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Synthesis of block copolymers through umpolung or treatment of propagating end of living cationic polytetrahydrofuran

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Abstract

Block copolymers containing polytetrahydrofuran segments were synthesized by umpolung or propagating end of the cationic living polymer and successive anionic polymerization of methacrylates (RMAs) or radical polymerization of RMAs, acrylonitrile (AN), and styrene (St). Living polytetrahydrofuran (poly-THF) was prepared by cationic polymerization of tetrahydrofuran (THF), whose propagation end was reduced by samarium(II) iodide (SmI_2). Anionic polymerizations of RMAs were conducted by addition of the monomers to the reduced poly-THF to obtain poly(THF-*b*-RMAs). On the other hand, the 2-bromoisobutyrate group, which can act as an initiator of radical polymerization, was introduced to the cationic propagating end of poly-THF by adding sodium 2-bromoisobutyrate. Block copolymers were synthesized by living radical polymerization of RMAs, St, or AN using the 2-bromoisobutyrate-capped poly-THF as a macroinitiator and copper(I) bromide (CuBr) as a catalyst.

Keywords Block copolymer · Umpolung · Living cationic polymerization · Living anionic polymerization · Living radical polymerization

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Introduction

Block copolymers have unique properties both in solution and in bulk [1]. Many kinds of block copolymers have been synthesized. The general method of synthesis is living polymerization where the propagating chain ends of polymer are still living after all monomers in the vessel are completely used [2–7]. So when another monomer is added, the living polymerization restarts from the propagating chain ends, and the corresponding block copolymer is synthesized (Fig. 1a). The block copolymer is effectively synthesized generally by the same polymerization method in the first and second steps. Living polymerization is not appropriate for synthesis of block copolymers composed of monomers, which are polymerized by different mechanisms. A solution to this problem is to utilize copper(I)-catalyzed cycloaddition between the azide group and ethynyl group, generally called "click reaction" (Fig. 1b) [8]. This method can be applied to many polymers and can be used to prepare a wide variety of block copolymers. However, the procedure for introducing the azide and ethynyl groups into the end of the polymers is tedious. Another method for synthesis of block copolymers is using umpolung (Fig. 1c) [9–31].

Synthesis of block copolymers using umpolung has been reported [9–31]. Richards et al. [9–15] reported the synthesis of block copolymers of styrene (St) and tetrahydrofuran (THF) using silver salt. First, St was polymerized by living anionic polymerization, after which the propagating ends were brominated by reaction with excess bromine. Finally, THF was polymerized by cationic polymerization from the ends of poly-St using silver salt. On the other hand, Tseng et al. [16] reported the synthesis of block copolymers of THF and methyl methacrylate (MMA) using primary amine. At first, THF was polymerized by living cationic polymerization. Then, the propagating ends were treated with excess primary amine, and the amine terminals were changed to anions by abstraction of the amine protons to polymerize MMA by living anionic polymerization. We previously reported the transformation of cationic active species of poly-THF into anionic ones via electron transfer in the SmI_2/HMPA system [22–25]. The obtained poly-THF macroanion reacted

(a) using living polymerization
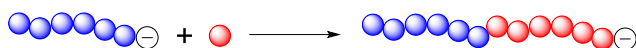
(b) using click reaction
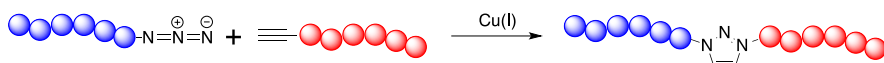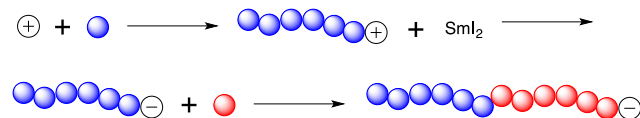

(c) using umpolung

Fig. 1 Several ways to synthesize block copolymers

with a variety of electrophiles including aldehydes, ketones, and isocyanates [22]. Furthermore, we polymerized *tert*-butyl methacrylate (tBMA) by living anionic polymerization from the poly-THF macroanion and obtained a block copolymer [23, 24]. In addition, we polymerized δ-valerolactone and ε-caprolactone with the poly-THF macroanion, and synthesized poly(THF-*b*-δ-valerolactone) and poly(THF-*b*-ε-caprolactone), respectively [25, 26]. Using this method, we conducted living cationic and anionic polymerization continuously in one pot. Using lanthanoid elements, we could effectively reduce cationic propagating ends to anionic ones without other side reactions. In recent years, much attention has been paid to lanthanoid elements including Sm, Eu, and Yb, which undergo efficient electron transfer reduction under mild reaction conditions [32–34].

On the other hand, transition metal elements such as Cu, Fe, and Ru are known as efficient catalysts for living radical polymerization such as atom transfer radical polymerization (ATRP) [2, 3]. In radical polymerization, a propagating radical chain end can be generated by one-electron reduction in the cationic propagating end or one-electron oxidation of the anionic propagating end. Therefore, if this transformation is achieved, block copolymers can be obtained from radically polymerizable monomers and anionicaly polymerizable or cationicaly polymerizable monomers [35].

