

Formation of Block Copolymers by Transformation of Cationic Ring-Opening Polymerization to Atom Transfer Radical Polymerization (ATRP)

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Received October 2, 1997; Revised Manuscript Received March 26, 1998

ABSTRACT: Transformation of cationic ring-opening polymerization to atom transfer radical polymerization (ATRP) to form AB and ABA type block copolymers was performed. Syntheses of AB type block copolymers initiated by polyTHF (poly(tetramethylene glycol)) containing one bromopropionyl end group were successful for styrene, methyl methacrylate (MMA), and methyl acrylate (MA). Block copolymers were characterized by GPC, ¹H NMR spectroscopy, and thermal analysis (DSC). An ABA type triblock copolymer formed from a telechelic bifunctional polyTHF backbone that contained bromopropionyl groups at both ends was clearly formed in the case of successive ATRP of MMA. The triblock copolymer was characterized by GPC, ¹H NMR, and DSC. In the case of styrene and MA, the formation of triblock copolymers was significantly slower.

Introduction

Controlled/"living" polymerization methods offer the best way to prepare well-defined polymers (controlled molecular weight, polydispersities, and terminal functionalities). In these systems the contribution of chain-breaking reactions is small^{1,2} and the polymerization proceeds until all of the monomer has been consumed, with further additions of monomer resulting in continued polymerization. Controlled/"living" polymerizations proceed by anionic,^{3,4} cationic,⁵ group transfer,⁶ metathesis,^{7,8} Ziegler–Natta,⁹ or radical mechanisms.^{10–14}

Controlled/"living" polymerization techniques provide several powerful tools for the synthesis of block and graft copolymers with well-defined structure:¹⁵ (a) sequential monomer addition, (b) coupling reaction of "living" chains, and (c) reaction of end-functionalized polymers. The sequential monomer addition for formation of block copolymers can be achieved easily in a one-pot synthesis; however, this method is restricted by relative monomer reactivities.¹ Another approach for block copolymer synthesis is the coupling reaction of two "living" homopolymers with opposite charges (e.g., carbocationic with group transfer polymerization) or using coupling agents of two living chains of the same type (e.g., anionic or cationic).

The reaction of end-functionalized polymers involves the transformation of chain ends (after the first monomer polymerization is complete) into another type of initiating site with a completely different nature. Using this approach, Richards and co-workers developed several methods to interconvert anionic polymerizations to cationic or Ziegler–Natta processes.^{16–18} Several papers report well-defined block copolymers by transformation of initiating sites from "living" cationic to "living" anionic "initiating sites".^{19–22} These techniques require many steps, and the monomers available are limited to those that can be polymerized by cationic and anionic methods.

Recently, we reported a general method for the transformation of "living" carbocationic polymerizations into "living" radical polymerizations with the successful

preparation of block copolymers without any modification of initiating sites.²³ For example, polystyrene with chlorine termini synthesized by "living" cationic polymerization was used as an efficient macroinitiator for the homogeneous "living" atom transfer radical polymerization of styrene and (meth)acrylates.

A one-pot transformation from radical polymerization to ring-opening cationic polymerization, in the presence of electron acceptor to oxidize the propagating radical to a propagating cation, is reported in the combination of *p*-methoxystyrene polymerization and cyclohexene oxide ring-opening polymerization.²⁴ Although the synthesis of block and graft copolymers by combination of ring-opening polymerization with TEMPO-mediated radical polymerization have already been described,²⁵ the application of atom transfer radical polymerization (ATRP) for such systems has not yet been reported.

In cationic ring-opening polymerization (CROP), the propagation reaction can be described as nucleophilic substitution in which the positively charged active species is the electrophile and the monomer is the nucleophile. Ring-opening polymerization of cyclic monomers by a cationic mechanism provides several important industrial polymers, for example, thermoplastic polyacetals (copolymer of 1,3,5-trioxane with either ethylene oxide or with 1,3-dioxolane), polytetrahydrofuran, polysiloxane, and polyphosphazene.²⁶ The monomers can be cyclic ethers (epichlorohydrine, tetrahydrofuran), cyclic acetals (1,3,5-trioxane, 1,3-dioxolane, 1,3-dioxepane), lactones, sulfides, or lactams. Many initiating systems based on carbenium ion salts, triflic acid, anhydrides, esters, or Lewis acids are active for CROP.²⁶

