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ARTICLE

Syntheses and Characterization of Polyisobutylene Macromonomers with Methacrylate, Acrylate, Glycidyl Ether, or Vinyl Ether End-Functionality

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ABSTRACT: The syntheses of new polyisobutylene macromonomers with methacrylate, acrylate, vinyl ether, and glycidyl ether end-functionality have been accomplished using simple nucleophilic substitution reactions of bromoallyl end-functional polyisobutylene. Use of a phase transfer catalyst tetrabutylammonium bromide significantly increased the rate of substitution reactions. The macromonomers were characterized by ^{1}H, COSY, and ^{13}C NMR spectroscopic, GPC, and MALDI-TOF MS analyses. The end-functionality was calculated to be ~2 in all the cases. The GPC-RI traces were identical to the precursor bromoallyl telechelic PIB, indicating the absence of side reactions affecting the chain length in the corresponding substitution reactions.

Introduction

Polyisobutylene (PIB)-based networks and graft copolymers have gained substantial attention in recent times owing to their many important applications such as controlled drug delivery matrixes, polymeric surfactants, compatibilizers, surface modifiers, and scaffolds for tissue engineering.[1] For instance, Ivan et al. reported amphiphilic networks based on methacryloyl end-capped telechelic PIB that possessed controlled drug release abilities.[2] PIB-toughened poly(methyl methacrylate) (PMMA) networks have also found application as bone cements.[3] Polymeric networks based on acrylate (Acr) end-capped PIB are useful as microprocessor and medical device coatings since they possess strong adherence to the substrate, flexibility, thermal stability, and impermeability to moisture.[4] Radiation curable coatings based on vinyl ether end-functional PIB exhibited high refractive index, good adhesion, dampening, and barrier properties and could be used for encapsulating electronic devices and as high refractive index coatings for optical fibers.[5] The incorporation of PIB as rubbery segment into epoxy networks[6] greatly reduces the brittleness and moisture sensitivity of conventional epoxy resins.[7] Thus, networks based on epoxy functional PIB find widespread application as chemical resistance coatings, underwater paints, coatings subject to humid environments, and wire insulation.[8]

The synthesis of such advanced materials relies on well-defined telechelic polymers with controlled molecular weight and narrow molecular weight distribution. Previously reported synthetic routes to the above PIB macromonomers, however, are cumbersome and involve expensive transformations. For example, Ivan and co-workers have reported Acr or methacrylate (MA) telechelic PIB by hydroboration and oxidation of allyl end-capped PIB followed by esterification with acryloyl or methacryloyl chloride.[9] Kennedy et al. reported the synthesis of glycidyl ether end-functional PIB from phenol end-capped PIB using a multistep synthetic procedure[10] utilizing a large excess of epichlorohydrine to avoid a concomitant side reaction of phenoxide ion with epoxy end-group of the resulting polymer. Epoxidation of allyl end-functional PIB offered another method to prepare epoxy end-capped PIB.[11] Similarly, PIB chloride was treated with *n*-BuLi/*t*-BuOK followed by chloroethyl vinyl ether to obtain vinyl ether end-functional PIB.[12]

Faust and co-workers have recently reported the synthesis of haloallyl functional PIBs, which offers a promising new route to obtain functional PIBs by simple nucleophilic substitution reactions as exemplified by syntheses of various end-functional PIBs.[13,14] In this article the syntheses and characterization of Acr, MA, vinyl ether (VE), and epoxy (EP) end-functional PIBs are reported. These macromonomers were obtained with quantitative functionality using a one-step S$_N$2 reaction utilizing inexpensive reagents.