In this paper, we synthesized block copolymers using umpolung of a living cationic propagating end. THF was polymerized by living cationic polymerization, and the obtained cationic propagation end was reduced by SmI$_2$. After that, some methacrylate monomers other than tBMA were polymerized by living anionic polymerization. On the other hand, the cationic propagating end of poly-THF was exposed to sodium 2-bromoisobutyrate to introduce 2-bromoisobutyrate groups. To synthesize block copolymers composed of poly-THF with polymethylmethacrylate (poly-MMA), poly-St, or polyacrylonitrile (poly-AN), which cannot be prepared by a simple sequential monomer addition, we used this Br-end poly-THF as a macroinitiator with CuBr as a catalyst, and ATRPs of MMA, St, and AN. This two-batch synthesis could be used as another type of umpolung of a cationic propagation end.

Experimental section

Materials

THF was purchased from the Wako Pure Chemical Industry (Osaka, Japan) and distilled over sodium with benzophenone before use. Methyl methacrylate (MMA), ethyl methacrylate (EMA), and *tert*-butyl methacrylate (tBMA) were purchased from Wako Pure Chemical Industry (Osaka, Japan) and distilled before use. Dodecyl methacrylate (DMA) was purchased from Tokyo Chemical Industry (Tokyo, Japan) and distilled before use. Phenyl methacrylate (PMA) was prepared from methacryloyl chloride according to the reported procedures [36].[1] Methacryloyl chloride,

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[1] See supporting information.

anisole, *N*,*N*-dimethylformamide (DMF), CuBr, and 2,2-bipyridyl were purchased from Wako Pure Chemical Industries (Osaka, Japan) and used as received. THF solution of SmI_2 was prepared as reported [37, 38]. Hexamethylphosphoric triamide (HMPA) was purchased from Wako Pure Chemical Industry (Osaka, Japan) and distilled on CaH_2 under reduced pressure. Methyl trifluoromethanesulfonate (MeOTf) was purchased from Tokyo Chemical Industry (Tokyo, Japan) and used as received. Sodium 2-bromoisobutyrate was prepared by treatment of 2-bromoisobutyric acid with NaH in THF and washed with dry THF and dried by freeze dehydration [27].

Measurements

^{1}H and ^{13}C NMR spectra were recorded with a JEOL JNM-ECS 400 spectrometer at a resonance frequency of 400 and 100 MHz for ^{1}H and ^{13}C with tetramethylsilane (TMS) as an internal standard. NMR chemical shifts were reported in delta units (δ). Infrared (IR) spectra were recorded with a Thermo Scientific Nicolet iS10 spectrometer equipped with a Smart iTR Sampling Accessory. Number-average and weight-average molecular weights (M_n, M_w) and polydispersity indices (M_w/M_n) of the polymers were estimated by size exclusion chromatography (SEC) using DMF containing 10 mM lithium bromide as the eluent at a flow rate of 0.5 mL/min at 40 °C, performed on Tosoh chromatograph model HLC-8220GPC equipped with Tosoh TSKgel Super AW 2500 columns (6.0 mmI.D.×15 cm), TSKgel Super AW 3000 columns (6.0 mmI.D.×15 cm), and TSKgel Super AW 4000 columns (6.0 mmI.D.×15 cm), refractive index (RI) detector. The molecular weight calibration curve was obtained with polystyrene standards. Thermogravimetric analysis (TGA) was performed on a Seiko Instrument Inc. TG–DTA 6200 with an aluminum pan under a 200 mL/min N_2 flow at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was carried out with a Seiko Instrument Inc. DSC-6200 using an aluminum pan under a 50 mL/min N_2 flow at a heating rate of 10 °C/min.

Synthesis of block copolymers by umpolung of living cationic propagating ends

The typical synthesis procedure is as follows. Details of synthesis are on supporting information. In a glove box, to a 50-mL round flask, THF (5 mL) and MeOTf (10 μL, 14.5 mg, 0.088 mmol) were added. The mixture was stirred for 10 min at room temperature. To the mixture, HMPA (251 μL, 258 mg, 1.44 mmol, 16 eq. for MeOTf) and a 0.1 M THF solution of SmI_2 (2.5 mL, 0.25 mmol) were added, and the whole mixture was stirred for 30 min at room temperature. Into the reaction mixture was added PMA (1.35 mL, 1.43 g, 8.8 mmol, 100 eq. for MeOTf) and the reaction mixture was stirred for 24 h at room temperature. A 3% HCl solution was added, and the products were extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, and concentrated. Then, a large amount of methanol (200 mL) was added to the residue with stirring, and the resulting precipitate was collected by centrifugation and dried in vacuo to give 120 mg of poly(THF-*b*-PMA) as a pale yellow oil.

poly(THF-b-PMA): ^{1}H NMR (400 MHz, 293 K, CDCl$_3$, δ): 7.40–7.00 (m, Ph–*H*), 3.43 (m, –OC*H*$_2$CH$_2$–), 3.40 (s, 3 H, –C*H*$_3$), 2.60–2.10 (m, –C*H*$_2$C(CH$_3$)(C=O)–), 2.00–1.40 (m, –CH$_2$C(C*H*$_3$)(C=O)–), 1.60 (m, –OCH$_2$C*H*$_2$–) ppm; IR (ATR): ν_{max} = 3065 (w, C–H), 1728 (s, C=O), 1474 (m, C=C), 1342 (w, C=C), 1180 (s, C–O), 1116 (s, C–O), 764 (s, C–H), 743 (s, C–H) cm^{-1}.

