

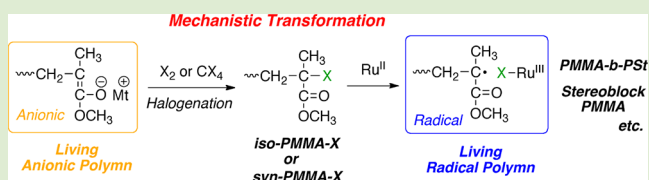
Direct Mechanistic Transformations from Isotactic or Syndiotactic Living Anionic Polymerizations of Methyl Methacrylate into Metal-Catalyzed Living Radical Polymerizations

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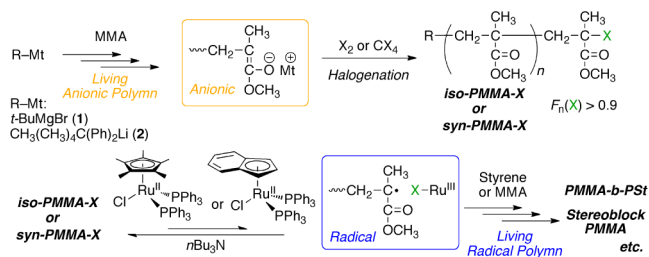
Supporting Information

ABSTRACT: The mechanistic transformations from living anionic polymerizations into living radical polymerizations were examined after halogenating the growing terminal during the stereospecific living anionic polymerization of methyl methacrylate (MMA), directly forming a macroinitiator with a covalent carbon–halogen terminal for subsequent transition metal-catalyzed living radical polymerizations. The quantitative halogenation of the living isotactic or syndiotactic PMMA anion, prepared using *t*BuMgBr in toluene or diphenylhexyllithium (DPHLi) in THF, respectively, was achieved using CCl₃Br or CCl₄ as a halogen source in the presence of strong Lewis bases, such as 1,8-diazabicyclo[5.4.0]undec-7-ene, to generate stereoregular PMMA with a C–X (X = Br or Cl) bond. The halogenated terminal was then transformed into the radical species through a one-electron redox reaction of the ruthenium catalysts to allow the living radical polymerization of styrene or MMA, resulting in block copolymers that consisted of stereoregular PMMA and polystyrene segments or stereoblock PMMAs.



A large number of controlled/living polymerizations currently exist,¹ some of which have versatile uses in

Scheme 1. Mechanistic Transformation from Living Anionic Polymerization into Metal-Catalyzed Living Radical Polymerization



various vinyl monomers as often observed in recently developed controlled/living radical polymerizations. Not many of these controlled/living polymerizations enable additional control, such as stereoregularity of the polymers or highly precise control of the molecular weights and chain end groups, as is sometimes observed in ionic and coordination polymerizations. A combination of the latter systems with the former general methods could broaden the scope of well-defined synthetic polymers that possess not only additional specificity but also versatility (e.g., a variety of block copolymers that retain stereoregular structures).

Since the discovery of the living anionic polymerization of styrene in 1956, various vinyl monomers, including nonpolar conjugated monomers and polar monomers such as methacrylic

monomers, have been successfully polymerized in a controlled fashion using various designed anionic initiating systems.² Among these systems, the stereospecific living anionic polymerization of methyl methacrylate (MMA) has been achieved using *t*BuMgBr in toluene or diphenylhexyllithium (DPHLi) in THF to generate highly isotactic or syndiotactic polymers, respectively, with controlled molecular weights.^{3,4} Both of these polymerizations proceed via the enolate-growing species associated with the specific metal counterions. In addition to their highly controlled structures, these polymers exhibit interesting properties, including glass transition temperatures that vary from 50 to 130 °C depending on the polymers' tacticities⁵ and the formation of stereocomplexes between the *iso*- and syndiotactic polymers with melting points over 150 °C.⁶

Over the last two decades, tremendous progress has been attained in controlled/living radical polymerizations, enabling the control of molecular weights and the synthesis of a wide variety of well-defined polymers such as block, graft, and star polymers from a number of vinyl monomers.⁷ Among this variety of methods, metal-catalyzed living radical polymerization, or atom transfer living radical polymerization (ATRP), is one of the most widely employed strategies. This technique is based on the reversible activation of a dormant carbon–halogen bond, which can be easily introduced into low and high molecular weight initiators, via a one-electron redox reaction of

