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Facile synthesis of diphenylethylene end-functional polyisobutylene and its applications for the synthesis of block copolymers containing poly(methacrylate)s

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Abstract

The convenient synthesis of methoxy-free 1,1-diphenylethylene end-functionalized polyisobutylene (PIB–DPE) has been accomplished by capping living PIB with 1,4-bis(1-phenylethenyl)benzene, followed by hydride transfer reaction with tributylsilane. The proposed method eliminates the need for methylation of the capped living PIB in which large excess of dimethylzinc must be used, resulting in a large amount of inorganic salt contamination. The obtained PIB–DPE was quantitatively lithiated with 1.5-fold excess *n*-butyllithium in tetrahydrofuran (THF) at room temperature. The methine proton at the chain end remained intact during the lithiation procedure. The resulting macroanion efficiently initiated the polymerization of alkyl methacrylates. Poly(methyl methacrylate) (PMMA)-*b*-PIB-*b*-PMMA, poly(2-hydroxyethyl methacrylate) (PHEMA)-*b*-PIB-*b*-PHEMA and poly(*tert*-butyl methacrylate) (P^{t}BMA)-*b*-PIB-*b*-P^{t}BMA have been prepared with high blocking efficiency by the proposed methodology. Complete hydrolysis of P^{t}BMA-*b*-PIB-*b*-P^{t}BMA into poly(methacrylic acid) (PMAA)-*b*-PIB-*b*-PMAA was realized in THF/1,4-dioxane, as confirmed by FTIR, ^{1}H NMR, and DSC analyses.
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Keywords: Block copolymer; Polyisobutylene; Poly(methacrylate)

1. Introduction

Many research efforts have been dedicated to the synthesis of block copolymers due to their potential applications in advanced technologies, such as nanopatterning, drug delivery, etc. [1]. The potential applications of block copolymers are based on their ability to self-assemble, in bulk or in selective solvents, into ordered nanostructures. Conventionally, block copolymers have been synthesized via the sequential living or living/controlled polymerization of different monomers. These polymerization methods include anionic, cationic, controlled radical, ring-opening metathesis and coordination polymerizations [2]. Recently, unique block copolymers not available by a single method have been synthesized by the combination of different polymerization mechanisms [3,4]. Polyisobutylene (PIB) based block copolymers have attracted much attention for biomedical applications due to their superior biostability and biocompatibility [5]. Triblock copolymers comprising IB and polar monomers, such as methacrylates, combine the unique properties of PIB with those of polar polymers. Since IB undergoes only cationic polymerization while methacrylates can be polymerized by anionic or radical polymerization, the combination of cationic and anionic or radial polymerizations is essential for the synthesis of block copolymers consisting of PIB and poly(methacrylate). Many attempts have already been reported to synthesize these block copolymers [6–8]. For instance, Müller et al. reported the synthesis of PIB-*b*-P^{t}BMA and PMMA-*b*-PIB-*b*-PMMA by metalation of DPE end-capped PIB with Na/K alloy or cesium followed by the anionic polymerization of methacrylates [6]. Another attempt demonstrated by Müller et al. involved the preparation of thiophene end-functionalized PIB and the subsequent

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metalation of the polymer chain end with an alkyllithium compound, followed by the polymerization of *tert*-butyl methacrylate with the generated macroanion [7]. Storey and coworkers reported the synthesis of poly(*tert*-butyl acrylate)-*b*-PIB-*b*-polystyrene (PS) triblock and poly(acrylic acid)-*b*-PS-*b*-PIB-*b*-PS-*b*-poly(acrylic acid) pentablock copolymers by the combination of carbocationic and atom transfer radical polymerization techniques [8,9]. In a recent publication, we also reported the synthesis of PIB-*b*-PMMA by a novel coupling approach combining living cationic and anionic polymerization techniques [10]. Bromoallyl end-functionalized PIB (PIB−AllylBr) was coupled with living PMMA anion in THF at −78 °C to yield a PIB-*b*-PMMA diblock copolymer with high coupling efficiency (>95%). Fang and Kennedy reported the synthesis of PIB-*b*-PMAA diblocks, PMAA-*b*-PIB-*b*-PMAA triblocks and three arm star block copolymers by the combination of cationic polymerization and ATRP, followed by the hydrolysis of the corresponding ^{t}BMA block copolymers [11].

The synthesis of poly(alkyl methacrylate)-*b*-PIB-*b*-poly(alkyl methacrylate) was also realized by utilizing a novel site transformation technique from living cationic to living anionic polymerization [12]. This method involved the synthesis of 1,1-diphenylethylene end-functionalized PIB (PIB−DPE) and quantitative lithiation with *n*-butyllithium (*n*-BuLi) at room temperature, followed by initiating the polymerization of methacrylates. PIB−DPE was obtained by the monoaddition of 1,4-bis(1-phenylethyl)benzene (*para*-double diphenylethylene, PDDPE) to living PIB and the subsequent methylation with large excess of dimethylzinc. The use of a large excess of dimethylzinc, however, resulted in a large amount of inorganic salt contamination, which made the purification of the product cumbersome. Therefore, it is desirable to avoid the methylation process. The synthesis of halogen-free PIB was recently reported by hydride transfer reaction between living PIB capped with 1,1-ditolylethylene (PIB−DTE$^+$) and tributylsilane [13]. Preliminary studies showed that the ditolyl methine proton (PIB−DTE−*H*) is stable towards *n*-BuLi at room temperature. Following this concept, herein we report on the synthesis of PIB−DPE by hydride transfer between tributylsilane and the diphenyl carbenium ion generated by a capping reaction of living PIB with PDDPE and its application for the synthesis of PIB−PMA diblock and triblock copolymers.

