

Synthesis of poly(ϵ -caprolactone-*b*-isobutylene) diblock copolymer and poly(ϵ -caprolactone-*b*-isobutylene-*b*- ϵ -caprolactone) triblock copolymer

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Summary

Poly(isobutylene-*b*- ϵ -caprolactone) diblock and poly(ϵ -caprolactone-*b*-isobutylene-*b*- ϵ -caprolactone) triblock copolymers have been prepared and characterized. The synthesis involved the living cationic polymerization of IB, followed by capping with 1,1-diphenylethylene or 1,1-*p*-ditolylethylene and end-quenching with 1-methoxy-1-trimethylsiloxy-2-methyl-propene to yield methoxycarbonyl functional PIB. Hydroxyl end-functional PIB polymers were quantitatively obtained by the subsequent reduction of methoxycarbonyl end-functional PIB with LiAlH₄. The structure of hydroxyl end-functional PIBs was confirmed by ¹H NMR and IR spectroscopy. Poly(ϵ -caprolactone-*b*-isobutylene) diblock copolymers and poly(ϵ -caprolactone-*b*-isobutylene-*b*- ϵ -caprolactone) triblock copolymers were synthesized by the living cationic ring-opening polymerization of ϵ -caprolactone with hydroxyl end-functional PIB as macroinitiator in the presence of HCl•Et₂O *via* the “activated monomer mechanism”. The block copolymers exhibited close to theoretical M_ns and narrow molecular weight distributions.

Introduction

Controlled ring-opening polymerization of a cyclic ester, such as lactide, glycolide, cyclic carbonate, and/or ϵ -caprolactone (ϵ -CL), attracts much attention because the obtained polymers are biodegradable [1]. ABA type triblock copolymers consisting of elastomeric polyisobutylene (PIB) middle block and styrenic end blocks are valuable thermoplastic elastomers [2]. PIB triblock copolymers with end segments formed from the above cyclic esters are expected to be novel thermoplastic elastomers with semicrystalline, biodegradable end blocks. Therefore, some attempts have already been reported to synthesize block copolymers of IB and lactide [3] or ϵ -CL [4]. Both methods employed HO-telechelic PIB, obtained by hydroboration-oxidation of olefin telechelic PIB, as macroinitiator for the anionic ring opening polymerization of cyclic esters. Recently, we have reported on a synthesis of novel triblock copolymers based on IB and pivalolactone by anionic ring-opening polymerization with carboxyl anion end-functional PIB as macroinitiator [5]. The carboxyl anion, however, is too weak to initiate ring opening polymerization of lactide or ϵ -CL.

In this article, we report a new method for the preparation of hydroxyl end-functional PIB and the synthesis of PIB-PCL diblock and PCL-PIB-PCL triblock copolymers. The block copolymer synthesis involves the combination of living cationic polymerization of IB and living cationic ring-opening polymerization of ϵ -CL *via* the “activated monomer mechanism” as the most powerful method to suppress unfavorable backbiting and transesterification reactions [6,7].

Experimental

Materials

1,1-Diphenylethylene (DPE, Aldrich), 1-methoxy-1-trimethylsiloxy-2-methyl-propene (MTSP, Aldrich), lithium aluminum hydride (LiAlH_4 , Acros), 2,6-di-*tert*-butylpyridine (DTBP, Aldrich), and HCl (Aldrich; 2.0 M solution in diethyl ether) were used as received. 1,1-*p*-Ditolylethylene (DTE) was synthesized according to the reported method [8]. ϵ -CL was distilled over CaH_2 under nitrogen. Tetrahydrofuran (THF) was dried over Na–benzophenone and distilled under dry nitrogen atmosphere. CH_2Cl_2 was distilled sequentially from CaCl_2 and CaH_2 under nitrogen before use. All reactions were carried out in an MBraun 150-M glovebox in glassware dried at 160 °C under a dry nitrogen atmosphere.