Among cyclic ethers, THF is known to polymerize in an almost "living" fashion; therefore, this polymerization has been frequently employed to produce telechelic polymers either by use of a functional initiator or by end-capping. THF can be polymerized by the bifunctional initiator, triflic anhydride, to produce polyTHF containing oxonium ions at both polymer chain ends.²⁷

This paper reports that polyTHF with one or two bromopropionyl termini, synthesized by "living" cationic

polymerization, is an efficient macroinitiator for "living" ATRP for styrene, MMA, and MA to make AB type block copolymers and for MMA to make ABA type triblock copolymers.

Experimental Section

Cationic Ring-Opening Polymerization. General Information. Tetrahydrofuran (THF) was purified by distillation over Na–benzophenone. 2-Bromopropionyl bromide was distilled under reduced pressure after drying over CaH₂. Sodium 2-bromopropionate was synthesized by the reaction of bromopropionic acid with NaOH. Commercial grade silver triflate (silver(I) trifluoromethanesulfonate (AgOTf)) and triflic anhydride (trifluoromethanesulfonic acid anhydride, O(Tf)₂) were used without further purification.

Molecular weights of obtained polymers and copolymers were roughly estimated by means of gel permeation chromatography (GPC). A Waters HPLC system was used for GPC analysis. THF, toluene, and polystyrene were used for eluent, reference, and standard sample, respectively.

¹H NMR spectra were recorded on a Bruker WM300 NMR spectrometer in CDCl₃ at 25 °C. All thermal measurements were conducted on a Rheometrics DSC Plus using mercury, indium, and tin as calibration standards. Unless otherwise stated, all heating rates are 20 °C/min. Glass transition temperatures were read as the middle in the change of heat capacity.

Procedure. Bulk Polymerization of THF. Bromopropionyl bromide, 216 mg (0.10 mL, 1 mmol), was dissolved in 100 mL of THF at 25 °C. A solution of AgOTf, 257 mg (1 mmol), in 10 mL of THF was added. Silver bromide precipitated immediately and polymerization was initiated by the bromopropionyl ion. After 1 h, the polymerization was quenched by addition of 1 mL of H₂O and this mixture was stirred overnight.

The mixture was poured into a large excess of methanol at –30 °C. The precipitated elastic solid was collected and dried under ambient conditions. The elastic solid turned to a viscous oil at room temperature. The resulting polymer was dissolved in 300 mL of THF and filtered to remove AgBr. The filtrate was reprecipitated from methanol. The final yield was ~10%. $M_n = 15\,400$, $M_w/M_n = 1.39$.

ATRP of Styrene Initiated with Cationically Prepared polyTHF-Br. With reagent ratios styrene:[pTHF-Br]:CuBr:dNbipy = 150:1:1:2, the solution polymerization in toluene (50 vol %) at 110 °C was performed. A THF solution of polyTHF-Br, 400 mg (0.025 mmol), was placed in a glass tube, and the THF was evaporated completely under reduced pressure (residual THF might interfere with the ATRP by ligation to copper). CuBr, 3.8 mg (0.025 mmol), and dNbipy, 22 mg (0.05 mmol), were added to the glass tube. The tube was flushed with argon by standard Schlenk techniques. Styrene, 0.50 mL (4.1 mmol), and toluene (0.50 mL) were then added to the tube. The mixture was degassed three times with a vacuum pump, sealed under high vacuum, and polymerized at 110 °C. The color of the mixture turned from pale brown to deep red brown immediately. The viscosity of the mixture increased gradually over several hours, and the polymerization was terminated after 24 h. The tube was opened, and the reaction mixture was added to THF (30 mL). The THF solution was passed through an alumina column to remove copper complexes. After precipitation from THF–methanol, a colorless powder was obtained. $M_n = 29\,000$ (calcd $M_n = 30\,600$), $M_w/M_n = 1.55$ (based on polystyrene standard).