2. Experimental

2.1. Materials

2-Chloro-2,4,4-trimethylpentane (TMPCl) and 5-*tert*-butyl-1,3-*bis*(1-chloro-1-methylethyl)benzene (^{t}BuDiCumCl) were synthesized according to the literature [14,15]. PDDPE was prepared by using procedures analogous to those reported by Tung and Lo [16]. 2,6-Di-*tert*-butylpyridine (DTBP, Aldrich, 97%), titanium tetrachloride ($TiCl_4$, Aldrich, 99.9%), *n*-butyllithium (*n*-BuLi, FMC lithium, 15 wt% solution in hexanes), 1,1-diphenylethylene (DPE, Aldrich, 97%), chlorotrimethylsilane (Me_3SiCl, Aldrich, 99%), 1,4-dioxane and tributylsilane (Bu_3SiH, Aldrich, 97%) were used as-received. The active concentration of an *n*-BuLi solution was determined by the polymerization of styrene. Tetrahydrofuran (THF, Aldrich, 99+%) and hexanes (Hex) for anionic polymerizations were finally dried by distillation over 1,1-diphenylhexyllithium (DPHLi) on a vacuum line (10^{-6} torr). Methyl methacrylate (MMA, Aldrich, 99%), *tert*-butyl methacrylate (^{t}BMA, Aldrich, 99%) and 2-[(trimethylsilyl)oxy]ethyl methacrylate (TMSHEMA, Gelest, >95%) were distilled over CaH_2 then distilled over triethylaluminum (Aldrich, 1.9 M solution in toluene) on the vacuum line [17]. Hex, methyl chloride (MeCl), methylene dichloride (CH_2Cl_2), and isobutylene (IB, Airgas) were purified as described previously [15].

2.2. Synthesis of DPE monofunctionalized PIB (PIB−DPE)

The preparation of PIB−DPE was carried out at −80 °C under a dry nitrogen atmosphere in an Mbraun 150-M glove box. To a prechilled 500 mL three-neck flask equipped with a mechanical stirrer were added Hex/MeCl (60/40, v/v), TMPCl, DTBP and IB sequentially. $TiCl_4$ was added to polymerize IB. After the completion of the polymerization, 2 equiv. of PDDPE relative to TMPCl dissolved in CH_2Cl_2 was added to the reactor. After 3 h, 5 equiv. of Bu_3SiH to TMPCl was added. The reaction mixture was quenched with prechilled methanol and poured into an excess 10% ammoniacal methanol solution. After the evaporation of solvent, the crude product was dissolved in hexanes and the inorganic salts were removed by filtration. The polymer was dissolved in hexanes again and precipitated into acetone twice.

2.3. Synthesis of DPE difunctionalized PIB (DPE−PIB−DPE)

DPE−PIB−DPE was prepared using ^{t}BuDiCumCl as an initiator for the polymerization of IB in the similar manner as PIB−DPE.

2.4. Synthesis of PIB-b-poly(methacrylate) (PMA) copolymer

The polymerization was carried out in THF at −78 °C under high vacuum ($<10^{-6}$ torr) in a sealed glass reactor with break seals. In a typical experiment, THF (45 mL) was added to a 100 mL round bottom flask equipped with break seals by trap-to-trap distillation over DPHLi. After degassing the solution at −78 °C for 10 min, the apparatus was cut off from a vacuum line by heat-sealing. PIB−DPE (0.63 g, M_n 6300, 0.1 mmol) dissolved in 7 mL of THF was then added. Dilute DPHLi solution was added dropwise to the reactor at room temperature until the color of the polymer solution turned to light red, indicating the absence of protic impurities in the polymer solution. Lithiation was performed by adding 1.5-fold excess *n*-BuLi (0.15 mmol) at room temperature for 10 min. Then, the polymer solution was cooled down to

−78 °C and MMA monomer in THF was added with vigorous stirring to start the polymerization. After the completion of the polymerization of MMA at −78 °C in 30 min, the polymer solution was quenched with 1 mL methanol.

2.5. Synthesis of PMA-b-PIB-b-PMA

The synthesis of triblock copolymer was carried out using DPE−PIB−DPE in the similar manner as PIB-*b*-PMA except that a THF/Hex (70/30 v/v) solvent mixture was used.

2.6. Benzoylation of PHEMA [18]

PHEMA-*b*-PIB-*b*-PHEMA (0.5 g) was dissolved in 6 mL of anhydrous pyridine. Under a nitrogen atmosphere, 4.5 g of benzoic anhydride was added slowly at 0 °C. The reaction mixture was stirred at room temperature for 48 h. The reaction solution was then poured into a large amount of water to precipitate the polymer. The polymer was purified by reprecipitation using THF and methanol twice.

2.7. Hydrolysis of P^{t}BMA-b-PIB-b-P^{t}BMA

Hydrolysis of P^{t}BMA-*b*-PIB-*b*-P^{t}BMA to PMAA-*b*-PIB-*b*-PMAA was performed with 10-fold molar excess of HCl towards ^{t}BMA units in THF/dioxane at reflux temperature for 6 h. Typically, 0.25 g of P^{t}BMA-*b*-PIB-*b*-P^{t}BMA was dissolved in 20 mL THF/1,4-dioxane (2/1 v/v) mixture, and 0.5 mL concentrated HCl solution (60 mmol) was added. The hydrolyzed product was precipitated by pouring the reaction solution into methanol, filtered and then washed with THF before drying in a vacuum oven overnight.

2.8. Nuclear magnetic resonance

^{1}H NMR spectra were measured on a Bruker 500 MHz spectrometer using $CDCl_3$ as a solvent. ^{1}H NMR spectra of solutions in $CDCl_3$ were calibrated to tetramethylsilane (TMS) as an internal standard ($\delta_H = 0.00$).

2.9. Molecular weight characterization

Molecular weights and molecular weight distributions of polymers were measured at room temperature using a Waters HPLC system equipped with a model 510 HPLC pump, model 410 differential refractometer, model 486 UV/visible detector, online multiangle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc.), model 712 sample processor, and five Waters ultraStyragel® columns connected in the series (500, 10^3, 10^4,10^5 and 100 Å). THF was used as an eluent at a flow rate of 1 mL/min. The known d*n*/d*c* values of PIB ($dn/dc = 0.115 \times (1-122/M_n)$) [19] and PMMA ($dn/dc = 0.090$) [20] in THF were used for the determination of absolute molecular weights and molecular weight distributions of polymers from MALLS data. The d*n*/d*c* value of PMMA was used for other PMAs.