Synthesis of block copolymers by radical polymerization of 2-bromoisobutyrate-capped poly-THF

The typical synthesis procedure is as follows. Details of synthesis are on supporting information. In a glove box, to a 100-mL round flask, THF (40 mL) and MeOTf (272 µL, 394 mg, 2.4 mmol) were added. The mixture was stirred for 10 min at room temperature. To the mixture, sodium 2-bromoisobutyrate (900 mg, 4.76 mmol, 4.25 eq. for MeOTf) was added, and the whole mixture was stirred for 3 h at room temperature. Then, the resulting mixture was taken out from the glove box, filtered to remove solid salts, and concentrated. A large amount of water was added to the residues, and the organic products were extracted with CH$_2$Cl$_2$. The organic layer was dried over MgSO$_4$, concentrated, and dried in vacuo to give 2.93 g of 2-bromoisobutyrate-capped poly-THF as a clear oil. The obtained poly-THF (200 mg, 0.106 mmol) was dissolved in DMF (1.80 mL, 1 M for PMA) in an ampoule tube, and CuBr (15.2 mg, 0.106 mmol), 2,2-bipyridyl (33.1 mg, 0.212 mmol), and PMA (324 µL, 344 mg, 2.12 mmol) were added. After the solution was degassed through three freeze–pump–thaw cycles, the ampoule tube was sealed, and the mixture was stirred for 12 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into a large amount of methanol (300 mL), and the resulting precipitate was collected by decantation. Obtained solids were dissolved in CH$_2$Cl$_2$, and the solution was washed with water. The organic layer was dried over MgSO$_4$, filtered, concentrated, and dried in vacuo to give 120 mg of poly(THF-*b*-PMA) as a pale green oil.

poly(THF-b-PMA): ^{1}H NMR (400 MHz, 293 K, CDCl$_3$, δ): 7.40–7.00 (m, Ph–*H*), 4.10 (t, 2 H, –OC*H*$_2$CH$_2$–), 3.43 (m, –OC*H*$_2$CH$_2$–), 3.40 (s, 3 H, –C*H*$_3$), 2.60–2.10 (m, –C*H*$_2$C(CH$_3$)(C=O)–), 2.00–1.40 (m, –CH$_2$C(C*H*$_3$)(C=O)–), 1.60 (m, –OCH$_2$C*H*$_2$–) ppm; IR (ATR): ν_{max} = 3065 (w, C–H), 1728 (s, C=O), 1474 (m, C=C), 1342 (w, C=C), 1180 (s, C–O), 1116 (s, C–O), 764 (s, C–H), 743 (s, C–H) cm^{-1}.

Results and discussion

Umpolung of living cationic propagating end to anionic propagating end

THF was chosen as the cationic polymerization monomer. The reasons for this are as reported previously [23, 24]: First, the polymerization of THF gives a living polymer without termination and chain transfer reaction at the initial stage of the polymerization when the initiators are properly selected [39, 40]. Second, the growing
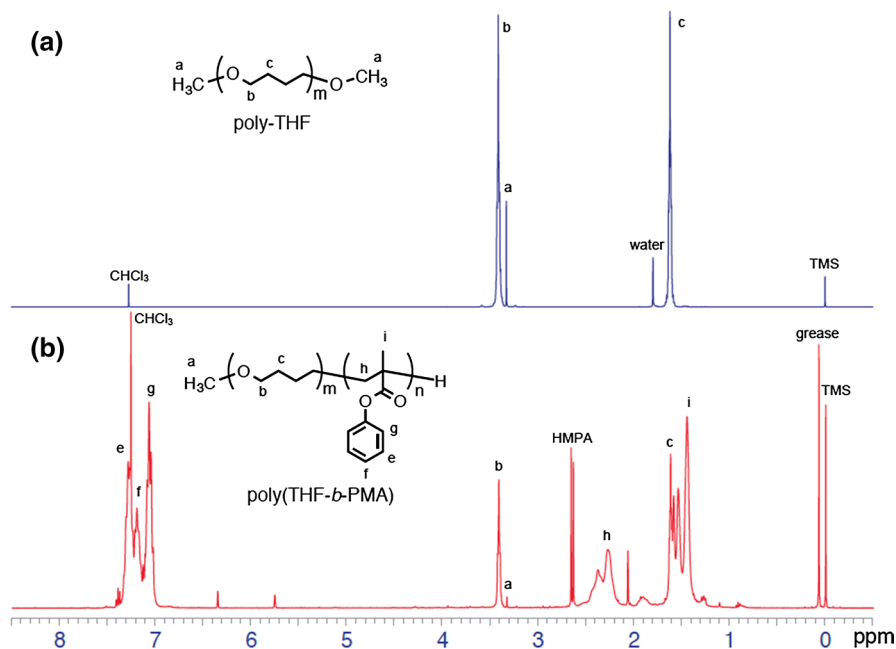
Fig. 2 ^{1}H NMR spectra of **a** poly-THF and **b** poly(THF-*b*-PMA) (400 MHz, CDCl[3], 293 K)