ATRP of MMA Initiated with Cationically Prepared PolyTHF-Br. A solution polymerization in toluene (50 vol %) at 90 °C was performed with MMA:[polyTHF-Br]:CuBr:dNbipy = 150:1:1:2 similarly to the styrene system. After several precipitations from methanol, a colorless elastic solid was obtained. $M_n = 56\,700$ (calcd $M_n = 35\,000$), $M_w/M_n = 1.21$ (based on polystyrene standard).

ATRP of MA Initiated with Cationically Prepared PolyTHF-Br. A solution polymerization in toluene (50 vol %) at 90 °C was performed with MA:[pTHF-Br]:CuBr:dNbipy

= 150:1:1:2 similarly to the styrene system. After several precipitations from methanol, a colorless elastic solid was obtained. $M_n = 28\,500$ (calcd $M_n = 29\,700$), $M_w/M_n = 1.32$ (based on polystyrene standard).

Bulk Two-Directional Polymerization of THF. Neat triflic anhydride, 0.39 g (0.2 mL, 1.39 mmol), was added to 100 mL of THF, and the polymerization was carried out at 25 °C. After 30 min, deactivation was performed by addition of 5 mL of a methanol solution of sodium bromopropionate, 990 mg (5.2 mmol). The mixture was stirred overnight and then was poured into a large excess of methanol at –30 °C. The precipitated elastic solid was collected and dried. The elastic solid turned to a viscous oil at ambient temperature. The resulting polymer was dissolved in 300 mL of THF and filtered. The filtrate was precipitated again. The yield was 10%. $M_n = 20\,000$, $M_w/M_n = 1.71$. A flame reaction showed the presence of Br.

ATRP of MMA Initiated with Cationically Prepared Bifunctional Br-PolyTHF-Br. A solution polymerization in toluene (50 vol %) at 90 °C was performed with MMA:[Br-pTHF-Br]:CuBr:dNbipy = 40:1:1:2 in a way similar to that of the styrene system. Br-polyTHF-Br, 250 mg (0.0125 mmol), CuBr, 1.8 mg (0.0125 mmol), and dNbipy, 10.2 mg (0.025 mmol), were placed in the glass tube. The atmosphere inside the tube was changed to argon. MMA, 0.6 mL (5 mmol), and toluene (0.6 mL) were then added into the tube. The mixture was degassed three times, sealed under high vacuum, and polymerized at 90 °C. The color of the mixture turned from pale brown to deep red brown immediately. The viscosity of the mixture increased gradually for a few hours, and the mixture turned to a solid after several hours. The polymerization mixture was terminated after 12 h of polymerization. The cooled tube was opened, and the mixture was dissolved in a small amount of THF. The THF solution was then passed through an alumina column to remove copper complexes. After several precipitations from THF to methanol, a colorless solid was obtained. $M_n = 71\,000$ (calcd $M_n = 60\,000$), $M_w/M_n = 1.34$ (based on polystyrene standard).

ATRP of Styrene Initiated with Cationically Prepared Bifunctional Br-PolyTHF-Br. A solution polymerization in toluene (50 vol %) at 90 °C was performed with styrene:[Br-pTHF-Br]:CuBr:dNbipy = 40:1:1:2. After several precipitations from methanol, an elastic colorless solid was obtained. $M_n = 28\,000$ (bimodal) (calcd $M_n = 60\,000$), $M_w/M_n = 1.82$ (based on polystyrene standard).

ATRP of MA Initiated with Cationically Prepared Bifunctional Br-PolyTHF-Br. A solution polymerization in toluene (50 vol %) at 90 °C was performed with MA:[Br-pTHF-Br]:CuBr:dNbipy = 40:1:1:2 in a way similar to that of the styrene system. After several precipitations from methanol, a colorless elastic solid was obtained ($M_n = 27\,000$ for the THF-soluble part, calcd $M_n = 60\,000$; $M_w/M_n = 1.38$, based on polystyrene standard).

Results and Discussion

AB Type Block Copolymers. Macroinitiators based on polyTHF with a bromine-terminated chain end were obtained by cationic ring-opening polymerization of THF with a bromopropionyl bromide/AgOTf initiating system in bulk under argon at 25 °C, according to Scheme 1.