2.10. Differential scanning calorimetry

The glass transition temperatures (T_gs) of the triblock copolymers were determined by a DuPont 910 differential scanning calorimeter calibrated with indium for onset temperature and enthalpy change. The samples were heated to 150 °C at 10 °C/min, at 60 °C for 5 min, and then cooled to −90 °C at 10 °C/min. Thermograms were recorded during the second heating cycle from −90 to 160 °C or 280 °C at 10 °C/min.

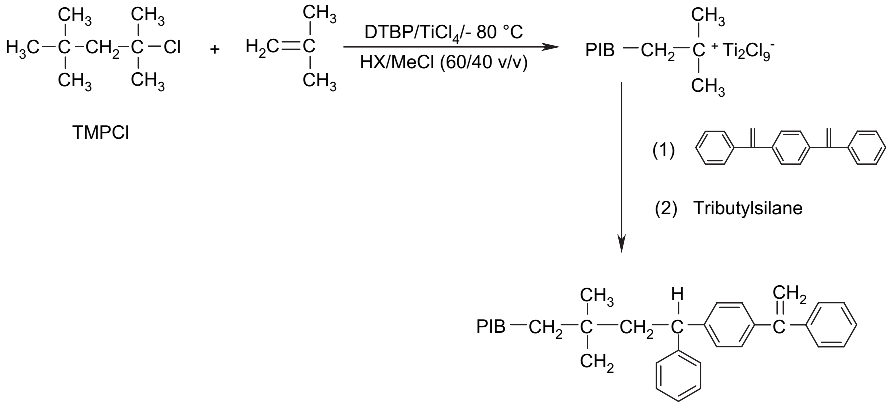
2.11. Mechanical properties

The tensile properties were measured on compression molded samples according to ASTM D638-02a. Compression molding was carried out at 240 °C for 30 min (10 min preheating at 240 °C, 10 min under 4500 psi at 240 °C, followed by 10 min cooling under pressure).

3. Results and discussion

3.1. PIB−DPE−H

The PIB precursor PIB−DPE−H was prepared by capping living PIB with 2-fold excess PDDPE followed by hydride transfer reaction between Bu_3SiH and diphenyl carbenium ion (Scheme 1). First, IB was polymerized by the TMPCl/



Scheme 1. Synthesis of DPE functionalized PIB (PIB−DPE).

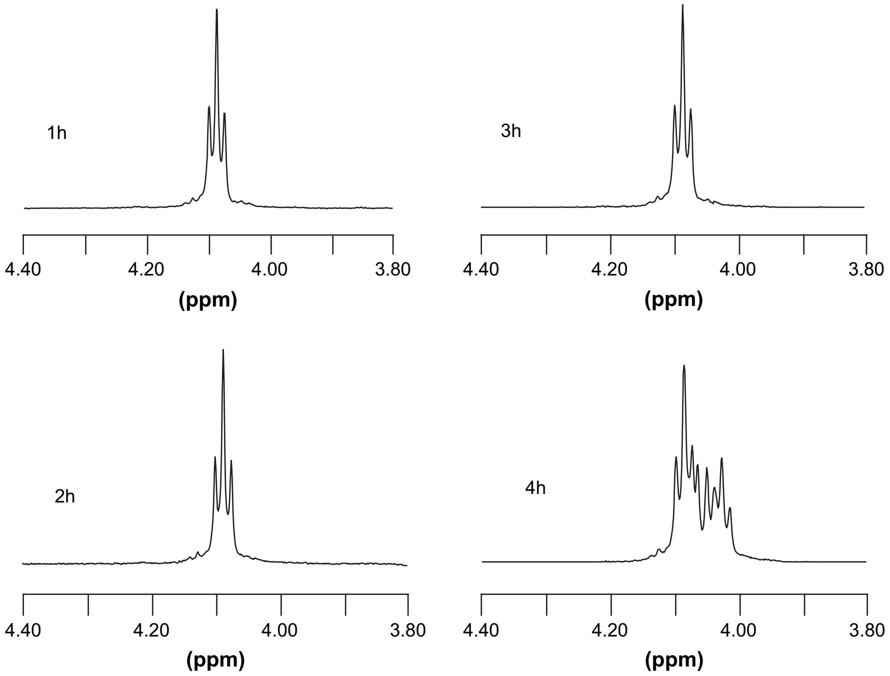


Fig. 1. ^{1}H NMR spectra of PIB–DPE after hydride transfer reaction at methine region using $[Bu_3SiH] = 0.01$ mol L^{-1}.

$TiCl_4$ initiating system in Hex/MeCl 60/40 (v/v) at −80 °C using $[TMPCl] = 0.002$ mol L^{-1}, $[DTBP] = 0.004$ mol L^{-1} and $[TiCl_4] = 0.036$ mol L^{-1}. The polymerization of IB was complete in 75 min. Then the capping agent PDDPE solution ($[PDDPE] = 0.004$ mol L^{-1}) was added to the reaction mixture containing living PIB to form the resulting diphenyl carbenium ion. Previous *in situ* UV–vis spectroscopic studies indicated that quantitative capping reaction can be achieved in 3 h [12]. Quenching diphenyl carbenium ion with methanol exclusively produces a methoxy end functionality. This functionality, however, is labile and therefore undesirable when *n*-BuLi is used to produce polymeric anions. The hydride transfer reaction between the resulting diphenyl carbenium ion and Bu_3SiH was studied in order to form a stable end functionality. To investigate optimal reaction conditions, the hydride transfer reaction was performed using four different Bu_3SiH concentrations of 0.006, 0.01, 0.02 and 0.03 mol L^{-1}. For each concentration, the reaction was run for 1, 2, 3, and 4 h. The reactions at different concentrations showed similar results. Fig. 1 shows the ^{1}H NMR spectra of the products after hydride transfer reaction at the methine region. When the reaction time was less than 3 h, a clean triplet was obtained, and the integration ratio of this triplet over the peak at $\delta = 1.44$ for methylene protons at the PIB main chain agreed very well with the degree of polymerization, indicating quantitative reaction. When the reaction time was 4 h, extra peaks at upper field were observed due to side reactions. It is hypothesized that this side reaction involves addition of Bu_3SiH to the double bond at the DPE chain end. The observed reduced DPE chain-end functionality and NMR simulation support this assumption.