Experimental Section

Materials. Sodium methacrylate (Aldrich, 99%), sodium acrylate (Aldrich, 97%), glycidol (Aldrich, 96%), ethylene glycol vinyl ether (Aldrich, 97%), *N*,*N*-dicyclohexylcarbodimide (DCC, Alfa Aesar, 99%), tetra-*n*-butylammonium bromide (TBAB, Aldrich, 99%), sodium hydride (NaH, Aldrich, 60% dispersion in mineral oil), potassium hydroxide (KOH, Aldrich), sodium sulfate (Na$_2$SO$_4$, Aldrich), and 1,4-benzoquinone (Aldrich, 98%) were used as received. Hexanes (Hex, Doe & Ingals, Technical grade) and methanol (Doe & Ingals, Technical grade) were purified by refluxing over sulfuric acid for 24 h. They were washed with aqueous solution of KOH three times followed by distilled water. Then they were stored over sodium sulfate overnight at room temperature. Finally, they were distilled over CaH$_2$ under a nitrogen atmosphere before use. Tetrahydrofuran (THF, Aldrich, 99%) was refluxed over sodium metal and benzophenone overnight and distilled under a nitrogen atmosphere prior to use. In a typical purification procedure, the polymer (~200 mg) was dissolved in 2 mL of hexanes. The solution was added to 10 mL of methanol and kept undisturbed until the entire polymer settled down. The supernatant liquid was slowly decanted, and the same procedure was repeated with the precipitate three times. Finally, the precipitate was dried under vacuum at room temperature for 12 h.

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Measurements. ^{1}H and ^{13}C NMR spectroscopy for structural analysis was carried out on a Bruker 500 MHz spectrometer using $\mathrm{CDCl_3}$ (Cambridge Isotope Laboratories, Inc.) as a solvent. ^{1}H or ^{13}C NMR spectra of solution in $\mathrm{CDCl_3}$ were calibrated to tetramethylsilane (TMS) as internal standard (δ H or δ C 0.00). Absolute molecular weights were measured with a Waters HPLC system equipped with a model 510 HPLC pump, a model 410 differential refractometer (λ = 930 nm), a model 441 absorbance detector (λ = 254 nm), an online MALLS detector (MiniDawn, Wyatt Technology Inc., 120 V; three angles: 45°, 90°, and 135°; λ = 690 nm), a model 712 sample processor, and five Styragel HR GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. THF was used as an eluant at a flow rate of 1.0 mL/min at room temperature. MW and PDI data were calculated based on MALLS and RI with the ASTRA 4.9 software (Wyatt Technology Inc.). Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was carried out on a micromass M@LDI MALDI-TOF-MS (Waters Corp.) equipped with a 337 nm $\mathrm{N_2}$ laser for end-group analysis. All spectra were obtained in the positive ion mode using an accelerating voltage of 15 kV and low laser frequency. The sample was recorded in linear mode, and the average mass of each peak is reported to a dalton. The source voltage and delay time were optimized to achieve maximum signal-to-noise ratio. External calibration was performed using polystyrene standards (M_n = 2000 and 1600 Da, Polysciences, Inc.). The matrix solution was prepared by dissolving dithranol in THF at a concentration of 20 mg/mL. $\mathrm{CF_3COOAg}$ (AgTFA) was dissolved in THF (10 mg in 1 mL) to prepare the stock solution. The polymer solution was made by dissolving 10 mg in 1 mL of THF. The polymer, dithranol, and AgTFA solution were mixed in 10:10:1 volume ratio, and 1 μL of the resulting solution was evaporated on the sample holder.

