz, CDCl_3 , 55 °C) of polymers obtained by the mechanistic transformation from anionic to radical (co)polymerizations with $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$ in the same experiments as for Figure 4.

The formation of the block copolymers was further confirmed by analyzing the structure using ^1H NMR (Figure 5). The polystyrene obtained after the extension reaction by radical polymerization showed again the terminal-chlorinated structure as in the case by living cationic polymerization with increasing the styrene unit from the macroinitiator (A). In the spectra of the other copolymers, there were characteristic signals of each monomer unit, of which the peak intensity ratios of agreed well with the calculated values from the monomer feed ratios and the conversions of each monomer (B–D). Thus, the mechanistic transformation from anionic polymerization into radical polymerization was also demonstrated via the C–Cl bonds.

TABLE 1 Mechanistic Transformation from Anionic to Radical Copolymerization for Synthesis of St-*b*-(St-*r*-MMA) Block Copolymers via C–Cl bond

entry	PSt–Cl ^a		PSt- <i>b</i> -P(St- <i>r</i> -MMA) ^b	
	M_n	M_w/M_n	M_n	M_w/M_n
1	2,500	1.07	12,400	1.19
2	9,800	1.04	19,700	1.14
3	22,800	1.06	38,900	1.15
4	32,600	1.07	53,700	1.15

^aBy anionic polymerization of styrene: $[\text{styrene}]_0/[\text{sec-BuLi}]_0 = 1000/40, 10, 5.0, \text{ or } 3.3$ in methylcyclohexane/THF = 1/1 at -78°C , and $[\text{CCl}_4]_{\text{add}} = 40$ equiv to sec-BuLi . ^bBy radical copolymerization of styrene and MMA from PSt–Cl: $[\text{styrene}]_0/[\text{MMA}]_0/[\text{PSt–Cl}]_0/[\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2]_0/[\text{Et}_3\text{N}]_0 = 1000/1000/20, 10, \text{ or } 6.7/4.0/40$ mM in toluene at 80°C ; and the styrene/MMA conversions (%) were 87/87 (for entry 1), 95/94 (for 2), 74/74 (for 3), and 70/69 (for 4), respectively.

We further examined the transformation using higher molecular weight polystyrenes into radical polymerization. A series of PSt–Cl with the M_n of ca. 10K, 20K, and 30K was also synthesized by anionic polymerization followed by halogenation with CCl_4 according to the aforementioned procedure by changing the initial feed ratio of sec-BuLi and styrene monomer (Table 1). Although the functionality of terminal chloride was not exactly estimated because the terminal peaks in the ^1H NMR spectra became too small, these polymers were also amenable to the Ru-catalyzed radical

copolymerization of styrene and MMA as the macroinitiators. Even from the higher molecular weight PSt–Cl, the radical copolymerization of styrene/MMA proceeded well to afford the St-*b*-(St-*r*-MMA) block copolymer, of which the SEC curves shifted clearly and quantitatively retaining narrow MWDs (see also Figure S6).

Synthesis of Unprecedented Gradient Block Copolymers Through Anionic, Cationic, and Radical Polymerizations

On the success of transformation from anionic polymerization into cationic or radical polymerization, we further investigated the combination of all of the polymerizations (Figure 6). First, PSt–Cl was synthesized by living anionic polymerization of styrene from sec-BuLi followed by halogenation as described above (A). After purification, the polymer was further employed as the macroinitiator for living cationic polymerization of styrene with the $\text{SnCl}_4/n\text{-BuN}_4\text{Cl}$ initiating system to form the second block of polystyrene (B). And finally, the obtained PSt–PSt–Cl was used for the living radical polymerization of styrene using the ruthenium complex to result in the final PSt–PSt–PSt–Cl (C). Throughout the mechanistic transformations, the M_n of the produced polymer proportionally increased in agreement with the calculated value assuming that one molecule of the original sec-BuLi generates one PSt chain, and the SEC curves also shifted to the high molecular weight region maintaining narrow MWDs. Although the obtained polymer is just a polystyrene, it was generated in a controlled and living fashion through the career of various active species, i.e., anionic, cationic, and radical growing species, via terminal carbon-halogen bond.

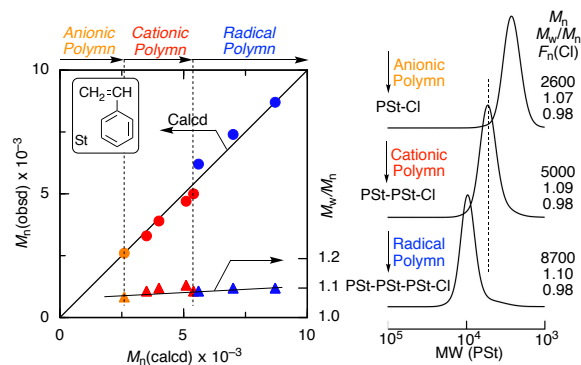


FIGURE 6 Polymerizations of styrene by mechanistic transformation direct through anionic, cationic, and radical active species. The conditions are same as in Figure 1 (for anionic), Figure 3 (for cationic), and Figure 4 (for radical polymerization), respectively. The diagonal indicates the calculated values assuming that one *sec*-BuLi molecule generates one polymer chain.