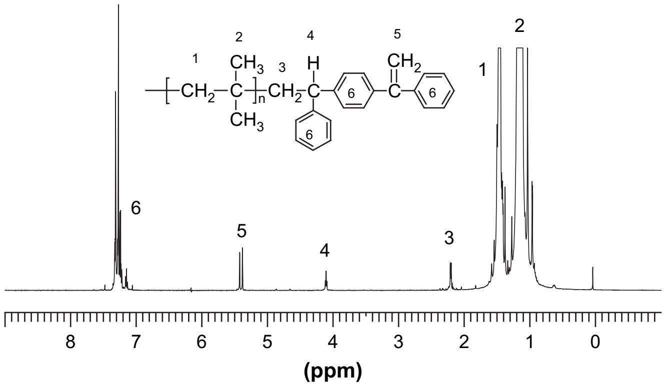


Fig. 2. ^{1}H NMR spectrum of PIB–DPE after hydride transfer reaction at $[Bu_3SiH] = 0.01$ mol L^{-1} for 1 h.

Fig. 2 shows the ^{1}H NMR spectrum of PIB–DPE after the hydride transfer reaction at $[Bu_3SiH] = 0.01$ mol L^{-1} for 1 h. Quenching living PIB diphenyl carbenium ion with methanol prior to hydride transfer reaction yields a methoxy group (PIB–CH$_2$–C(OCH_3)(Ph)–Ph–C(=CH$_2$)–Ph) at the chain end, which exhibits characteristic resonances at $\delta = 3.07$ and 2.50 ppm, corresponding to the methoxy protons and methylene protons next to the methoxy group, respectively. Instead, after the hydride transfer reaction, a new triplet at $\delta = 4.10$ ppm and a doublet at $\delta = 2.20$ ppm appeared, corresponding to the methine proton and the methylene protons (PIB–CH_2–C(H)(Ph)–Ph–C(= CH$_2$)–Ph), respectively. The absence of resonance signals at $\delta = 3.07$ and 2.50 ppm indicates quantitative reaction between Bu_3SiH and diphenyl carbenium ion. In addition, the integration ratio (1:0.51) of peaks at $\delta = 5.35$–5.48 and 4.10 ppm is close to the theoretical ratio (2:1), indicating quantitative chain-end functionalization. The GPC RI trace of PIB–DPE (Fig. 3(A)) shows a monomodal peak together with a very small shoulder (<3%) at the high molecular weight region. This may be attributed to the undesired coupled product generated by the addition of

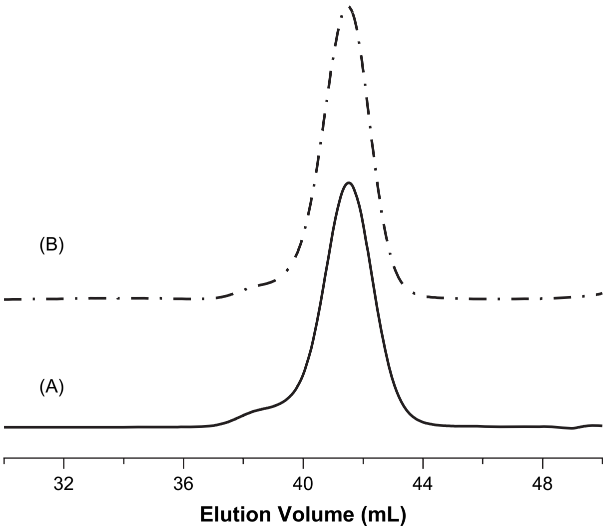


Fig. 3. GPC RI traces of PIB–DPE (A) before and (B) after lithiation.

both double bonds of PDDPE to the living PIB cation. The major fraction of the peak corresponds to the molecular weight, $M_n = 6300$, with low $M_w/M_n = 1.17$. The quantitative functionality can also be confirmed by the good agreement between $M_{n\,(GPC)}$ and $M_{n\,(NMR)}$ (= 5900). This hydride transfer process avoids large amount of inorganic contamination in comparison with the methylation process, simplifying the purification of PIB–DPE. The excess PDDPE and Bu_3SiH can be removed by precipitation of PIB–DPE hexane solution into acetone.

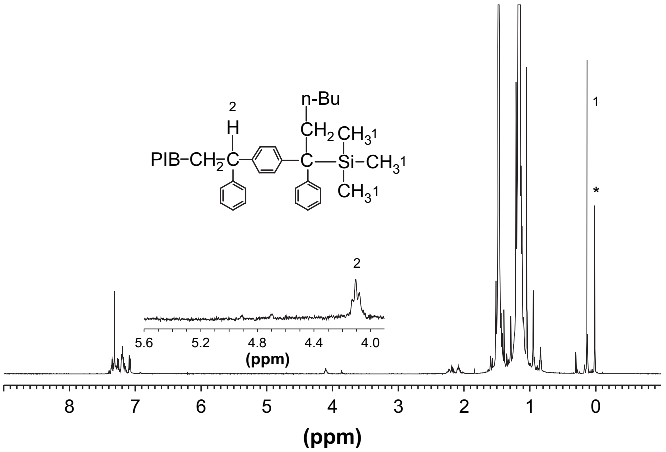


Fig. 4. ^{1}H NMR spectrum of trimethylsilyl-terminated PIB–DPE.