Synthesis of hydroxyl end-functional PIB macroinitiator (**PIB-OH**)

PIB having carboxylate end group was synthesized as follows: IB ([IB] = 0.09 M), DTBP ([DTBP] = 0.003 M) as a proton trap, and 2-chloro-2,4,4-trimethylpentane (TMPCl) ([TMPCl] = 0.002 M) as an initiator in hexane/methyl chloride (MeCl) (60/40 v/v) were added to a prechilled 400 mL round flask. The polymerization of IB was initiated by addition of TiCl_4 stock solution ([TiCl_4] = 0.036 M) at -80 °C. After 1 h polymerization, PIB was capped *in-situ* by the addition of 2 equiv. of DPE stock solution. After 1 h capping time, 2 equiv. of MTSP stock solution was added into the reaction mixture. After 1 h reaction time, the reaction mixture was quenched with prechilled methanol and poured into NH_4OH /methanol (10/90 v/v). The obtained methoxycarbonyl end-functional PIB was purified by repeated precipitation from hexane into methanol, followed by drying in vacuum.

Hydroxyl end-functional PIB (**PIB-OH**) was obtained by the reduction of methoxycarbonyl group of the above polymer: To a suspension of LiAlH_4 (1.51 g, 39.8 mmol) in THF (20 mL) a solution of methoxycarbonyl end-functionalized PIB polymer (1.90 g, 0.6 mmol) in THF (20 mL) was added at 0 °C under nitrogen. The resulting solution was stirred at room temperature for 1 h and then refluxed for 50 h. Then, under nitrogen a solution of 2% aqueous H_2SO_4 (30 ml) at 0 °C was added, followed by the addition of hexanes (100 ml). The solution was washed with water and a dilute aqueous sodium bicarbonate solution several times. The organic phase was dried over anhydrous sodium sulfate and concentrated by evaporation. The obtained polymer was precipitated from hexane into methanol, and dried in vacuum at 50 °C.

Synthesis of dihydroxyl end-functional PIB macroinitiator (HO-PIB-OH)

HO-PIB-OH was synthesized using 5-*tert*-butyl-1,3-dicumyl chloride as an initiator for the living cationic polymerization of IB and DTE for the capping, similarly to the synthesis of **PIB-OH**.

*Synthesis of Poly(ϵ -caprolactone-*b*-isobutylene) diblock copolymer (PIB-PCL)*

To ϵ -CL (0.11 g, 1 mmol) a solution of **PIB-OH** (0.1 g, 0.033 mmol) in CH_2Cl_2 (2 mL) was added. The polymerization was initiated by the addition of 2.0 M solution of HCl in diethyl ether (66 μL , 0.132 mmol) at 25 °C. After 24 h, the reaction mixture was poured into methanol to precipitate a polymer, which was separated from the supernatant by decantation and dried in vacuum. The ϵ -CL monomer conversion was determined by ^1H NMR spectroscopy before precipitation with methanol.

*Synthesis of Poly(ϵ -caprolactone-*b*-isobutylene-*b*- ϵ -caprolactone) triblock copolymers*

The triblock copolymer was synthesized using **HO-PIB-OH** as a macroinitiator in a similar manner to that described for **PIB-PCL**.

Characterization

^1H NMR spectra were recorded with a Bruker 250 MHz instrument in CDCl_3 . IR spectra were measured with a PERKIN ELMER FT-IR spectrophotometer 1720X. Molecular weights and molecular weight distributions of the **PIB-OH**, **HO-PIB-OH**, **PIB-PCL**, and **PCL-PIB-PCL** polymers were measured by a Viscotek GPC system (a Model 250 RI/viscosity detector) using five ultrastryragel columns connected in the following series: 500, 10^5 , 10^4 , 10^5 and 100 Å. THF was used as the eluent at a flow rate of 1 mL/min. The M_n of the PCL segment in the copolymers was determined by ^1H NMR spectroscopy from the intensity of the PIB aromatic end group signal at $\delta = 7.6 \sim 7.7$ ppm and the signal of the PCL methylene group at $\delta = 4.10$ ppm. Differential scanning calorimetry (DSC) was performed with a 2910 Modulated DSC (TA Instruments) using a heating/cooling scan rate of 10°C/min in the temperature range from -100 °C to 200 °C.

Result and Discussion

Synthesis of hydroxyl end-functional PIB macroinitiator (PIB-OH)

Living cationic polymerization of IB was carried out with the TMPCl/TiCl_4 initiating system in the presence of DTBP as a proton trap in hexanes/MeCl (60/40 v/v) solvent mixture at -80 °C. Methoxycarbonyl end-functional PIB was synthesized by *in-situ* capping with DPE, followed by quenching with MTSP. **PIB-OH** was finally obtained by reduction of carboxyl end-functional PIB with LiAlH_4 (Scheme 1).