center of poly-THF is stable in solution. Third, the living cationic polymerization of THF is propagated slowly at room temperature, so it is easy to control the polymerization. Cationic polymerization of THF was conducted at room temperature for 10 min using MeOTf as an initiator. Reduction in the propagating end was carried out at a low THF conversion intentionally (within 3–5%), far below the equilibrium monomer concentration. The reversible propagation and chain transfer to the polymer can be avoided under these conditions, resulting in the formation of poly-THF with a narrow molecular weight distribution (Fig. 2). Thus, the generated cationic propagating end of poly-THF was reduced by SmI[2] with HMPA as a ligand. The color of the THF solution of SmI[2] changed from blue to purple after the addition. Under normal circumstances, the color of the mixture should change gradually to yellow–brown from purple [23, 24].[2] In this case, however, the color of the mixture remained purple, because we added excess SmI[2] to MeOTf (2.5 eq. to MeOTf). After this umpolung of the cationic propagating end, RMA was added to the reaction mixture at room temperature. PMA, EMA and DMA were copolymerized from the thus prepared anionic propagating end of poly-THF (Scheme 1, Table 1). We already reported synthesis of poly(THF-*b*-tBMA) by umpolung; however, we have not considered polymerization with other methacrylate monomers. In this paper, we studied the polymerization with a methacrylate monomer with an alkyl group or a

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[2] Broad absorptions are observed at 557 and 618 nm for the divalent samarium derivatives [37, 38] and 363 nm for the trivalent ones.
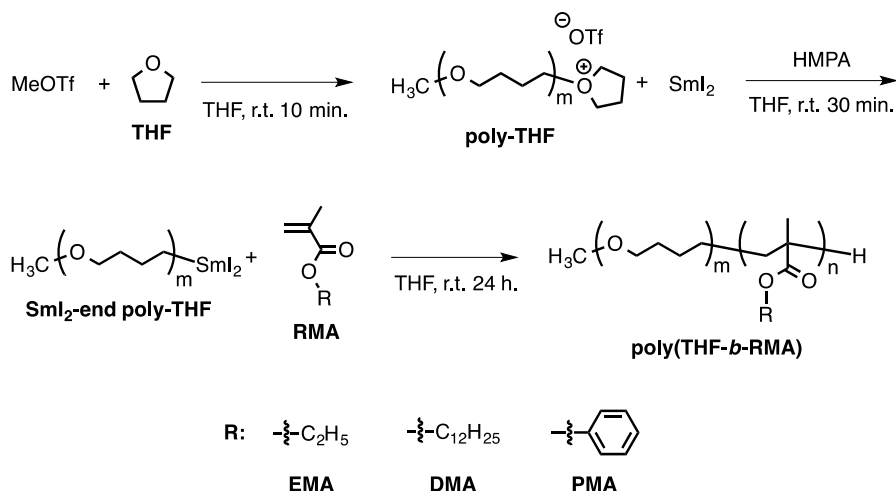
Scheme 1 Living cationic polymerization of THF followed by umpolung and living anionic polymerization of RMAs

Table 1 Results for synthesis of block copolymers

	M_n^a	M_w^a	M_w/M_n^a	M^b	m^b	n^b	$T_g\ (°C)^c$	$T_{d5}\ (°C)^d$
Poly-THF	2400	3100	1.29	1670	23	0	− 128	281
Poly(THF-*b*-PMA)	39,500	56,900	1.44	16,600	23	92	152	265
Poly(THF-*b*-EMA)	208,500	261,900	1.26	25,710	23	211	54	280
Poly(THF-*b*-DMA)	7100	10,000	1.40	4450	23	11	− 43	248

[a]Determined by GPC (eluent = DMF, polystyrene standards)

[b]The molecular weights and numbers of repetitions were calculated from results of ^{1}H NMR. Integration of main chain peak was divided by termination peak