Synthesis of Methacrylate (MA)−PIB−MA. Bromoallyl-telechelic PIB (M_n = 2200, PDI = 1.16, 200 mg, 0.09 mmol) was dissolved in dry THF (10 mL) and was added into a two-necked glass reactor followed by the addition of sodium methacrylate (500 mg, 4.6 mmol), DCC (350 mg, 1.69 mmol), TBAB (1.92 g, 5.9 mmol), and 1,4-benzoquinone (5 mg, 0.005 mmol); the mixture was refluxed under a dry nitrogen atmosphere for 6 h. The reaction mixture was cooled to room temperature, and THF was evaporated using a rotary vacuum evaporator. The residue was dissolved in hexanes, the solution was filtered, and the filtrate (polymer solution) was precipitated in methanol. The polymer was allowed to settle down. The supernatant liquid was decanted, and the sticky mass was dried under vacuum at room temperature for 12 h. Gravimetric yield: 98%. ^{1}H NMR ($\mathrm{CDCl_3}$, ppm, δ): 4.6 (d, 2H, $\mathit{C}\boldsymbol{H}_2\mathrm{OCOCH_3C{=}CH_2}$), 5.65 (m, 1H, $-\mathit{C}\mathrm{H{=}C}\boldsymbol{H}\mathrm{CH_2OCOCH_3C{=}CH_2}$), 5.85 (m, 1H, $-\mathit{C}\boldsymbol{H}{=}\mathit{C}\mathrm{H}\mathit{C}\mathrm{H_2OCOCH_3C{=}CH_2}$), 5.6 and 6.15 (s, 2H, $-\mathrm{C}\boldsymbol{H}_2$), 2.0 (s, 3H$-\mathrm{C}\boldsymbol{H}_3\mathrm{C{=}CH_2}$). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm, δ): 167 ($\mathrm{O}\boldsymbol{C}\mathrm{OCH_3C{=}CH_2}$), 149 ($=\boldsymbol{C}$, Ar), 148.5 ($\boldsymbol{C}\mathrm{{=}CH}$, Ar), 137 ($-\mathrm{CH_3}\boldsymbol{C}\mathrm{{=}CH}$), 133.5 ($-\mathit{C}\mathrm{H}{=}\boldsymbol{C}\mathrm{H}\mathit{C}\mathrm{H_2OCOCH_3C{=}CH_2}$), 126.5 ($-\mathrm{CH_3C}{=}\boldsymbol{C}\mathrm{H_2}$), 125 ($\boldsymbol{C}\mathrm{H{=}CH}\ \mathit{C}\mathrm{H_2OCOCH_3}\mathit{C}\mathrm{{=}CH_2}$), 121 ($-\boldsymbol{C}\mathrm{H{=}C}$, Ar), 120 ($-\boldsymbol{C}\mathrm{H{=}C}$, Ar), 65.5 ($\boldsymbol{C}\mathrm{H_2OCOCH_3C{=}CH_2}$).

Synthesis of Acrylate (Acr)−PIB−Acr. Bromoallyl-telechelic PIB (M_n = 2200, PDI = 1.16, 200 mg, 0.09 mmol) was dissolved in dry THF (10 mL) and was added into a two-necked glass reactor followed by the addition of sodium acrylate (500 mg, 5.3 mmol), DCC (350 mg, 1.69 mmol), TBAB (1.92 g, 5.9 mmol), and 1,4-benzoquinone (5 mg, 0.005 mmol). The mixture was refluxed under a dry nitrogen atmosphere for 6 h. The reaction mixture was cooled to room temperature, and THF was evaporated. The residue was dissolved in hexanes, the solution was filtered, and the filtrate (polymer solution) was precipitated in methanol. The polymer was allowed to settle down at the bottom. The supernatant liquid was decanted, and the sticky mass was dried under vacuum at room temperature for 12 h. Yield: 100%. ^{1}H NMR ($\mathrm{CDCl_3}$, ppm, δ): 4.65 (d, 2H, $\mathit{C}\boldsymbol{H}_2\mathrm{OCOCH{=}CH_2}$), 5.60 (m, 1H, $-\mathit{C}\mathrm{H}{=}\mathit{C}\boldsymbol{H}\mathit{C}\mathrm{H_2OCOCH{=}CH_2}$), 5.85 (m, 1H, $-\mathit{C}\boldsymbol{H}{=}\mathit{C}\mathrm{H}$-$\mathit{C}\mathrm{H_2OCOCH{=}CH_2}$), 5.85 (s, 1H,$-\mathrm{C}\boldsymbol{H}$), 6.15 (m, 1H, $\mathrm{C}\boldsymbol{H}\mathrm{{=}CH_2}$), 6.4 (d, 1H, $-\mathrm{C}\boldsymbol{H}$). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm, δ): 166 ($\mathrm{O}\boldsymbol{C}\mathrm{OCH{=}CH_2}$), 149 ($=\boldsymbol{C}$, Ar), 148.5 ($\boldsymbol{C}\mathrm{{=}CH}$, Ar), 134 ($\mathit{C}\mathrm{H}{=}\boldsymbol{C}\mathrm{H}\mathit{C}\mathrm{H_2OCOCHC{=}CH_2}$), 128.5 ($-\boldsymbol{C}\mathrm{H{=}CH_2}$), 131 ($-\mathrm{CH}{=}\boldsymbol{C}\mathrm{H_2}$), 126 ($\boldsymbol{C}\mathrm{H{=}CH}\mathit{C}\mathrm{H_2OCOCHC{=}CH_2}$), 121 ($-\boldsymbol{C}\mathrm{H{=}CH}$, Ar), 120 ($-\boldsymbol{C}\mathrm{H{=}C}$, Ar), 65.5 ($\boldsymbol{C}\mathrm{H_2OCOCHC{=}CH_2}$).