Received: November 6, 2012

Accepted: December 26, 2012

Published: December 31, 2012

Table 1. Halogenation of Living Anionic PMMA Terminal^a

entry	initiator/solvent	halogenating agent	additive	M_n^b	M_w/M_n^b	$F_n(C-X)^c$
1		none		2400	1.14	—
2		Br ₂		2300	1.23	0.46
3		CBr ₄	none	2500	1.16	0.89
4		CCl ₃ Br		2500	1.17	0.90
5		CCl ₄		2500	1.16	0.39
6		CBr ₄		2500	1.18	1.00
7	<i>t</i> BuMgBr/toluene ^d	CCl ₃ Br	DBU	2400	1.19	1.04
8		CCl ₄		2800	1.19	0.90
9		CCl ₃ Br		2400	1.16	1.02
10		CCl ₄	TMG	2600	1.19	0.95
11		CCl ₃ Br	Et ₃ N	2500	1.18	0.90
12				TMEDA	2500	1.24
13			PMDETA	2400	1.17	0.96
14			HMTETA	2600	1.19	0.86
15		none		2800	1.14	—
16	DPHLi/THF ^e	CCl ₃ Br	none	2900	1.14	0.95
17		CCl ₄		2900	1.18	0.96
18		CCl ₃ Br		2700	1.12	0.94
19		CCl ₄	DBU	3200	1.18	0.95

^a $[M]_0/[I]_0 = 25$, $[I]_0/[\text{halogenating agent}]_{\text{add}}/[\text{additive}]_{\text{add}} = 1/40/5$. ^bDetermined by SEC using PMMA standards in THF. ^cObtained from $M_n(\text{SEC})/M_n(\text{NMR})$. ^d $[\text{MMA}]_0 = 1.35$ M, polymerization: 25 h (-78 °C), halogenation: 2 h (-78 °C) and then 23 h (-78 to 0 °C). ^e $[\text{MMA}]_0 = 0.85$ M, polymerization: 0.25 h (-78 °C), halogenation: 2 h (-78 °C), and then 23 h (-78 to 0 °C).

the transition metal catalysts into the growing radical species.^{7a,b} However, the initiating system cannot principally control the stereochemistry of the resulting polymers due to the absence of the substantial interactions between the halogen or metal catalyst and the growing radical species, similar to all of the other controlled/living radical polymerizations that proceed via the reversible activation of the dormant species. Although stereochemical control has become possible even in radical polymerization⁸ by using bulky monomers, polar solvents, or Lewis acid additives, the regularity is moderate and lower than those attained in stereospecific anionic polymerization reactions.

A direct mechanistic transformation of the propagating species between different living polymerizations can expand the scope of polymerizable monomers per chain and now represents one of the most efficient methods of synthesizing well-defined block copolymers that consist of different monomer types.⁹ In addition, recent advances in direct mechanistic transformation have been achieved through the use of common dormant species, which can generate different propagating species depending on the stimulus, such as covalent carbon–halogen and related bonds via heterolytic and homolytic cleavage by Lewis acids and transition metal catalysts for living cationic and radical polymerizations, respectively.¹⁰

Because anionic living polymerizations can allow for highly well-controlled polymers when compared to the radical processes mentioned above, a mechanistic transformation that switches from anionic to radical polymerization should provide a highly efficient strategy for novel block copolymer syntheses. However, a direct mechanistic transformation from a carbanion into a carbon radical species has been limited¹¹ in comparison to many reports regarding an indirect method^{9,12} (i.e., the initiating moiety for living radical polymerization is introduced at the functionalized chain end obtained after the modification of the anionic polymerization terminal).

Halogenation of a carbanion can be achieved and is widely employed in organic synthesis.¹³ Thus, this study aims for the straightforward halogenation of the living anionic species, especially the enolate chain end in the stereospecific living anionic polymerization of MMA, into the carbon–halogen terminal for successive transition-metal-catalyzed living radical polymerization via a mechanistic transformation. This communication reports the quantitative halogenation of the growing terminal in the isotactic and syndiotactic living anionic polymerizations of MMA to produce halogen-capped polymers. Furthermore, the subsequent ruthenium-catalyzed living radical polymerizations of styrene or MMA blocking from the halogen-capped stereoregular PMMA to generate novel block copolymers (Scheme 1) are reported and quantitated here.