[c]Determined by DSC

[d]Determined by TGA

phenyl group, instead of a bulky functional group like tBMA. EMA and DMA were chosen as the methacrylate monomers with alkyl chain, and PMA was chosen as the methacrylate monomer with phenyl group. After charging RMAs to the reaction mixture, the GPC curve shifted to the high molecular weight regions without any tailings attributed to the original poly-THF, and the obtained block copolymers showed a narrow molecular weight distribution as illustrated in Fig. 3 and supporting information. In addition, signals attributed to both THF and RMA units were observed in the ^{1}H NMR spectra (Fig. 2 and supporting information). The "M" in Table 1 is molecular weight calculated from ^{1}H NMR spectrum. There are dissociations between "M" and "M_n, M_w" because "M_n, M_w" were calculated from SEC curves determined by polystyrene standards. These results suggest that the transformation of a cationic propagation end to an anionic end proceeded quantitatively and that the transformed macroanion initiated the polymerization of RMAs with high
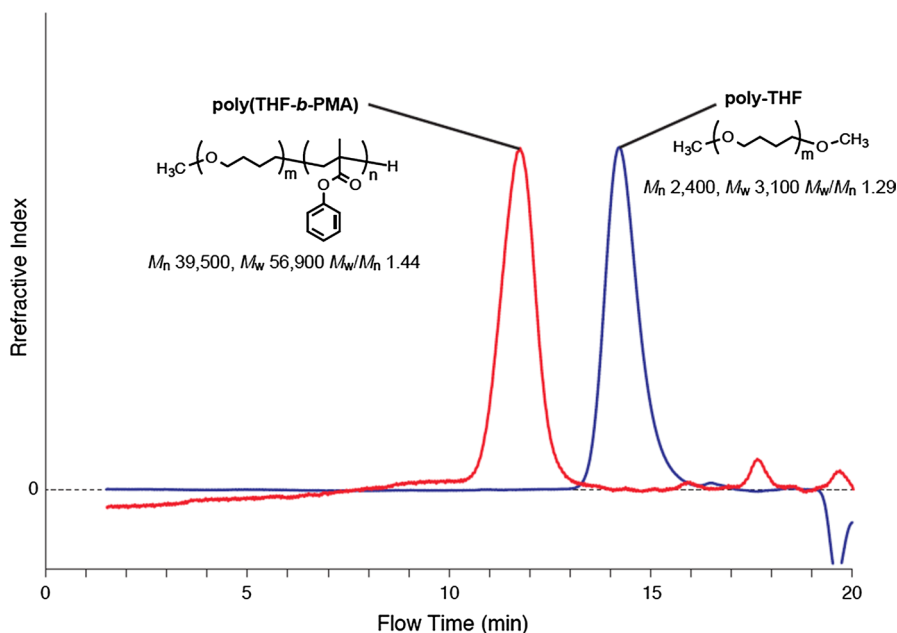
Fig. 3 SEC curves of poly-THF and poly(THF-*b*-PMA)

initiation efficiency. To confirm that the excess SmI_2 did not contribute to polymerization of RMA, the mixture of RMA, HMPA, and SmI_2 in THF solution was stirred at room temperature. After 24 h, there was no change in the mixture or polymers.

On the other hand, MMA was not polymerized with the anionic propagating end of poly-THF prepared by this method, and the block copolymer was not obtained at all. The transformed macroanion could not polymerize methacrylates with a small ester group such as MMA due to the hard character of alkylsamariums. Alkylsamariums exclusively attacked the carbonyl carbon of MMA [28–31]. In a similar manner, AN was not polymerized with the anionic propagating end of poly-THF. St was not polymerized either. However, the reasons for this were different from those of MMA and AN. The electrophilicity of St is not as strong as those of RMAs. To polymerize St using SmI_2, it is necessary to enhance the nucleophilicity of the anionic propagating end by other methods such as introduction of a phenyl group as previously reported [41–43].

Capping of a propagating end of a cationic living poly-THF with 2-bromoisobutyrate and its use as a macroinitiator for radical polymerization

2-Bromoisobutyrate group was introduced into the chain end of the poly-THF to synthesize block copolymers of THF and radically polymerizable monomers. Sodium 2-bromoisobuthyrate was added to the cationic propagation end of the poly-THF, and the desired end-capped poly-THF having α-bromo carbonyl group was
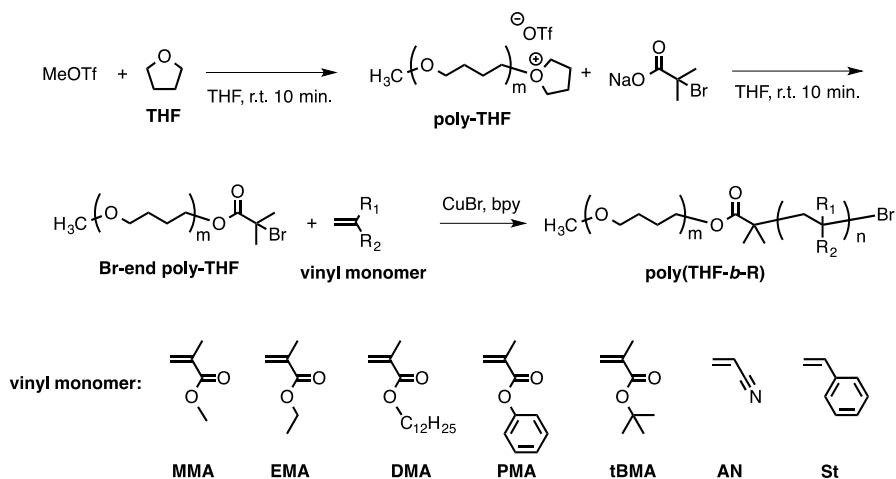
Scheme 2 Living cationic polymerization of THF and successive living radical polymerization of vinyl monomers