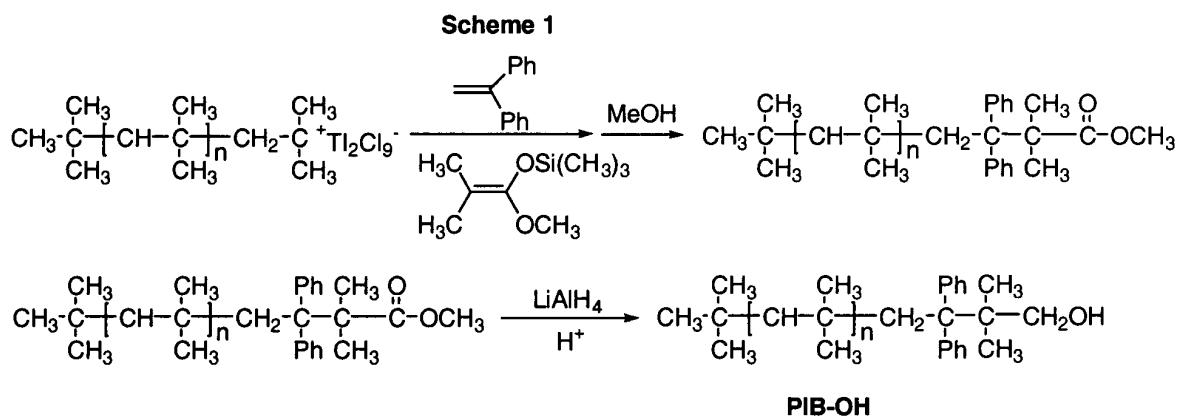


Figure 1 shows the ^1H NMR spectra of the PIB (a) before and (b) after reduction. In the spectrum after reduction, signals *a* and *b* assigned to methylene protons at the chain end appeared at 3.10 and 2.55 ppm, respectively. Moreover, the absorption attributed to C=O of carboxyl group at 1720 cm^{-1} completely disappeared in the IR spectrum after reduction, indicating the quantitative formation of hydroxyl end-functional PIB (**PIB-OH**) ($M_n=3000$, $M_w/M_n=1.09$).

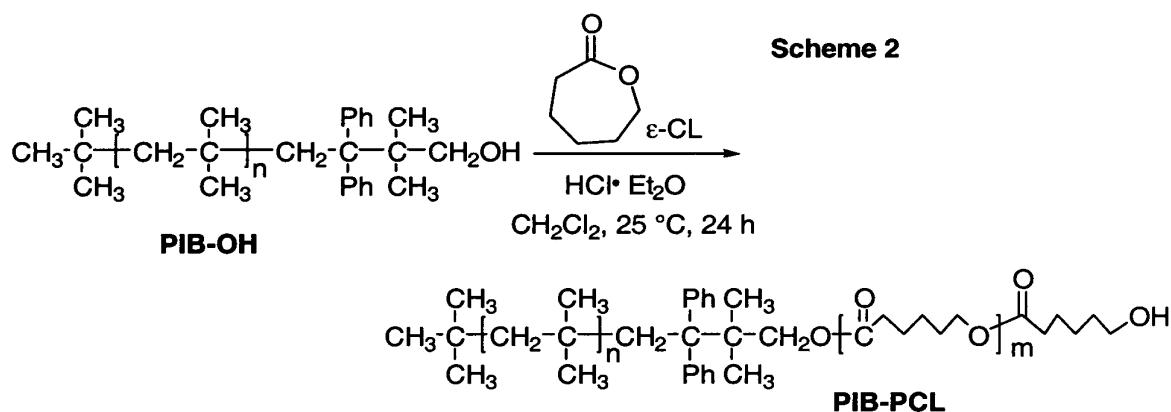
Table 1. M_n and M_w/M_n of poly(ϵ -CL-*b*-IB) diblock copolymers and poly(ϵ -CL-*b*-IB-*b*- ϵ -CL) triblock copolymers ^a