Synthesis of 2,3-Epoxy-1-propoxy (EP)−PIB−EP. Bromoallyl-telechelic PIB (M_n = 2200, PDI = 1.16, 200 mg, 0.09 mmol) was dissolved in dry THF (15 mL). Glycidol (370 mg, 5 mmol), NaH (80 mg, 3.33 mmol), and TBAB (1.61 g, 5 mmol) were added, and the mixture was refluxed under a dry nitrogen atmosphere for 6 h. The reaction mixture was cooled to room temperature, and THF was evaporated. The residue was dissolved in hexanes, the solution was filtered, and the filtrate was reprecipitated in methanol. The product obtained was further purified by dissolution and reprecipitation using hexanes and methanol. The product polymer was finally dried under vacuum at room temperature. Yield: 95%. ^{1}H NMR ($\mathrm{CDCl_3}$, ppm, δ): 4.05 (m, 2H, $\mathit{C}\boldsymbol{H}_2\mathrm{OCH_2(CHOCH_2)}$)), 5.55 (m, 1H, $\mathrm{CH}{=}\mathrm{C}\boldsymbol{H}\mathit{C}\mathrm{H_2OCH_2(CHOCH_2)}$)), 5.75 (m, 1H, $-\mathrm{C}\boldsymbol{H}\mathrm{{=}CH}\mathit{C}\mathrm{H_2}$-$\mathrm{OCH_2(CHOCH_2)}$)), 3.7 and 3.4 (d, 2H, $-\mathrm{OC}\boldsymbol{H}_2\mathrm{(CH_2OCH)}$)), 3.2 (m, 1H, $-(\mathrm{C}\boldsymbol{H}\mathrm{OCH_2}$), 2.8 and 2.6 (m, 1H, $(\mathrm{CHOC}\boldsymbol{H_2}$)). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm, δ): 149 ($\boldsymbol{C}\mathrm{{=}CH}$, Ar), 148.5 ($-\boldsymbol{C}\mathrm{{=}CH}$, Ar), 132.5 ($\mathrm{CH}{=}\boldsymbol{C}\mathrm{H}\mathit{C}\mathrm{H_2OCH_2(CHOCH_2)}$)), 128 ($-\boldsymbol{C}\mathrm{{=}CH}$, Ar), 121.5 ($-\boldsymbol{C}\mathrm{H{=}CH}\mathit{C}\mathrm{HOC(CHOCH_2)}$)), 120 ($\boldsymbol{C}\mathrm{H{=}C}$, Ar), 70 ($\mathrm{O}\boldsymbol{C}\mathrm{H_2(CHOCH_2)}$)), 72.5 ($\boldsymbol{C}\mathrm{H_2OCH_2(CHOCH_2)}$)), 51 ($\boldsymbol{C}\mathrm{HO}$-$\mathrm{CH_2}$), 45 ($\mathrm{CHO}\boldsymbol{C}\mathrm{H_2}$).