effectively obtained (Scheme 2) [27, 44]. Pure Br-end poly-THF was obtained after removal of the byproduct salts through filtration and drying completely. Using the obtained poly-THF having an active bromide as a macroinitiator, ATRP was carried out in the presence of CuBr(I) with 2,2-bipyridyl as a ligand (Scheme 2). The results of the ATRP are shown in Table 2. MMA and EMA were polymerized at room temperature to provide the corresponding block copolymers [45]. To obtain block copolymers from other vinyl monomers, polymerizations had to be carried out with heating. PMA [46] and AN [47] could be polymerized at about 60 °C, while DMA [48], tBMA [49], and St [50] needed more high temperature. This difference in polymerization temperatures may come from sterick bulkiness at the ester groups. Poly(THF-*b*-DMA), poly(THF-*b*-tBMA), and poly(THF-*b*-St) were not solved in DMF, so we chose anisole as solvent. After those polymerizations, the GPC curves shifted to the high molecular weight regions without any tailings attributed to the original poly-THF, and the obtained block copolymers showed a narrow molecular weight distribution as illustrated in Fig. 4 and supporting information. Moreover, signals attributed to both THF and vinyl monomer units were observed in the ^{1}H NMR spectra (Fig. 5 and supporting information). These results strongly suggest that the ATRP of vinyl monomers proceeded with high efficiency from the Br-capped chain end of the poly-THF. There is little difference in the two ^{1}H NMR spectra for the block copolymers synthesized by anion polymerization and radical polymerization (Figs. 2, 5). From these results, almost the same block copolymers were obtained from two different approaches. Since living anionic polymerization is faster than living radical polymerization, the molecular weights of block copolymers synthesized by umpolung are higher in the same block copolymers under mild conditions. For example, in the case of poly(THF-*b*-EMA), under the same room temperature condition for 24 h, the living anionic polymerization has a M_n 208,500, while the living radical polymerization has a M_n 3200. On the other hand, molecular

Table 2 Results for synthesis of block copolymers

	Solvent	Reaction temperature (°C)	Reaction time (h)	M_n^a	M_w^a	M_w/M_n^a	M^b	m^b	n^b	T_g (°C)^c	T_{d5} (°C)^d
Poly-THF	–	–	–	3000	3900	1.31	1880	24	0	– 133	285
Poly(THF-*b*-MMA)	DMF	r.t.	24	3200	5000	1.55	4380	24	25	75	281
Poly(THF-*b*-PMA)	DMF	60	12	7000	9300	1.32	8500	24	42	159	260
Poly(THF-*b*-EMA)	DMF	r.t.	24	3200	4700	1.44	4050	24	19	55	277
Poly(THF-*b*-DMA)	anisole	105	24	8000	11,200	1.40	6960	24	20	–53	242
Poly(THF-*b*-tBMA)	anisole	105	24	5000	7000	1.40	4010	24	15	133	219
Poly(THF-*b*-AN)	DMF	65	12	11,900	13,400	1.13	7500	24	106	215	290
Poly(THF-*b*-St)	anisole	105	24	4500	6000	1.32	2480	24	6	70	288

^{a}Determined by GPC (eluent = DMF, polystyrene standards)

^{b}The molecular weights and numbers of repetitions were calculated from results of ^{1}H NMR. Integration of main chain peak was divided by termination peak
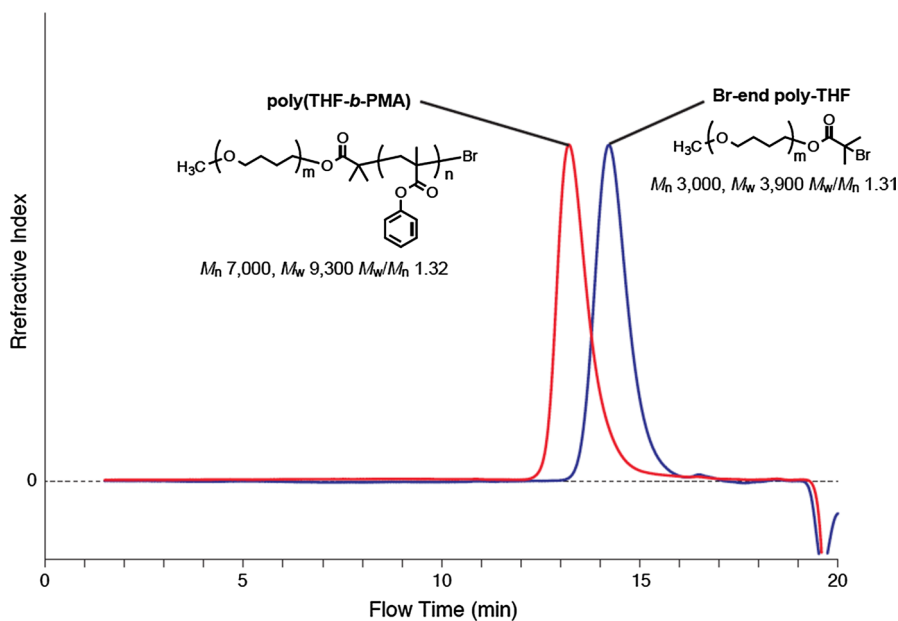
^{c}Determined by DSC