We investigated the halogenation of a growing enolate species by quenching the stereospecific anionic living polymerization of MMA using several halogenating agents in the presence and absence of Lewis base additives. The stereospecific living anionic polymerization of MMA was first performed using previously reported systems, i.e., *t*BuMgBr in toluene or diphenylhexyllithium (DPHLi) in THF at -78 °C. In both cases, the polymers obtained after quenching with methanol as control experiments possessed controlled molecular weights, agreeing well with the calculated values, assuming that one molecule of the organometallic compound generates one living polymer chain, and narrow molecular weight distributions (MWDs) ($M_w/M_n \sim 1.1$) (entries 1 and 15 in Table 1). In addition to the livingness, the Mg/toluene-based system produced highly isotactic PMMA ($mm/mr/rr = 91/8/1$), while the Li/THF-based system produced syndiotactic PMMA ($mm/mr/rr = 1/25/74$), as reported in the literature.^{3,4}

We then examined a reaction to end-cap the living PMMA anions using an excess amount of Br₂, CBr₄, and CCl₃Br for bromination and CCl₄ for chlorination as the halonium cation source (40 equiv to the anionic initiator). These reactions result in forming carbon–halogen bonds at the terminal along with the formation of a metal halide or metal trihalomethide and

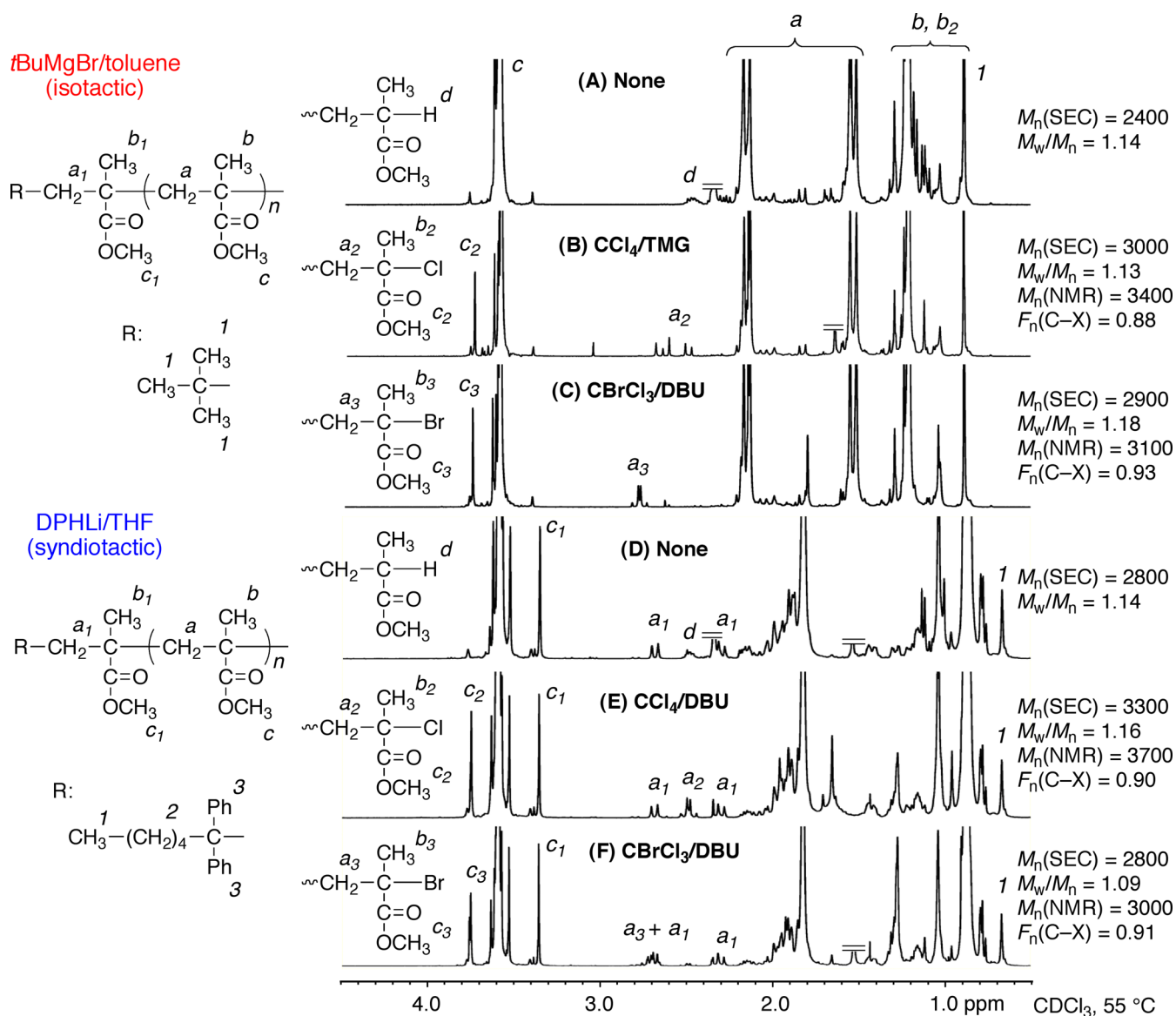


Figure 1. ^1H NMR spectra of PMMA-X (X = H, Cl, and Br) obtained with *t*BuMgBr in toluene (A–C) or diphenylhexyllithium in THF (D–F) at $-78\text{ }^\circ\text{C}$ using methanol (A and D), CCl_4 (B and E), or CCl_3Br (C and F) as the quenching agent in the presence of DBU or TMG (for halogenation).