After 30 min, the polymerization was terminated by the addition of excess water. The polymerization mixture was then poured into cooled methanol (–30 °C) to separate the polymer as a viscous oil. The polymer was purified by repeated dissolution–precipitation from THF/methanol and dried under vacuum. The experimental number average molecular weight ($M_{n,exp}$) was close to the theoretical value ($M_{n,th}$) calculated by means of eq 1, and the molecular weight distribution was relatively narrow ($M_w/M_n = 1.39$).

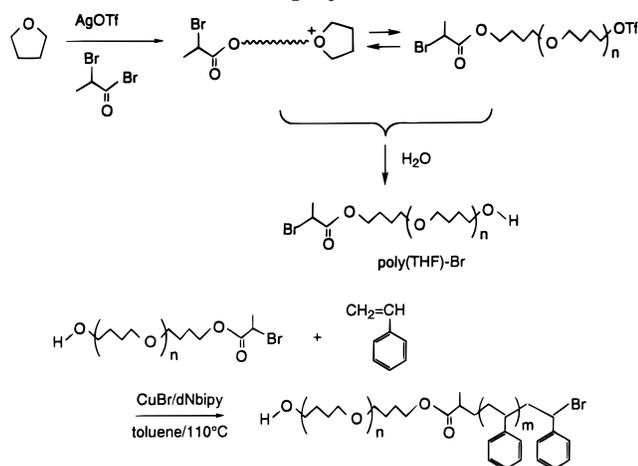
$$M_{n,th} = ([M]_0/[initiator]_0) \times (MW)_0 \times \text{conversion} \quad (1)$$

Table 1. Results Obtained by Transformation of Cationic Ring-Opening Polymerization of THF to ATRP^a

monomer	pTHF-Br:monomer:CuBr:dNbipy	temp, °C	$M_{n,th}$	$M_{n,exp}$	ratio of segments (NMR)	M_w/M_n
styrene	1:150:1:2	110	30 600	29 000		1.55
styrene	1:150:1:2	110	30 600	31 000	1:1.3	1.46
MMA	1:150:1:2	110	30 000	32 500		1.75
MMA	1:200:1:2	90	35 000	35 000	1:1.4	1.21
MA	1:150:1:2	110	27 900	27 900		2.74
MA	1:200:0.8:1.6	110	32 200	32 200	1:1.4	1.49
MA	1:150:1:2	90	28 000	28 500		1.32

^a Initiating system pTHF-Br/CuBr/dNbipy, polyTHF-Br $M_n = 15\ 400$, $M_w/M_n = 1.39$, time 24 h, conv > 97%.

Scheme 1. Reaction Scheme of Copolymerization of PolyTHF with Styrene To Form AB Type Block Copolymer



Although end group analysis by ¹H NMR did not show a clear signal for the bromopropionyl group due to the high degree of polymerization (DP = 190), the polymer should contain one bromopropionyl end group and one hydroxy end group. This approach provides better control than application of functional terminators, which may not efficiently terminate all growing chains. PolyTHF with a bromine terminal functionality was used as a macroinitiator in controlled/"living" radical polymerization (ATRP).

PolyTHF with a bromine chain end, polyTHF-bromopropionate (pTHF-Br), was used to initiate the homogeneous ATRP of styrene, methyl acrylate, and methyl methacrylate in the presence of CuBr/dNbipy (4,4'-di-(5-nonyl)-2,2'-bipyridine) catalyst. Table 1 summarizes polymerization results in the ring-opening cationic polymerization of THF, along with the homogeneous ATRP of styrene (St), methyl methacrylate (MMA), and methyl acrylate (MA), initiated with pTHF-Br and catalyzed by CuBr/dNbipy.

$M_{n,exp}$ values agree with $M_{n,th}$, which were calculated using eq 1 with the assumption that each polymer chain contains one terminal bromine. The GPC chromatograms of pTHF-Br, pTHF-*b*-St-Br, pTHF-*b*-MMA-Br, and pTHF-*b*-MA-Br copolymers are illustrated in Figure 1. GPC measurements showed that the molecular weight distribution of block copolymers are unimodal and narrow. No signal shoulder attributed to the starting macroinitiators has been detected.