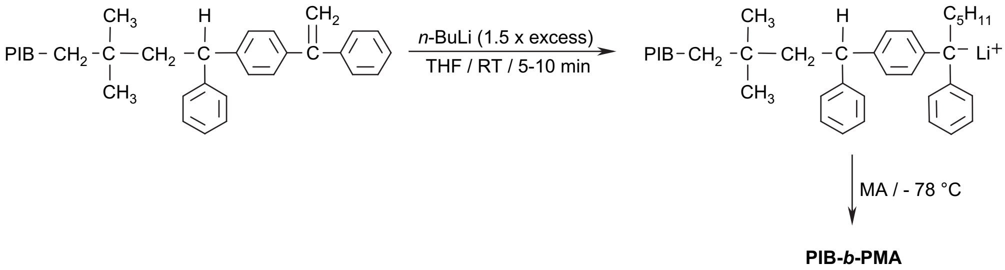
3.2. Lithiation of PIB–DPE

The lithiation of PIB–DPE precursor was performed at room temperature using 1.5-fold excess *n*-BuLi. Prior to the lithiation, a dilute DPHLi solution was added dropwise to the polymer solution until a light red color persisted. The utilization of DPHLi solution as a cleansing agent eliminated the need of critical purification of PIB–DPE precursor. Upon the addition of *n*-BuLi, a deep red color developed immediately, suggesting the instantaneous formation of PIB diphenyl carbanion. After 10 min, Me_3SiCl was added to the solution. The reaction product was analyzed by GPC and NMR spectroscopy. The GPC RI trace remained unchanged after lithiation (Fig. 3), indicating that the main chain remains intact during lithiation. Fig. 4 shows the ^{1}H NMR spectrum of the product after the lithiation. Quantitative lithiation is indicated by the disappearance of the peaks at $\delta = 5.35–5.48$ ppm corresponding to the double bond of DPE moieties. A new peak at $\delta = 0.12$ ppm appeared due to the presence of trimethylsilyl groups, while the methine proton at the chain end remained intact during the lithiation step. Therefore, the resulting PIB diphenyl carbanion can be used effectively for the living anionic polymerization of methacrylates, as demonstrated in the next section.

3.3. Synthesis of PIB-b-PMA

The diblock copolymers containing PMMA, PTMSHEMA or P^{t}BMA as the second blocks were synthesized to investigate the blocking efficiencies. A short PIB block and a longer PMA block were designed so that the peaks of the PIB precursor and diblock copolymer can be separated in the GPC eluogram. The GPC UV trace (254 nm) can be used to calculate blocking efficiencies because it only detects the phenyl rings at the chain end of PIB–DPE.

To prepare the diblock copolymer, the macroinitiator for anionic polymerization was obtained by the reaction of PIB–DPE with 1.5-fold excess *n*-BuLi at room temperature. The polymer solution was kept at room temperature for 10 min before adding methacrylate monomer to start the anionic polymerization at −78 °C (Scheme 2). A dilute DPHLi solution was used as a cleansing agent before lithiation. It is presumed that the slight excess of *n*-BuLi ($<10^{-3}$ M) is decomposed by THF in 10 min at room temperature. The blocking efficiency of PIB-*b*-PMA copolymers determined using the GPC UV trace (254 nm) was 83–91% (see Table 1 and Fig. 5). The application of LiCl was reported to suppress the



Scheme 2. Synthesis of PIB-*b*-PMA copolymer.

Table 1
Blocking efficiencies (B_{eff}) of diblock copolymers[a]

Block copolymer	M_n (block)	M_w/M_n (block)	B_{eff}[b]
IB-*b*-PMMA1	42,600	1.20	83
PIB-*b*-PMMA2[c]	38,200	1.05	85
PIB-*b*-PTMSHEMA	35,600	1.12	85
PIB-*b*-P^{t}BMA	34,100	1.09	91

[a] PIB block: $M_n = 6300$, $M_w/M_n = 1.17$.
[b] Determined by the GPC UV trace (254 nm).
[c] LiCl was added at [LiCl] = 0.006 mol L^{-1}.

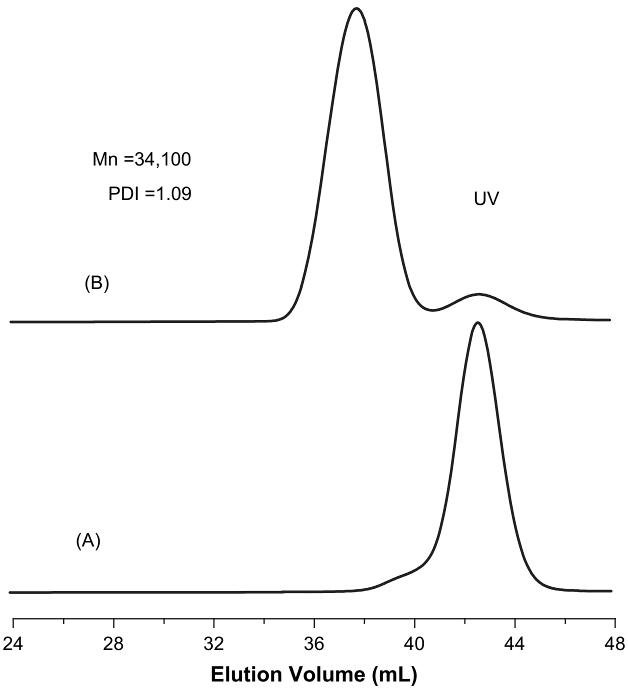


Fig. 5. GPC RI traces of (A) PIB–DPE (M_n 6300, M_w/M_n 1.17), and (B) UV trace of block copolymer PIB-*b*-P^{t}BMA.

backbiting reaction [21], however, the blocking efficiency remained the same with or without LiCl.

3.4. Synthesis of PMMA-b-PIB-b-PMMA, PHEMA-b-PIB-b-PHEMA and P^{t}BMA-b-PIB-b-P^{t}BMA

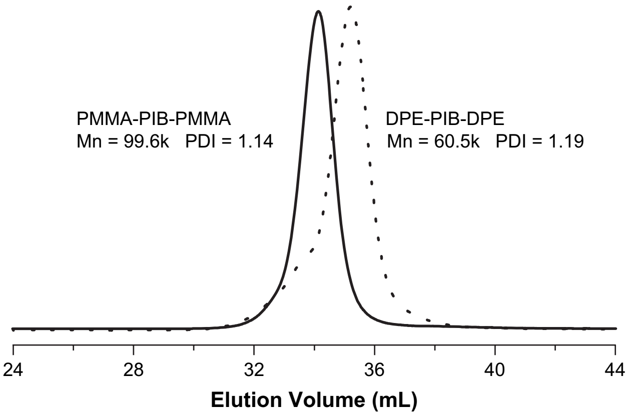


Fig. 6. GPC RI traces of PMMA-*b*-PIB-*b*-PMMA (solid line) and DPE–PIB–DPE (dotted line).