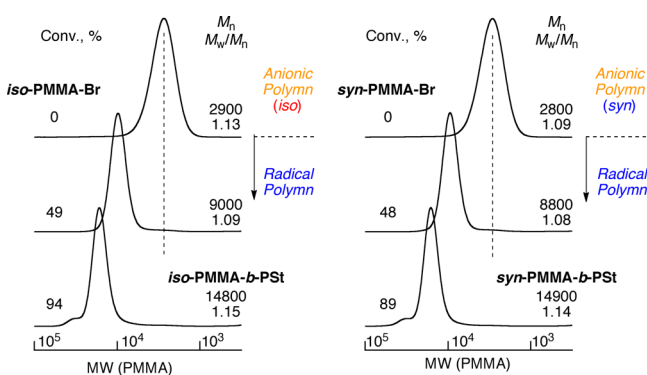


Figure 2. SEC curves of isotactic or syndiotactic PMMA-Br and PMMA-*b*-PSt obtained via the transformation from stereospecific living anionic polymerization of MMA to metal-catalyzed living radical polymerization of styrene: $[\text{styrene}]_0 = 4.0\text{ M}$, $[\text{PMMA-Br}]_0 = 40\text{ mM}$, $[\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2]_0 = 4.0\text{ mM}$, $[\text{nBu}_3\text{N}]_0 = 40\text{ mM}$ in toluene at $80\text{ }^\circ\text{C}$.

further possible decomposition into a carbene species in the case of polyhalogenated compounds. When the anionic polymerization was nearly completed, these halogenating agents were added directly to the polymerization mixture, which was maintained at $-78\text{ }^\circ\text{C}$ for 2 h and then gradually warmed to $0\text{ }^\circ\text{C}$ for an additional 23 h to complete the end-capping reaction. In addition, the halogenation was also investigated in the presence of a series of Lewis bases, including 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,1,3,3-tetramethylguanidine (TMG), Et_3N , N,N,N',N' -tetramethylethylenediamine (TMEDA), N,N,N',N',N'' -pentamethyldiethylenetriamine (PMDETA), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), which are used for similar end-functionalization reactions of the PMMA anion.¹⁴ As shown in Table 1, the obtained polymers exhibited narrow MWDs and controlled M_n values that agreed well with the calculated values regardless of the initiating systems, the halogenating agents, and the additives.

Figure 1 presents the ^1H NMR spectra of the isotactic (A–C) and syndiotactic PMMAs (D–F) with hydrogen terminals obtained by quenching with methanol (A and D) and by using CCl_4 (B and E) or CCl_3Br (C and F) in the presence of DBU or TMG. The polymers gave signals characteristic of repeating PMMA units, i.e., methoxy (*c*), methylene (*a*), and α -methyl (*b*) protons, which exhibited typical spectral patterns depending on their tacticities. The polymers obtained using *t*BuMgBr (A–C) exhibited primarily *mm* α -methyl (1.2 ppm) and double-doublet methylene (1.5 and 2.2 ppm) protons, while those obtained using DPHLi (D–F) exhibited primarily *rr* α -methyl (0.9 ppm) and singlet methylene (1.8 ppm) protons.

In addition to these large peaks, small signals that were ascribed to the halide ω -end (C–X), such as $-\text{OCH}_3$ (*c*₂ or *c*₃, 3.8 ppm) and $-\text{CH}_2-$ (*a*₂ or *a*₃, 2.5–2.8 ppm) groups adjacent to chlorine (B and E) or bromine atoms (C and F), respectively, were observed. In contrast, the hydrogen terminal only exhibited the indicative C–H peak (*d*, 2.5 ppm) (A and D). The terminal halogen functionality [$F_n(\text{C}-\text{X})$] at the ω -end was thus determined by comparing the $M_n(\text{NMR})$ values obtained from the peak intensity ratios of *c*₂ or *c*₃ to *c* against the $M_n(\text{SEC})$ measured by SEC based on the PMMA calibration [$F_n(\text{C}-\text{X}) = M_n(\text{SEC})/M_n(\text{NMR})$].