No	Initiator [I]	$[\epsilon\text{-CL}]/[\text{I}]$	Conv. ^d of $\epsilon\text{-CL}$	Yield ^e (%)	M_n , NMR ^d (M_n of $\epsilon\text{-CL}$)	M_w/M_n ^f
D10	PIB-OH ^b	10	100	90	900	1.02
D30		30	100	95	3300	1.10
D100		100	99	98	16700	1.18
T70	HO-PIB-OH ^c	70	97	96	7800	1.05
T90		115	87	86	10500	1.10

^a Condition: in CH_2Cl_2 at $25\text{ }^\circ\text{C}$ for 24 h, $[\epsilon\text{-CL}]=0.5\text{ mol/L}$, $[\text{HCl}]_0/[\text{I}]_0=4$.

^b **PIB-OH** : $M_n=3000$, $M_w/M_n=1.09$. ^c **HO-PIB-OH** : $M_n=3800$, $M_w/M_n=1.05$.

^d Determined by ^1H NMR. ^e Methanol-insoluble part. ^f Determined by GPC.



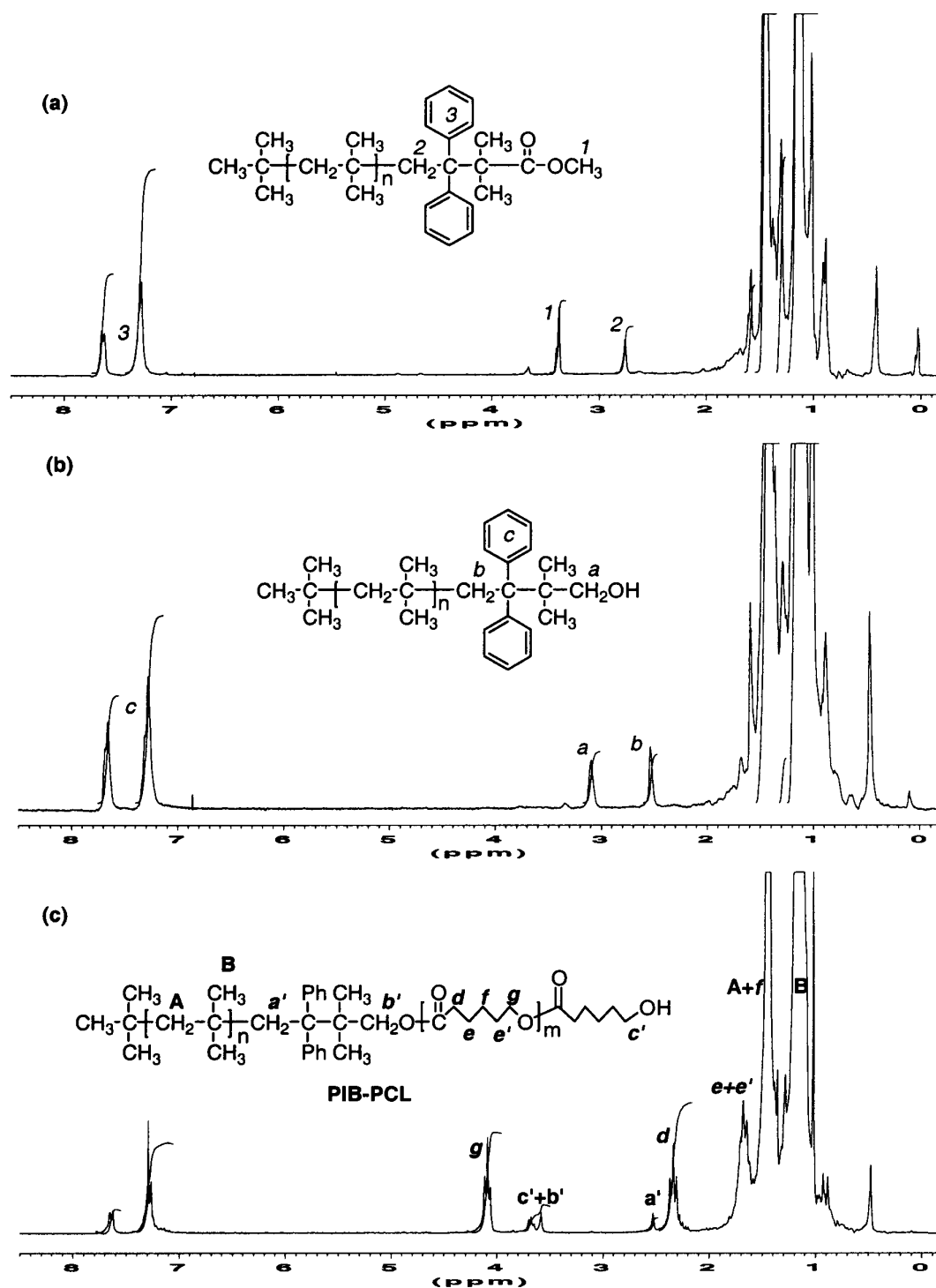


Figure 1. ^1H NMR spectra of the PIB (a) before, (b) after reduction, and (c) PIB-PCL (D10) diblock copolymer obtained by the polymerization of ϵ -CL with **PIB-OH** in the presence of $\text{HCl}\cdot\text{EtO}_2$ in CH_2Cl_2 for 24 h at 25 $^\circ\text{C}$. $[\epsilon\text{-CL}]_0 = 0.5$ M, $[\text{HCl}]/[\text{PIB-OH}]_0 = 4$.

*Synthesis of poly(ϵ -caprolactone-*b*-isobutylene) diblock copolymers*

The polymerization of ϵ -CL was carried out with **PIB-OH** as a macroinitiator in CH_2Cl_2 in the presence of $\text{HCl}\cdot\text{Et}_2\text{O}$ at 25 °C (Scheme 2) [7]. In these polymerizations close to quantitative ϵ -CL conversion was observed and the poly(ϵ -CL-*b*-IB) (**PIB-PCL**) diblock copolymer products were virtually free of homoPCL (Table 1). The GPC charts of **PIB-PCL** diblock copolymers obtained at varied ϵ -CL/**PIB-OH** ratio are shown in Figure 2 (a).