Table 2
M_n and IB wt% of triblock copolymers[a]

Triblock copolymers	M_n	M_w/M_n	IB[b] (wt%)	Deactivated PIB[c] (%)
PMMA-*b*-PIB-*b*-PMMA	99,600	1.14	61.2	1.0
PHEMA-*b*-PIB-*b*-PHEMA[d]	93,200	1.17	64.8	2.4
P^{t}BMA-*b*-PIB-*b*-P^{t}BMA[e]	114,700	1.15	53.5	–
PMAA-*b*-PIB-*b*-PMAA[f]	93,300	1.15	65.0	1.5

[a] PIB block: $M_n = 60{,}500$, $M_w/M_n = 1.19$.
[b] Determined by ^{1}H NMR.
[c] Hexanes' soluble part.
[d] Determined by GPC of the benzoylated derivative and ^{1}H NMR.
[e] Crude product.
[f] Calculated from P^{t}BMA-*b*-PIB-*b*-P^{t}BMA.

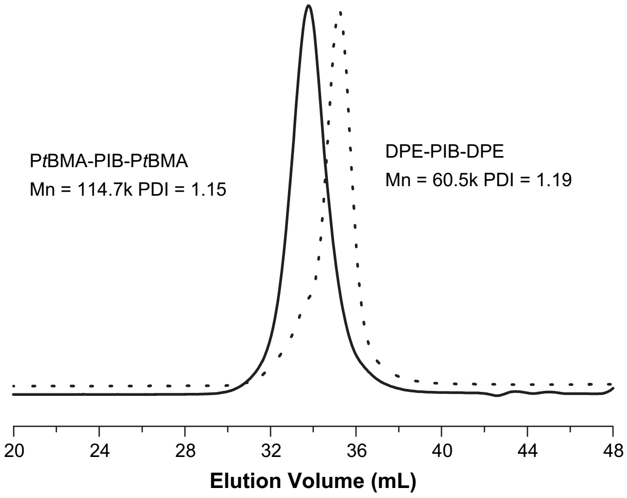


Fig. 7. GPC RI traces of P^{t}BMA-*b*-PIB-*b*-P^{t}BMA (solid line) and DPE–PIB–DPE (dotted line).

DPE–PIB–DPE with high molecular weight was prepared using ^{t}BuDiCumCl as an initiator. The obtained DPE–PIB–DPE ($M_n = 60{,}500$ and $M_w/M_n = 1.19$) showed a small shoulder on the high molecular weight side due to coupled PIB (Fig. 6, dotted line). We assume that the coupled PIB, however, still has DPE moieties at both chain ends. For the synthesis of a triblock copolymer, THF/Hex 70/30 (v/v) mixture solvent was used to increase the solubility of high molecular weight PIB in THF at low temperature. The DPE–PIB–DPE solution was titrated with a dilute DPHLi solution in THF to remove impurities. The macrodianion for the anionic polymerization was obtained in the reaction of DPE–PIB–DPE with 1.5-fold molar excess *n*-BuLi towards DPE moieties at room temperature, followed by the polymerization of MMA, TMSHEMA or ^{t}BMA at −78 °C. The polymer solutions were then poured into a large amount of methanol to isolate polymers. The crude products of PMMA-*b*-PIB-*b*-PMMA and PHEMA-*b*-PIB-*b*-PHEMA were purified by the extraction with hexanes for 24 h to isolate deactivated PIB precursors from triblock copolymers. A small amount of the unreacted PIB (<2.5 wt%) suggested excellent blocking efficiency.

The characterization data of triblock copolymers are summarized in Table 2. The GPC traces are shown in Figs. 6 and 7 for PMMA-*b*-PIB-*b*-PMMA and P^{t}BMA-*b*-PIB-*b*-P^{t}BMA, respectively. As expected, the obtained triblock

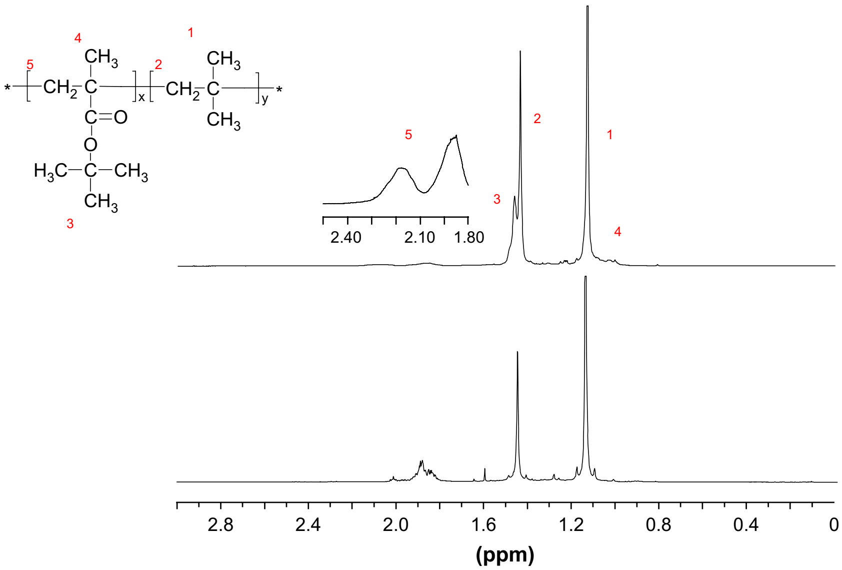


Fig. 8. ^{1}H NMR spectra of P^{t}BMA-*b*-PIB-*b*-P^{t}BMA and PMAA-*b*-PIB-*b*-PMAA.

copolymers exhibited designed molecular weights and narrow molecular weight distributions. Since the trimethylsilyl groups of PTMSHEMA-*b*-PIB-*b*-PTMSHEMA were cleaved during the work-up procedure and the resulting polymer was no longer soluble in THF, the benzoylated sample was used to determine M_n and M_w/M_n. Quantitative benzoylation can be reached at the selected condition [18]. The molecular weight of PHEMA-*b*-PIB-*b*-PHEMA is calculated based on its structure and the molecular weight of the benzoylated sample.