^{d}Determined by TGA

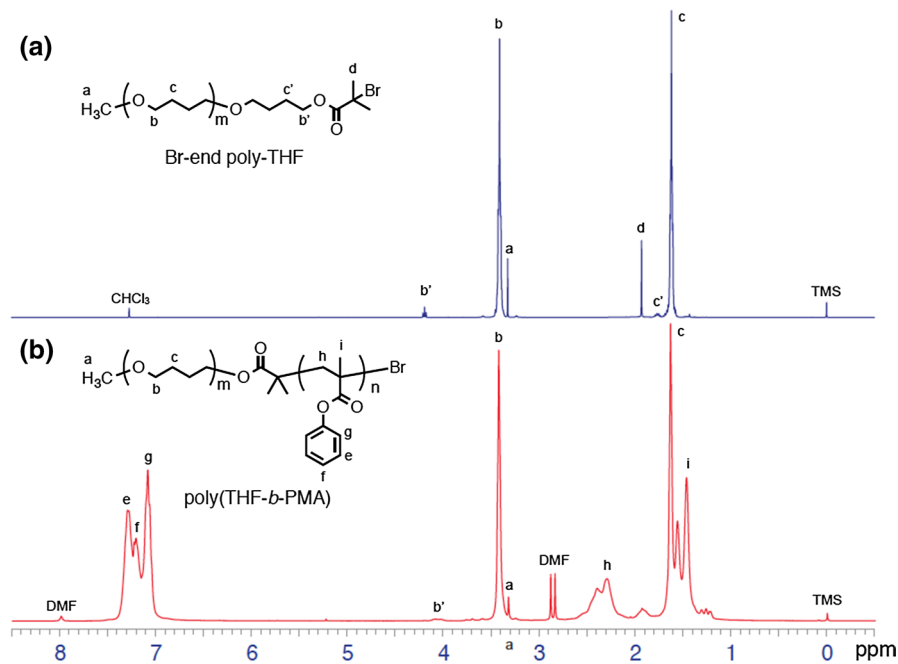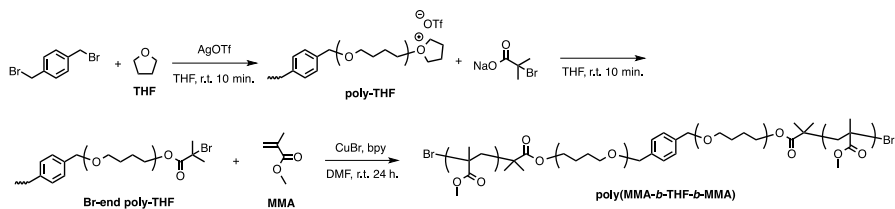**Fig. 4** SEC curves of Br-end poly-THF and poly(THF-*b*-PMA)

Fig. 5 ^{1}H NMR spectra of **a** Br-end poly-THF and **b** poly(THF-*b*-PMA) (400 MHz, CDCl$_3$, 293 K)

Scheme 3 Living cationic polymerization of THF using a difunctional initiator and successive living radical polymerization of MMA
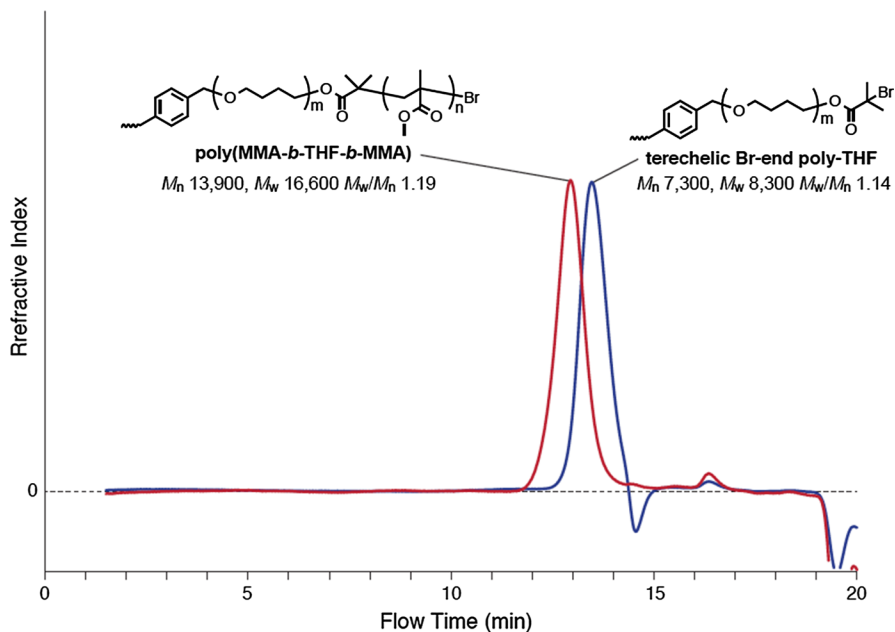

Fig. 6 SEC curves of terechelic Br-end poly-THF and poly(MMA-*b*-THF-*b*-MMA)

weight distributions are not differing greatly between the two polymerization methods, and it is considered that the polymerizations are proceeding in a living manner by either methods.