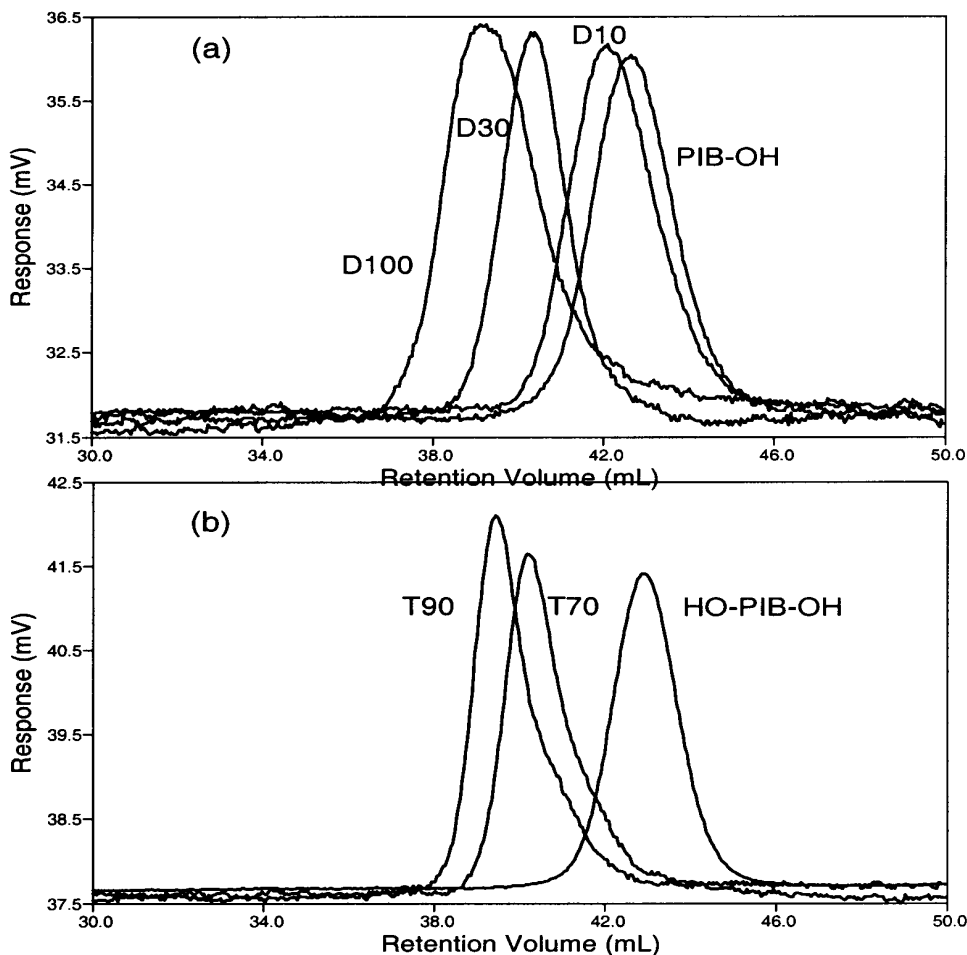


Figure 2. GPC RI traces of (a) **PIB-PCL** diblock copolymers and (b) **PCL-PIB-PCL** triblock copolymers obtained by polymerization of ϵ -CL with **PIB-OH** and **HO-PIB-OH** at 25 °C for 24 h. (D100 trace is that of the purified product.)

Relative to the starting **PIB-OH**, the GPC RI traces of **PIB-PCL** diblock copolymers shifted to higher molecular weight and the molecular weight distribution remained narrow ($\text{PDI} < 1.18$). The GPC RI trace of the crude **PIB-PCL** (D100) diblock copolymer, however, exhibited a small hump at the elution volume of the starting **PIB-OH**.