Synthesis of Vinyl Ether (VE)−PIB−VE. Bromoallyl-telechelic PIB (M_n = 2200, PDI = 1.16, 200 mg, 0.09 mmol) was dissolved in dry THF (15 mL) and charged into a two-necked glass reactor equipped with a condenser. Ethylene glycol vinyl ether (440 mg, 5 mmol), NaH (80 mg, 3.33 mmol), and TBAB (1.61 g, 5 mmol) were charged into the reactor under a slow stream of dry nitrogen atmosphere, and the mixture was refluxed for 4 h. The reaction mixture was cooled to room temperature, and THF was evaporated. The residue was dissolved in hexanes, the solution was filtered, and the filtrate was reprecipitated in methanol. The product was purified as mentioned above. Gravimetric yield: 97%. ^{1}H NMR ($\mathrm{CDCl_3}$, ppm, δ): 4.05 (d, 3H $\mathit{C}\boldsymbol{H}_2\mathrm{(OCH_2CH_2OC}\boldsymbol{H}\mathrm{{=}CH_2)}$)), 5.55 (m, 1H, $\mathrm{CH}{=}\mathrm{C}\boldsymbol{H}\mathrm{CH_2(OCH_2CH_2OCH{=}CH_2)}$)), 5.75 (m, 1H, $\mathrm{C}\boldsymbol{H}\mathrm{{=}CHCH_2}$-$\mathrm{(OCH_2CH_2OCH{=}CH_2)}$)), 3.7 (m, 2H, $\mathrm{C}\boldsymbol{H}_2\mathrm{CH_2OCH{=}CH_2}$), 3.8 (m, 2H, $\mathrm{C}\boldsymbol{H}_2\mathrm{OCH{=}CH_2}$), 4.2 (d, 1H, $\mathrm{CH_2OCH{=}C}\boldsymbol{H}_2$), 6.5 (q, 1H, $\mathrm{CH_2OCH{=}C}\boldsymbol{H}_2$). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm, δ): 152.5 ($\mathrm{OCH_2CH_2O}\boldsymbol{C}\mathrm{H{=}CH_2}$), 149 ($\boldsymbol{C}\mathrm{{=}CH}$, Ar), 148.5 ($\boldsymbol{C}\mathrm{{=}CH}$, Ar), 132.5 ($\mathrm{CH}{=}\boldsymbol{C}\mathrm{HCH_2OCH_2CH_2OCH{=}CH_2}$), 128.5 ($\boldsymbol{C}\mathrm{H{=}CHCH_2OCH_2CH_2OCH{=}CH_2}$), 121 ($-\boldsymbol{C}\mathrm{H{=}C}$, Ar), 120 ($-\boldsymbol{C}\mathrm{H{=}C}$, Ar), $=\mathrm{CH_2}$), 67.5 ($\boldsymbol{C}\mathrm{H_2OCH_2}\boldsymbol{C}\mathrm{H_2OCH{=}}$-$\mathrm{CH_2}$), 86.5 ($\mathrm{CH_2OCH}{=}\boldsymbol{C}\mathrm{H_2}$), 73 ($\mathrm{O}\boldsymbol{C}\mathrm{H_2\ CH_2OCH{=}CH_2}$).

Results and Discussion

The precursor bromoallyl-telechelic PIB (M_n = 2200, PDI = 1.2) was synthesized by halogen exchange from Cl−Allyl−PIB−Allyl−Cl (M_n = 2200, PDI = 1.2) as reported before.[13] The end-functional PIBs were synthesized according to Scheme 1.