The functionality depends on both the halogenating agents and the additives; Br_2 resulted in a lower functionality, as has been reported in nonstereospecific living anionic polymerizations of MMA,^{11a} while the polyhalogenated compounds totally provided higher functionalities. The functionality of the terminal carbon–halogen bond obtained with the DPHLi/THF system was almost one regardless of the polyhalogenated compounds (entries 16 and 17 in Table 1). The *t*BuMgBr/toluene system mostly resulted in lower functionalities (entries 2–5), especially for the least reactive halogenating agent, CCl_4 . The lower functionality produced using *t*BuMgBr/toluene was most probably due to aggregation of the growing anionic species in the less polar solvent toluene. However, the functionality was improved with the addition of Lewis bases to enable nearly quantitative conversions into the C–X bonds. The functionalities of bromide with CCl_3Br or CBr_4 in the presence of such additives were near unity (entries 6, 7, 9, 12, and 13), and that of the chloride with CCl_4 was much higher (entries 8 and 10) than that in the absence of the additives. These additives probably coordinated with the magnesium or lithium counteraction to result in both the disaggregation of the growing chain ends and the reactivity enhancement of the PMMA anion.

Isotactic or syndiotactic PMMA–Br, which were obtained after halogenation of the stereoregular living anionic PMMA with $\text{CCl}_3\text{Br}/\text{DBU}$, were then employed as the macroinitiators for the living radical polymerization of styrene catalyzed by $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$ with the *n*Bu₃N additive in toluene at 80 °C (Figure 2). In both cases, styrene was smoothly consumed to provide block copolymers consisting of isotactic or syndiotactic PMMA and polystyrene segments, and the SEC curves shifted to higher molecular weights while maintaining narrow MWDs. A small shoulder at high styrene conversions can be attributed to a small amount of coupling reaction between the propagating radical chain end of styrene. The monomer compositions of the obtained products were determined using ^1H NMR and were in good agreement with those calculated from the initial feed ratio of styrene to the macroinitiator and monomer conversions (Figure S1 in the Supporting Information). These results also indicated efficient

direct conversions of the growing living anionic species ($\sim\sim\sim\text{C}^-$) into covalent carbon–bromine bonds ($\sim\sim\sim\text{C}-\text{Br}$) that can be activated into the growing radical species using the transition metal complex in the subsequent metal-catalyzed living radical polymerizations.

A similar block ruthenium-catalyzed living radical polymerization of MMA was also attained via direct mechanistic transformation using isotactic or syndiotactic PMMA–X (X = Cl and Br) and $\text{Ru}(\text{Ind})\text{Cl}(\text{PPh}_3)_2$ to produce stereoblock PMMAs. The tacticities of the stereoblock PMMAs were changed from highly isotactic or syndiotactic enchainment, produced by stereospecific anionic polymerization, into moderate syndiotactic enchainment by radical polymerization (Figures S2 and S3, Supporting Information). Although stereoblock PMMAs have already been prepared through living anionic,¹⁵ coordination,¹⁶ and radical¹⁷ polymerizations without converting the polarity of the growing chain end, this result can broaden the scope of producing stereoblock copolymers with different tacticities.

In summary, we succeeded in the quantitative halogenation of the stereospecific living anionic PMMA-growing species by using appropriate halogenating agents and additives to produce highly isotactic or syndiotactic PMMAs with a covalent carbon–halogen terminal, which can be directly employed in subsequent metal-catalyzed living radical polymerizations. Thus, the direct mechanistic transformation from stereospecific living anionic polymerization into living radical polymerization was accomplished to produce block copolymers consisting of stereoregular PMMA segments and other radically polymerized segments, such as polystyrene and PMMA, with moderate syndiotacticity. This method not only developed a novel direct synthesis strategy for various block copolymers between living anionic and radical polymerizations but also would construct novel higher-ordered structures or provide novel polymeric materials that originate from possible stereocomplex formations using block copolymers.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and polymerization results (^1H NMR spectra, SEC curves, and ^{13}C NMR spectra). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported in part by JSPS Research Fellowships for Young Scientists for H.A. (No. 24-10127), a Grant-in-Aid for Young Scientists (A) for K.S. (No. 23685023) by the Japan Society for the Promotion of Science, and Program for Leading Graduate Schools “Integrative Graduate Education and Research Program in Green Natural Sciences”.

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