The structures of the block copolymers were analyzed by ¹H NMR spectroscopy. Figure 2 illustrates the ¹H NMR spectra of pTHF-Br, pTHF-*b*-St-Br, pTHF-*b*-MMA-Br, and pTHF-*b*-MA-Br (co)polymers. The ¹H NMR spectrum of pTHF-Br shows two kinds of methylene proton signals at 1.60 and 3.38 ppm. These signals do not overlap with signals from polySt, poly-

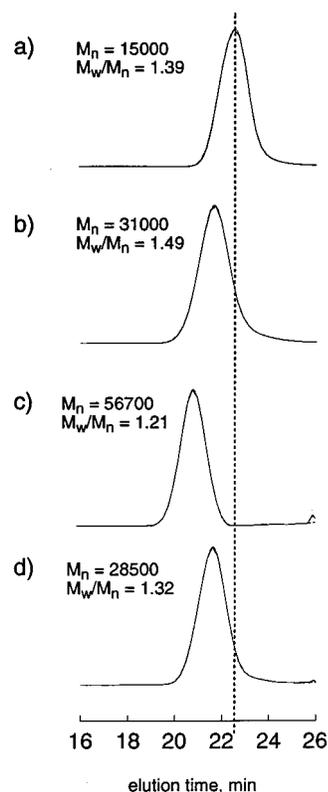


Figure 1. GPC elution diagrams of (a) monofunctional polyTHF, (b) poly(St-*b*-THF), (c) poly(MA-*b*-THF), and (d) poly(MMA-*b*-THF).

MMA, and polyMA. The spectra of block copolymers show simple superposition of signals from pTHF segments with the attached segments of styrene, MMA, or MA. This, along with GPC data, indicate formation of the block copolymer. The tacticity of the polyMMA segment in a block copolymer of polyTHF-*b*-MMA-Br (based on α -CH₃ group signals) was (rr) = 61%, (rm) = 34%, and (mm) = 5%.

Unfortunately, M_n of these copolymers cannot be calculated from the signal of a terminal group due to the low intensity of the terminal group signal, but segment ratios were determined (Table 2). Ratios of the segments for pTHF-*b*-St-Br, pTHF-*b*-MMA-Br, and pTHF-*b*-MA-Br copolymers were similar. These results are different from the results obtained from GPC, but the results from ¹H NMR may be more reliable, since the hydrodynamic volumes of segments of polyTHF observed in GPC may be different from those of the polystyrene standard.

ABA Type Block Copolymers. Bifunctional polyTHF was prepared by initiation with triflic anhydride, according to Scheme 2.

The polymerization system was terminated with addition of a methanol solution of sodium 2-bromopro-

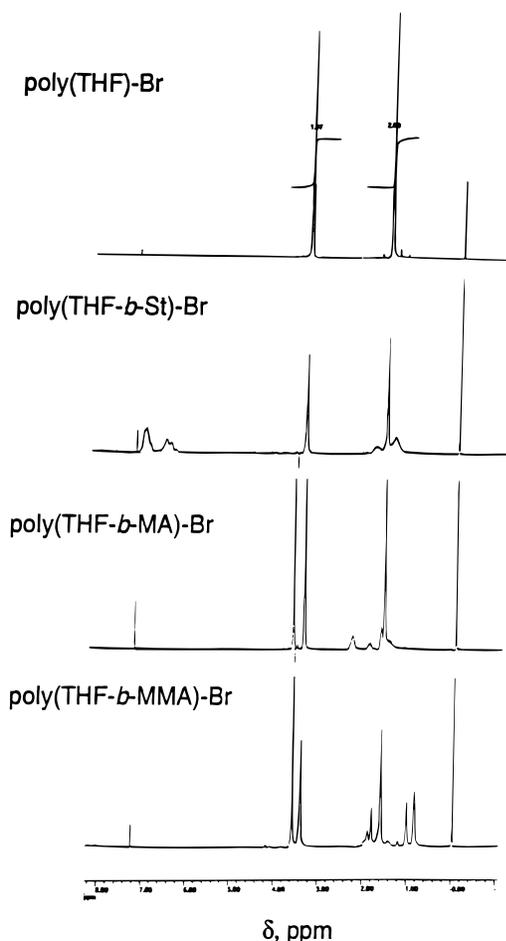
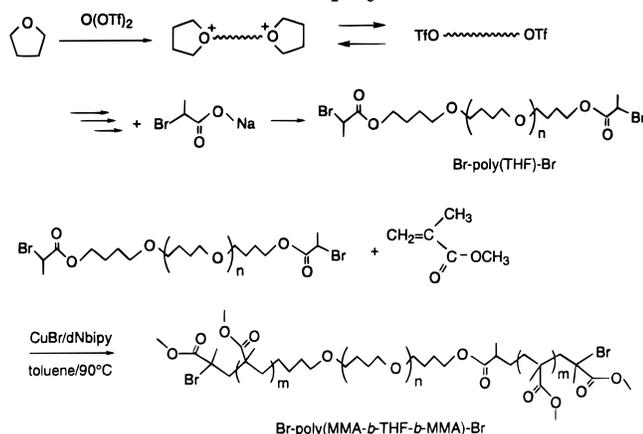