A terechelic ABA triblock copolymer was synthesized by applying this methodology changing the polymerization from cationic to radical (Scheme 3) [27, 44] (see footnote 1). THF was polymerized from a difunctional initiator with cationic activator, and the obtained poly-THF was treated with sodium 2-bromoisobuthyrate to introduce 2-bromoisobutyrate group into both ends of the poly-THF. The terechelic Br-end poly-THF was purified by removal of salt by-products with filtration and complete drying. By using this terechelic poly-THF having 2-bromoisobutyrate groups as macroinitiator, ATRP of MMA was carried out in the presence of CuBr(I) with 2,2-bipyridyl as a ligand in DMF at room temperature (see footnote 1).
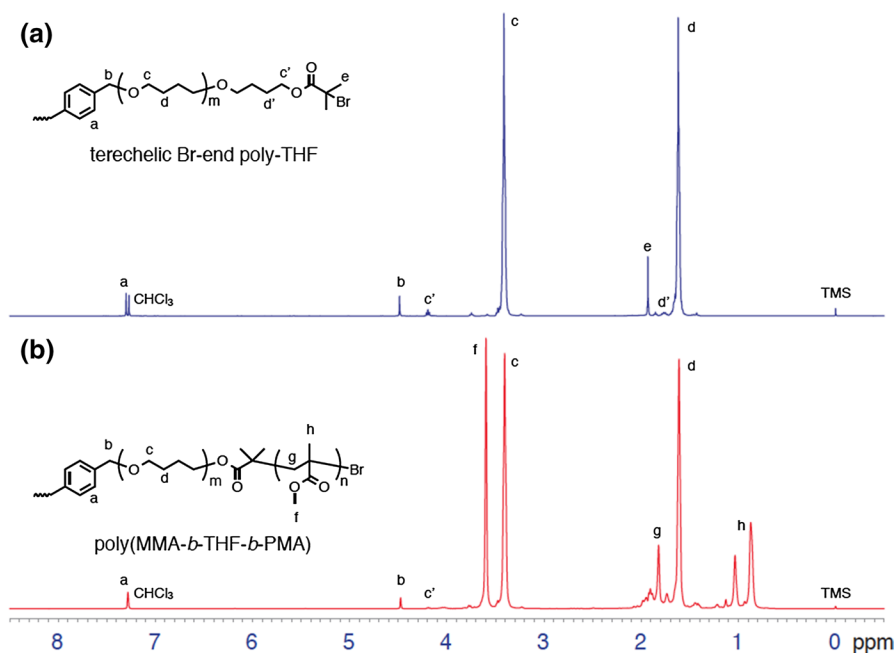
Fig. 7 ^{1}H NMR spectra of **a** terechelic Br-end poly-THF and **b** poly(MMA-*b*-THF-*b*-MMA) (400 MHz, CDCl$_3$, 293 K)

A monomodal and narrow GPC curve was observed for the resulting polymer, and there were no peaks corresponding to the original poly-THF or a diblock copolymer of THF and MMA (Fig. 6). In the ^{1}H NMR spectrum, signals attributed to THF, MMA, and the terechelic initiator were observed (Fig. 7). Furthermore, the ^{1}H NMR spectra of poly(THF-*b*-MMA) and poly(MMA-*b*-THF-*b*-MMA) showed no differences (see footnote 1). These results suggest that MMA was efficiently polymerized from the terechelic poly-THF to afford the desired ABA triblock copolymer.

Conclusions

In this paper, we synthesized block copolymers from two kinds of monomers which have completely different polymerization properties using umpolung or post-modification of a living cationic propagating end. First, poly-THF was synthesized by cationic polymerization and then umpolung of the cationic propagating end to anionic one for the second anionic polymerization. It was proved that other vinyl monomers, EMA, DMA, and PMA, than tBMA which had been reported previously [23, 24], could be polymerized from macroanions synthesized by umpolung of cationic propagating end. Using this manner, block copolymers could be synthesized from cationic polymerization monomer and anionic polymerization monomer by easy one-pot synthesis. On the other hand, the 2-bromoisobutyrate group was introduced by treatment of the living cationic propagating end of poly-THF, from which vinyl

monomers were polymerized by radical polymerization. It is not an one-pot synthesis, but it is easily applicable to many vinyl monomers to obtain block copolymers. The cationic polymerization of THF conducted here is living polymerization, and anionic polymerization using SmI_2 and radical polymerization using CuBr are also living polymerization. Therefore, one can access the block copolymers with well-controlled molecular weight with narrow molecular weight distributions. These block copolymers prepared here are expected to be valuable as new functional materials for various usages.

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