The compositions of triblock copolymers were calculated from ^{1}H NMR results. Again, the composition for PHEMA-*b*-PIB-*b*-PHEMA is based on the benzoylated samples. Fig. 8 (top) shows the ^{1}H NMR spectrum of P^{t}BMA-*b*-PIB-*b*-P^{t}BMA. The resonance of *tert*-butyl protons at $\delta = 1.46$ ppm is overlapped with that of methylene protons of PIB at $\delta = 1.44$ ppm. The signal for methyl protons of PIB is not well separated from that for methyl protons in P^{t}BMA. However, the composition can still be determined from the integration ratio of (signal 2 + signal 3)/(signal 1 + signal 4).

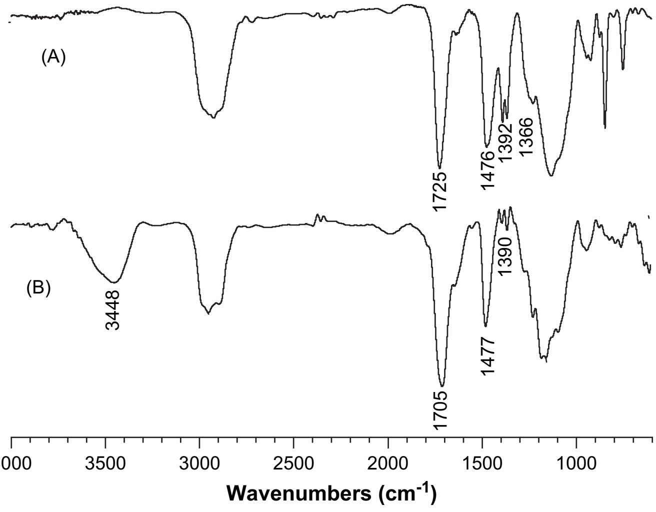


Fig. 9. FTIR spectra of (A) P^{t}BMA-*b*-PIB-*b*-P^{t}BMA and (B) PMAA-*b*-PIB-*b*-PMAA.

3.5. Hydrolysis of P^{t}BMA-b-PIB-b-P^{t}BMA into PMAA-b-PIB-b-PMAA

Amphiphilic block copolymers containing polyacid segment have found applications in colloid chemistry [22,23]. The strategy to prepare block copolymers containing a polyacid segment is usually to use a protected monomer for the polymerization followed by deprotection. This technique requires easy removal of the protecting groups. For example, P^{t}BMA is widely used as a precursor of poly(methacrylic acid) (PMAA) [11,12]. The quantitative hydrolysis of PMAA-*b*-PIB-*b*-PMAA can be accomplished using HCl solution in 1,4-dioxane when the molecular weight of PIB segment is low. Unfortunately, high molecular weight PIB is insoluble in 1,4-dioxane. Kennedy and his coworker reported successful hydrolysis of P^{t}BMA-*b*-PIB-*b*-P^{t}BMA in CH_3Cl/1,4-dioxane (2/1, v/v) with HCl [11]. Complete hydrolysis of our sample, P^{t}BMA-*b*-PIB-*b*-P^{t}BMA, was accomplished in THF/1,4-dioxane (2/1, v/v) at reflux temperature for 6 h. The FTIR spectra of P^{t}BMA-*b*-PIB-*b*-P^{t}BMA and PMAA-*b*-PIB-*b*-PMAA are shown in Fig. 9. The new absorbance at around 3500 cm^{-1} corresponds to O–H stretch (ν_{OH}) in PMAA. Since hydrogen bonding lowers the carbonyl group band frequency [24], the shift of the carbonyl stretch ($\nu_{C=O}$) from 1725 to 1705 cm^{-1} indicates close to complete hydrolysis. The doublet at 1392 and 1366 cm^{-1} characteristic of the *tert*-butyl group almost completely diminished after hydrolysis, supporting essentially quantitative hydrolysis of P^{t}BMA into PMAA.

The prepared PMAA-*b*-PIB-*b*-PMAA was also characterized by DSC. As shown in Fig. 10, two T_gs are observed in the DSC thermograms for P^{t}BMA-*b*-PIB-*b*-P^{t}BMA and PMAA-*b*-PIB-*b*-PMAA, indicating phase separation in both cases. The T_g for the PIB segment was detected at around −65 °C. The T_gs

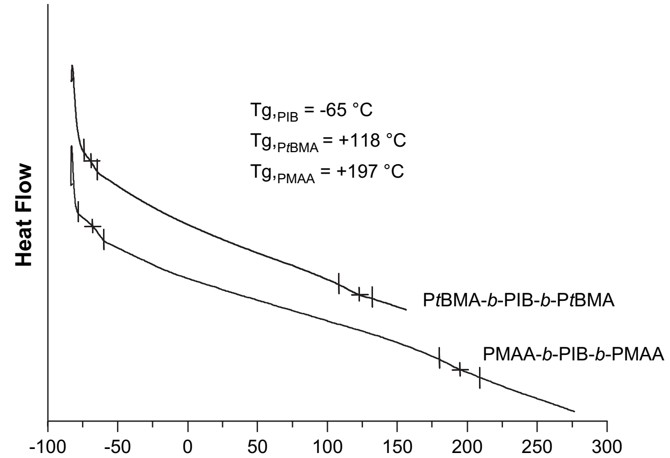


Fig. 10. DSC thermograms of P^{t}BMA-*b*-PIB-*b*-P^{t}BMA and PMAA-*b*-PIB-*b*-PMAA.