Figure 2. ^1H NMR spectra of polyTHF, polySt–polyTHF, polyMMA–polyTHF, and polyMA–polyTHF in CDCl_3 at 25°C .

Table 2. Ratio of Segments

copolymers	theor	GPC	NMR
p(THF- <i>b</i> -St)-Br	1:1	1:1	1:1.3
p(THF- <i>b</i> -MMA)-Br	1:1.3	1:1.6	1:1.4
p(THF- <i>b</i> -MA)-Br	1:1.3	1:1.9	1:1.4
Br-p(MMA- <i>b</i> -THF- <i>b</i> -MMA)-Br	1:1:1	1.3:1:1.3	1.4:1:1.4

Scheme 2. Reaction Scheme of Copolymerization of Bifunctional PolyTHF with MMA To Form ABA Type Block Copolymer



pionate. Presumably, the propionate anion reacts with oxonium cations faster than with methanol.

After the presence of bromine was confirmed by a flame reaction, polyTHF with bromine chain ends,

Table 3. Results Obtained by Transformation of Cationic Ring-Opening Polymerization of THF to ATRP ABA Triblock Copolymer

monomer	time, h	temp, $^\circ\text{C}$	conv, %	$M_{n,\text{exp}}$	M_w/M_n
styrene	48	110	~50	28 000	1.65 ^b
styrene (bulk)	48	110	~50	74 000	1.66 ^b
MMA	24	90	>99	71 000	1.34
MMA	24	90	>99	73 000	1.56
MA (bulk)	48	90	~60	135 000	2.73
MA	48	90	~20	27 000	1.38
MA	48	90	~20		

^a Initiating system Br-pTHF-Br/CuBr/dNbipy, Br-pTHF-Br $M_n \sim 20\,000$, $M_w/M_n \sim 1.71$, Br-pTHF-Br:monomer:CuBr:dNbipy = 1:40:1:2, $M_{n,\text{th}} = 60\,000$, time 24 h. ^b Bimodal.

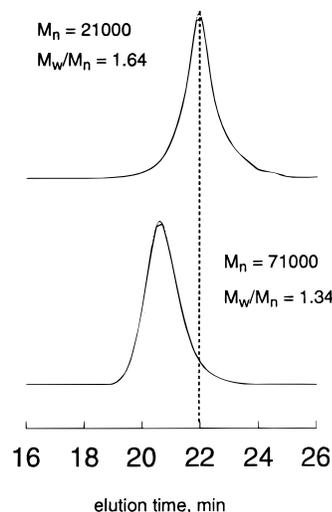


Figure 3. GPC elution diagrams of bifunctional polyTHF (top) and poly(MMA-*b*-THF-*b*-MMA) (bottom).

bromopropionate-polyTHF-bromopropionate, was used to initiate homogeneous ATRP of styrene, methyl acrylate, and methyl methacrylate in the presence of catalyst based on CuBr and dNbipy. Table 3 summarizes the polymerization results of ring-opening cationic polymerization of THF, along with the homogeneous ATRP of St, MMA, and MA, initiated with bifunctional bromopropionate-polyTHF-bromopropionate (Br-pTHF-Br) and catalyzed by CuBr/dNbipy.

In the case of ATRP of MMA, the polymerization proceeded very fast and the results showed good agreement with the theoretical prediction (Figure 3).