Synthesis of Epoxy-Functional Polyisobutylene. Glycidol has been frequently used in the literature to convert organic halides to epoxides under basic conditions.[15] Preliminary reaction of bromoallyl-telechelic PIB with glycidol was attempted using NaH in THF under reflux. The reaction was sluggish, yielding 20% end-group conversion in 24 h. This was attributed to the insolubility of sodium salt of glycidol in THF. The addition of a phase transfer catalyst TBAB increased the homogeneity of the reaction mixture, and the substitution was complete in 6 h.

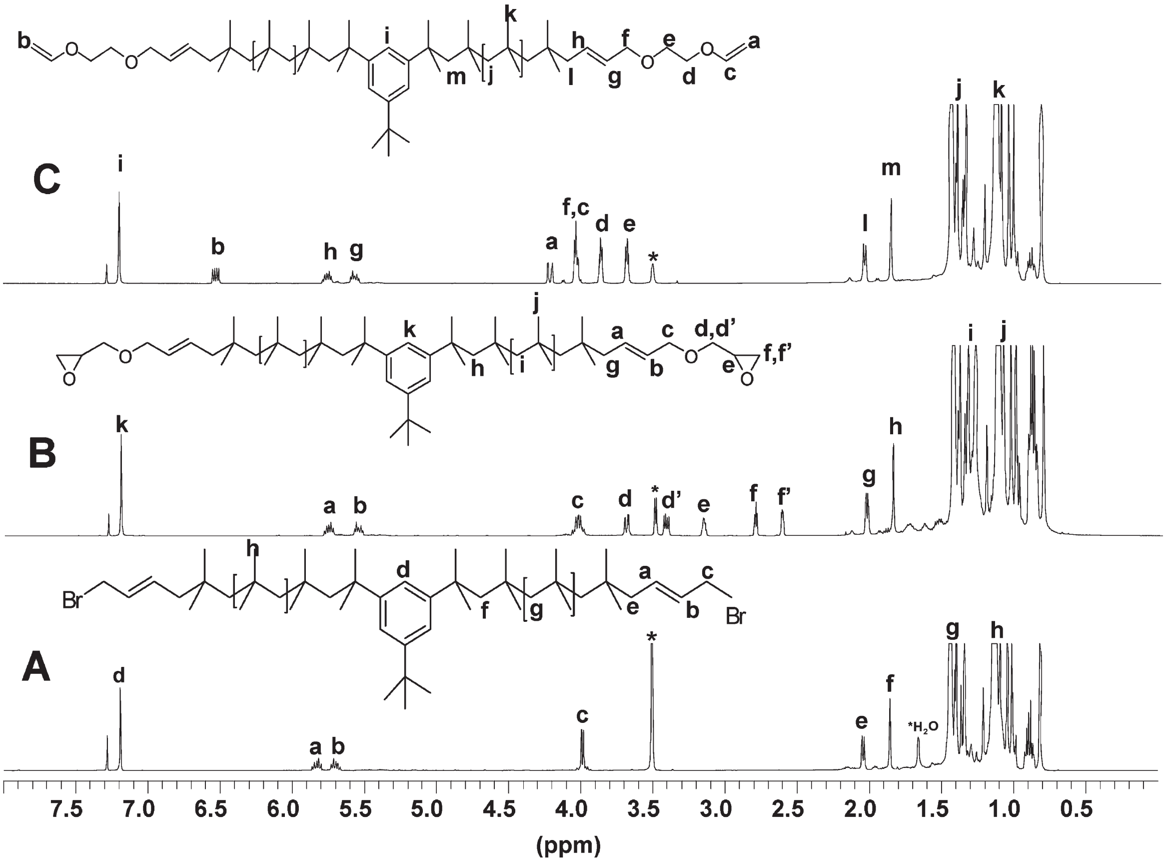
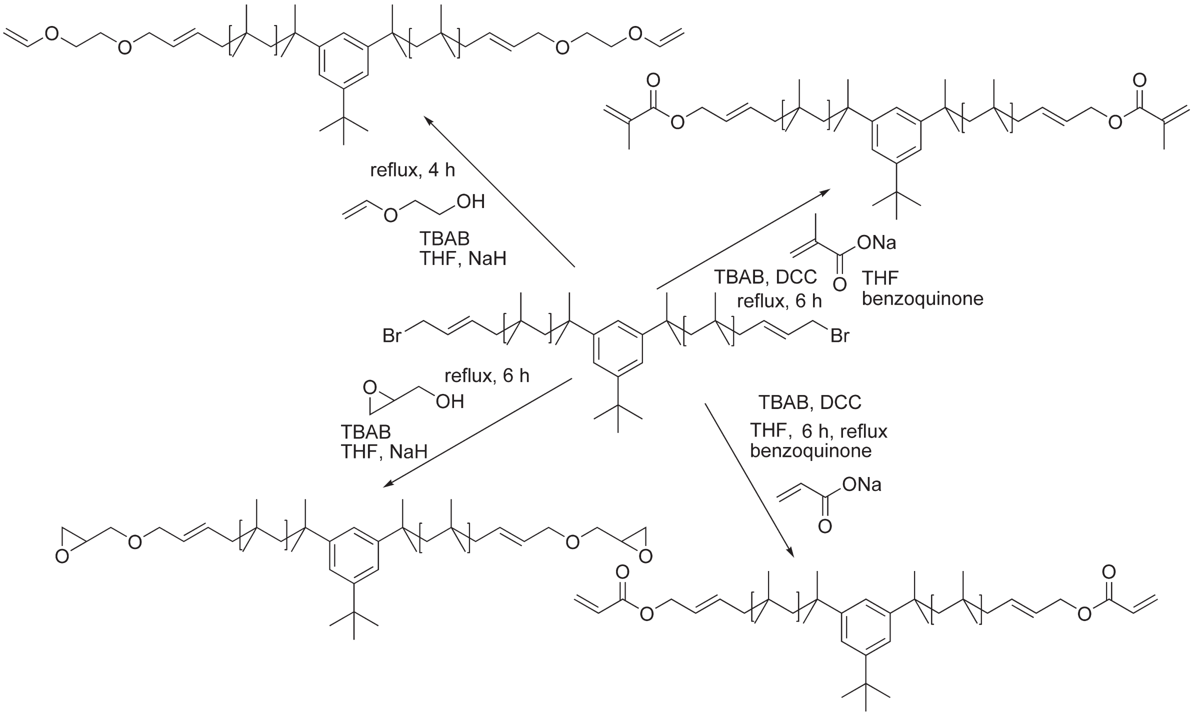