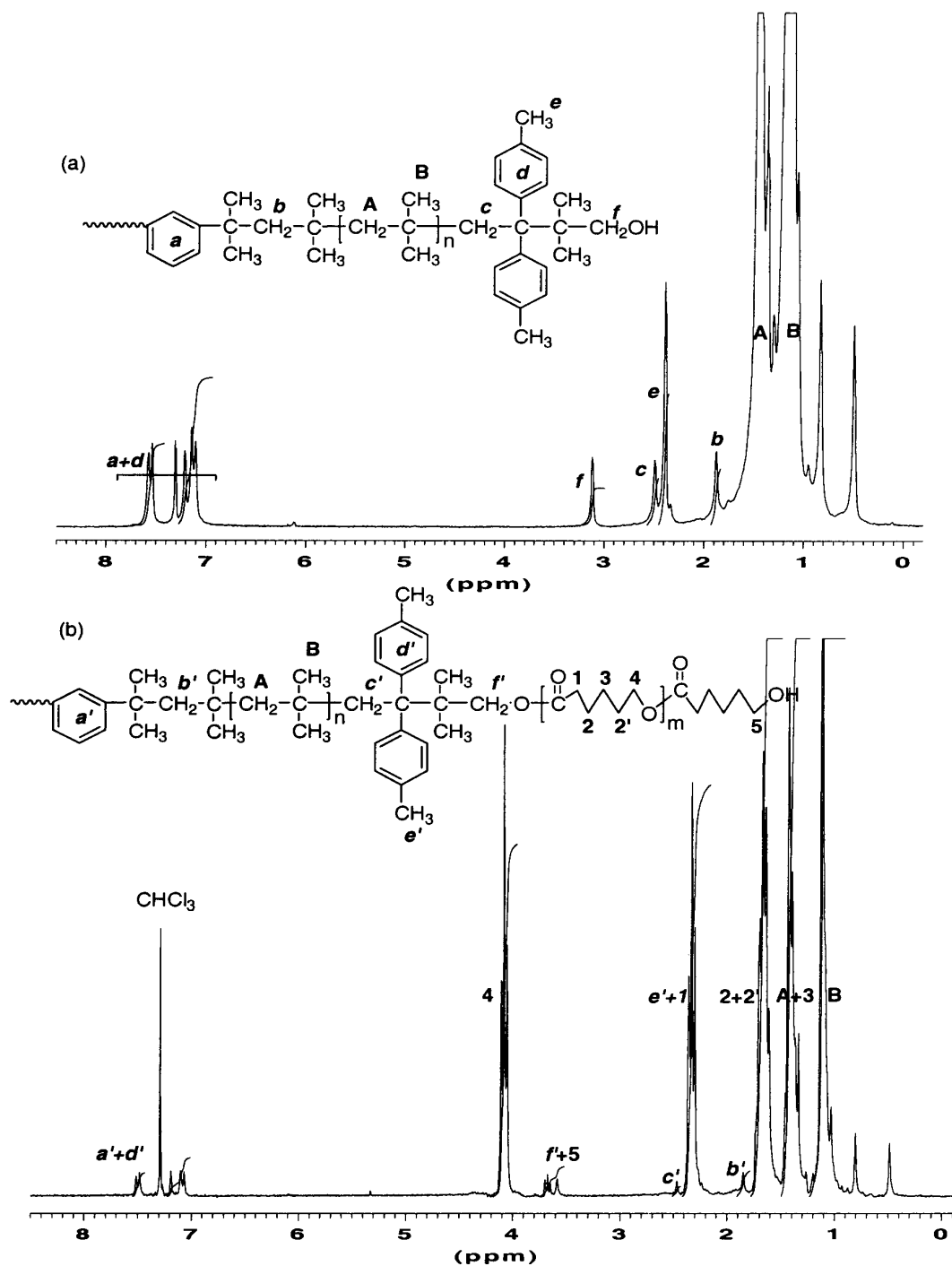


Figure 3. ^1H NMR spectra of the (a) **HO-PIB-OH** after reduction and (b) **PCL-PIB-PCL** (T70) triblock copolymer obtained by the polymerization of $\epsilon\text{-CL}$ with **HO-PIB-OH** in the presence of $\text{HCl}\cdot\text{EtO}_2$ in CH_2Cl_2 for 24 h at 25 °C. $[\epsilon\text{-CL}]_0 = 0.5$ M, $[\text{HCl}]_0/[\text{HO-PIB-OH}]_0 = 4$.

Based on column chromatography on silica gel using hexanes as eluent to separate

homoPIB, the initiation efficiency was estimated to be ~83%. This value agreed well with the number average –OH functionality, $F_n(\text{OH})$ of 0.85 calculated from the ^1H NMR spectrum of **PIB-OH**, attributed to incomplete capping of living PIB with DPE. Figure 1 (c) shows the ^1H NMR spectrum of **PIB-PCL**. The signal of methylene protons ($-\text{CH}_2\text{-OH}$) at 3.10 ppm completely disappeared, while methylene proton signals b' and c' were clearly observed around at 3.6~3.8 ppm, indicating initiation by the hydroxyl group. By DSC the T_g and T_m of **PIB-PCL** diblock copolymers were found to be around at -60 °C and 60 °C, respectively.

Synthesis of dihydroxyl end-functional PIB macroinitiator (HO-PIB-OH)

Methoxycarbonyl telechelic PIB was synthesized from 5-*tert*-butyl-1,3-dicumyl chloride with DTE as a capping reagent to assure complete capping of living PIB followed by end-quenching with MTSP. **HO-PIB-OH** ($M_n=3800$, $M_w/M_n=1.05$, $F_n(\text{OH})=2.0$) was obtained quantitatively after reduction of the end-group with LiAlH_4 . The structure of **HO-PIB-OH** was confirmed by ^1H NMR [Figure 3 (a)] and IR spectroscopy.

*Synthesis of Poly(ϵ -caprolactone-*b*-isobutylene-*b*- ϵ -caprolactone) triblock copolymers*

PCL-PIB-PCL triblock copolymer was obtained by the polymerization of ϵ -CL with **HO-PIB-OH** as macroinitiator in a similar procedure to that described for the synthesis of **PIB-PCL** diblock copolymer. The GPC traces of **PCL-PIB-PCL** triblock copolymers are shown in Figure 2 (b). The obtained **PCL-PIB-PCL** triblock copolymers exhibited narrow molecular weight distribution ($\text{PDI}<1.10$) indicating complete end-functionization of the macroinitiator and the molecular weight of PCL segments were in good agreement with the target molecular weight (Table 1).

Conclusion

In this article, we reported a new synthesis of hydroxyl end-functional PIB that is expected to be applicable for the preparation of high M_n HO- telechelic PIB. Cationic ring opening polymerization of ϵ -CL by the activated monomer mechanism using this macroinitiator is an efficient method, and can afford well-defined PIB-PCL diblock and triblock copolymers. This simple methodology may yield PIB based thermoplastic elastomer with a semicrystalline and biodegradable end segment.

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