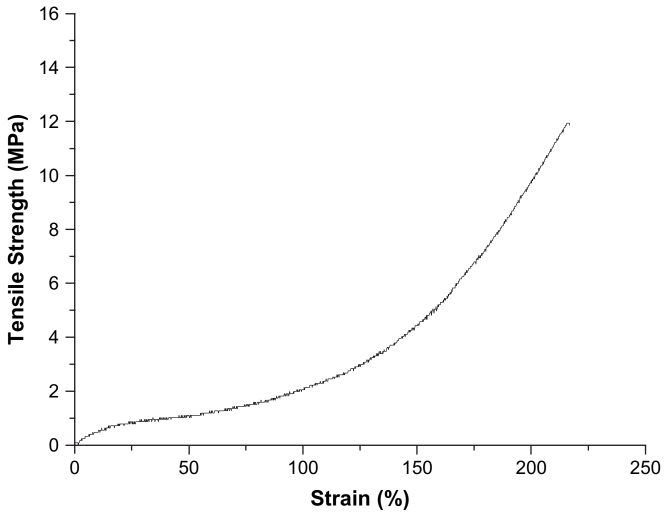


Fig. 11. Stress–strain plot of PMAA-*b*-PIB-*b*-PMAA.

for P^{t}BMA and PMAA blocks were observed at 118 and 197 °C, respectively. These values are close to the T_gs reported for the corresponding homopolymers [25]. The DSC results further support the efficient hydrolysis of P^{t}BMA-*b*-PIB-*b*-P^{t}BMA.

The tensile strength of PMAA-*b*-PIB-*b*-PMAA triblock copolymer was measured on compression molded films as shown by the stress–strain plot in Fig. 11. The sample exhibited 11.9 MPa in tensile strength and 220% elongation at break. The tensile strength is similar to that of the compression molded sample of PMMA-*b*-PIB-*b*-PMMA triblock copolymer (10.5 MPa) as previously reported by us [12]. However, the elongation at break is somewhat lower. Since there is little diblock contamination by the fact that only small amounts of homoPIB (1.5 wt%) was extracted, the low elongation may be attributed to insufficient microphase separation.

4. Conclusions

The synthesis of methoxy-free DPE end-functionalized PIB could be accomplished by capping living PIB with PDDPE followed by subsequent hydride transfer reaction with Bu_3SiH. The methine proton at PIB–DPE chain end is stable towards *n*-BuLi at room temperature in THF. The lithiation of PIB–DPE or DPE–PIB–DPE with 1.5-fold excess *n*-BuLi at room temperature is quantitative and the resulting macroanion could efficiently initiate the polymerization of methacrylate monomers. PMMA-*b*-PIB-*b*-PMMA, PHEMA-*b*-PIB-*b*-PHEMA and P^{t}BMA-*b*-PIB-*b*-P^{t}BMA have been prepared with high blocking efficiency. Complete hydrolysis of P^{t}BMA-*b*-PIB-*b*-P^{t}BMA into PMAA-*b*-PIB-*b*-PMAA was realized in THF/1,4-dioxane with HCl. This methodology avoids a methylation process using large excess of dimethylzinc and is suggested to be the most convenient for the synthesis of PIB–PMA block copolymers.

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References

[1] Almdal K. In: Hawley IW, editor. Developments in block copolymer science and technology. John Wiley & Sons Ltd; 2004 [chapter 2].
[2] Hadjichristidis N, Pitsikalis M, Iatrou H. Adv Polym Sci 2005;189:1–124.
[3] Yagci Y, Tasdelen MA. Prog Polym Sci 2006;31:1133–70.
[4] Bernaerts KV, Du P, Filip E. Prog Polym Sci 2006;31:671–722.
[5] Stone GW, Ellis SG, Cox DA, Hermiller J, O'Shaughnessy C, Mann JT, et al. N Engl J Med 2004;350:221–31.
[6] Feldthusen J, Ivan B, Müller AHE. Macromolecules 1998;31:578–85.
[7] Martinez-Castro N, Lanzendoerfer MG, Müller AHE, Cho JC, Acar MH, Faust R. Macromolecules 2003;36:6985–94.
[8] Breland LK, Murphy JC, Storey RF. Polymer 2006;47:1852–60.
[9] Storey RF, Scheuer AD, Achord BC. Polymer 2006;46:2141–52.
[10] Higashihara T, Feng D, Faust R. Macromolecules 2006;39:5275–9.
[11] Fang Z, Kennedy JP. J Polym Sci Part A Polym Chem 2002;40:3662–78.
[12] Cho JC, Cheng G, Feng D, Faust R, Richard R, Schwarz M, et al. Biomacromolecules 2006;7:2997–3007.
[13] De P, Faust R. Polym Bull 2006;56:27–35.
[14] Fodor Z, Gyor M, Wang HC, Faust R. J Macromol Sci Pure Appl Chem 1993;A30:349–63.
[15] Hadjikyriacou S, Faust R. Macromolecules 1996;29:5261–7.
[16] Tung LH, Lo GY-S. US Patent 4,182,818; 1980.
[17] Allen RD, Long TE, McGrath JE. Polym Bull 1986;15:127–34.
[18] Hirao A, Kato H, Yamaguchi K, Nakahama S. Macromolecules 1986;19:1294–9.
[19] Chance RR, Baniukiewicz SP, Mintz D, Ver Strate G, Hadjichristidis N. Int J Polym Anal Charact 1995;1:3–34.
[20] Andrews RJ, Grulke EA. In: Brandrup J, Immergut EH, Grulke EA, Abe A, Bloch DR, editors. Polymer handbook. 4th ed. New York: Wiley; 1998. p. VII/432.
[21] Wang JS, Jerôme R, Warin R, Teyssié P. Macromolecules 1993;26:5984–90.
[22] Hautekeer JP, Varshney SK, Fayt R, Jacobs C, Jerôme R, Teyssié P. Macromolecules 1990;23:3893–8.
[23] Zhang LF, Shen HW, Eisenberg A. Macromolecules 1997;30:1001–11.
[24] Crews P, Rodriguez J, Jaspars M. Organic structural analysis. Oxford University Press; 1998 [chapter 8].
[25] Andrews RJ, Grulke EA. In: Brandrup J, Immergut EH, Grulke EA, Abe A, Bloch DR, editors. Polymer handbook. 4th ed. New York: Wiley; 1998. p. VI/201.