Subsequently, we investigated the copolymerization of styrene and *p*-methylstyrene (pMS) through a series of active species (Figure 7). pMS exhibited different reactivity from styrene in ionic polymerizations due to the electron-donating substituent on the aromatic ring. The monomer reactivity ratio of styrene (M_1) and pMS (M_2) for each copolymerization had been reported as follows: $r_1 = 2.5$ and $r_2 = 0.26$ for anionic, $r_1 = 0.54$ and $r_2 = 3.6$ for cationic, and $r_1 = 0.83$ and $r_2 = 0.96$ for radical copolymerization.^{48–50} First, in the anionic copolymerization of the 1:1 mixture of styrene and pMS, styrene was consumed faster than pMS to afford living copolymers with a controlled M_n and narrow MWDs ($M_w/M_n = 1.09$). This indicates a gradient copolymer of P(St-*grad*-pMS)-Cl was produced, in which the content of pMS units gradually increased along with the living polymer chain. On the other hand, the subsequent cationic copolymerization from the macroinitiator by $\text{SnCl}_4/n\text{-Bu}_4\text{NCl}$ produced a gradient segment with the opposite distribution, in which pMS reacted faster than styrene (pMS-*grad*-St). As in the case of the homopolymerization of styrene, the M_n further increased after the living cationic copolymerization. And finally, in the radical copolymerization, the consumption rates of both monomers are almost the same, indicating the formation of random copolymer segments (St-*r*-pMS). Throughout these transformations, the

polymerizations proceeded in controlled manners to give living copolymers with narrow MWDs (Figure S7).

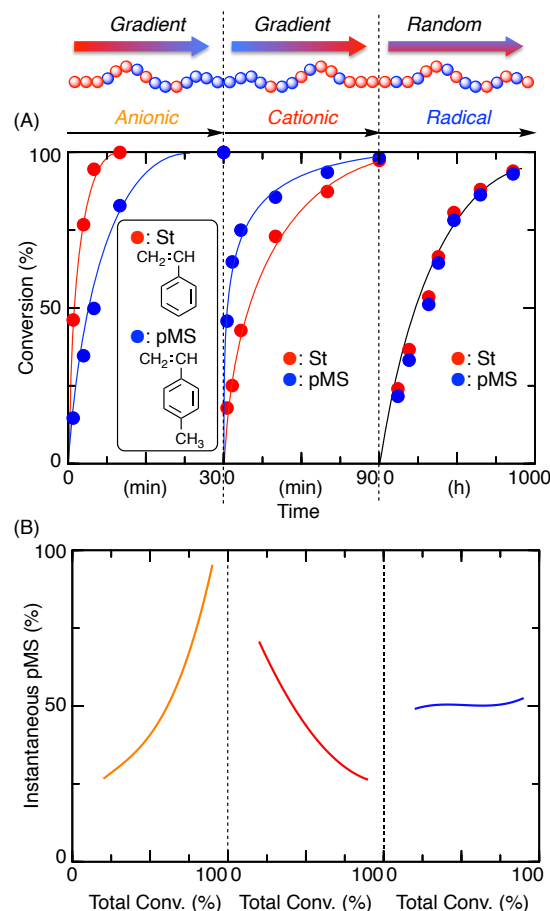


FIGURE 7 Time-conversion (A) and instantaneous incorporation of pMS unit (B) in the synthesis of gradient block copolymer of styrene and pMS via mechanistic transformation through anionic, cationic, and radical active species under the same conditions as in Figure 6 using the 1:1 mixture of styrene and pMS in place of styrene.

Figure 7B shows the instantaneous composition of pMS as the function of total conversions for each polymerization, which was calculated by using the consumption of two monomers. The composition by the monomer consumption agreed well with the incorporation into the produced copolymer by ^1H NMR analysis (Figure S8). It was confirmed that the instantaneous introduction of pMS gradually increased in anionic copolymerization, while it gradually decreased in cationic

copolymerization and almost constant at ca. 50% during radical copolymerization. Thus, through the transformations of active species, the unprecedented gradient block copolymer composed of (St-*grad*-pMS)-*b*-(pMS-*grad*-St)-*b*-(pMS-*r*-St) was synthesized, which could not be obtained by conventional synthetic methods. The thermal property of the obtained gradient copolymers was almost same as that of the random copolymer, because the segments were miscible and the glass transition temperatures of the corresponding homopolymers were not so different. However, since the pMS unit can be further converted into functional moiety using the reaction at the benzyl position, such as bromination and chlorination, this procedure may be applicable for creating novel functional materials.

CONCLUSIONS

It was demonstrated that the quantitative end chlorination in living anionic polymerization of styrene and its derivatives could be achieved, which allowed the subsequent mechanistic transformation into living cationic and radical polymerizations through the dormant C–Cl bond. The system could expand the scope of the applicable monomers for the synthesis of block copolymers, which were composed of various segments prepared via anionic, cationic, and radical polymerizations, including unprecedented gradient block copolymers.

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GRAPHICAL ABSTRACT

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Direct through Anionic, Cationic, and Radical Active Species: Terminal Carbon-Halogen Bond for "Controlled"/Living Polymerizations of Styrene

The direct mechanistic transformation during "controlled"/living polymerizations of styrene derivatives was accomplished through anionic, cationic, and radical growing active species via terminal carbon-halogen bond. The terminal chlorination in the anionic polymerization proceeded quantitatively under an appropriate condition, which consequently produced a macroinitiator for living cationic and radical polymerizations. The transformation allowed the synthesis of novel block copolymers including gradient block copolymers composed of styrene and *p*-methylstyrene.

GRAPHICAL ABSTRACT FIGURE