The ^1H NMR spectrum of this copolymer showed simple superposition of the polyTHF and polyMMA segments (Figure 4). The tacticity of polyMMA (based on $\alpha\text{-CH}_3$ group signals) was similar to that in diblock copolymer. The calculated value of the segment ratios of these two segments is shown in Table 2. This result indicates that the macroinitiator is effective for making a triblock copolymer; however, in the case of styrene and methyl acrylate, the rate of polymerization was significantly lower and the block copolymer formation was low in both bulk and solution polymerizations.

Thermal Behavior of Block Copolymers. Thermal behavior of these block copolymers was examined by differential scanning calorimetry (DSC) in the range of -50 to $+150^\circ\text{C}$. Melting points (mp) of the polymers were observed at 31, 16, 17, 19, and 18°C for pTHF-Br, p(THF-*b*-St)-Br, p(THF-*b*-MMA), p(THF-*b*-MA), and Br-p(MMA-*b*-THF-*b*-MMA)-Br, respectively. Sharp and clear melting transitions indicate the presence of long polyTHF segments that could have been slightly plasti-

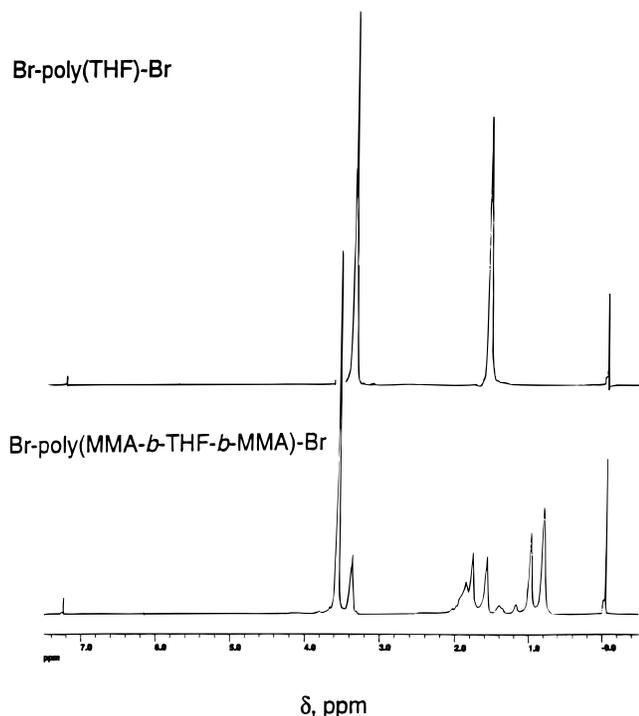


Figure 4. ^1H NMR spectra of Br-polyTHF-Br and Br-poly(MMA-*b*-THF-*b*-MMA)-Br in CDCl_3 at 25 $^\circ\text{C}$.

cized by vinyl polymers, reducing the melting points. This is additionally confirmed by the reduced enthalpies for melting transition, e.g., $\Delta H = 55.8 \text{ J/g}$ for Br-pTHF-Br and $\Delta H = 5.9 \text{ J/g}$ for Br-p(MMA-*b*-THF-*b*-MMA)-Br.

Typical T_g 's of polystyrene, polyMMA, and polyMA are reported to be 100, 110, and 10 $^\circ\text{C}$.²⁸ The T_g 's of block copolymers with polyMMA and polystyrene segments have values lower by 5–20 deg. These results might also indicate the plasticizing effect of polyTHF segments in these copolymers. T_g of polyMA could not be detected due to overlap with the intense melting transition of polyTHF.

Conclusion

We report two methods for the transformation of cationic ring-opening polymerization into a controlled radical polymerization system using either functional initiators or functional terminating agents and successful preparation of di- and triblock copolymers. We have demonstrated that polyTHF-Br and Br-polyTHF-Br prepared by CROP can be used as efficient macroinitiators for homogeneous "living" ATRP of styrene (for diblock), MMA (for di- and triblock), and MA (for diblock).

Acknowledgment. Financial support from the donors of the Petroleum Research Foundation administered by the American Chemical Society and by the industrial members of the ATRP Consortium at CMU

is gratefully acknowledged. A.K. acknowledges the Ministry of Education, Science, and Culture, Japan, for financial support.

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MA971445J