Figure 1. ^{1}H NMR spectra of (A) Br−Allyl−PIB−Allyl−Br, (B) EP−PIB−EP, and (C) VE−PIB−VE. The peak marked with an asterisk is designated as solvent (methanol) peak.

Scheme 1. Synthesis of Vinyl Ether (VE)−Polyisobutylene (PIB)−VE, Methacrylate (MA)−PIB−MA, Acrylate (Acr)−PIB−Acr, and Epoxy (EP)−PIB−EP in the Presence of Tetrabutylammonium Bromide (TBAB)



^{1}H NMR spectroscopy showed the disappearance of peaks at 4.0, 5.7, and 5.75 ppm assigned to the bromomethylene and bromoallylmethine protons and new signals at 4.05, 5.55, and 5.75 ppm assigned to $-\mathit{CH}_2\mathrm{OCH_2(CHOCH_2)}$, $-\mathrm{CH{=}C}\boldsymbol{\mathit{H}}\mathit{C}\mathrm{H_2OCH_2(CHOCH_2)}$, and $-\mathrm{C}\boldsymbol{\mathit{H}}\mathrm{{=}CH}\mathit{CH}_2\mathrm{OCH_2(CHOCH_2)}$ appeared, indicating close to quantitative conversion (Figure 1B). The $-\mathrm{OC}\mathit{H}_2\mathrm{(CHOCH_2)}$ exhibited two multiplets at 3.7 and 3.4 ppm whereas the

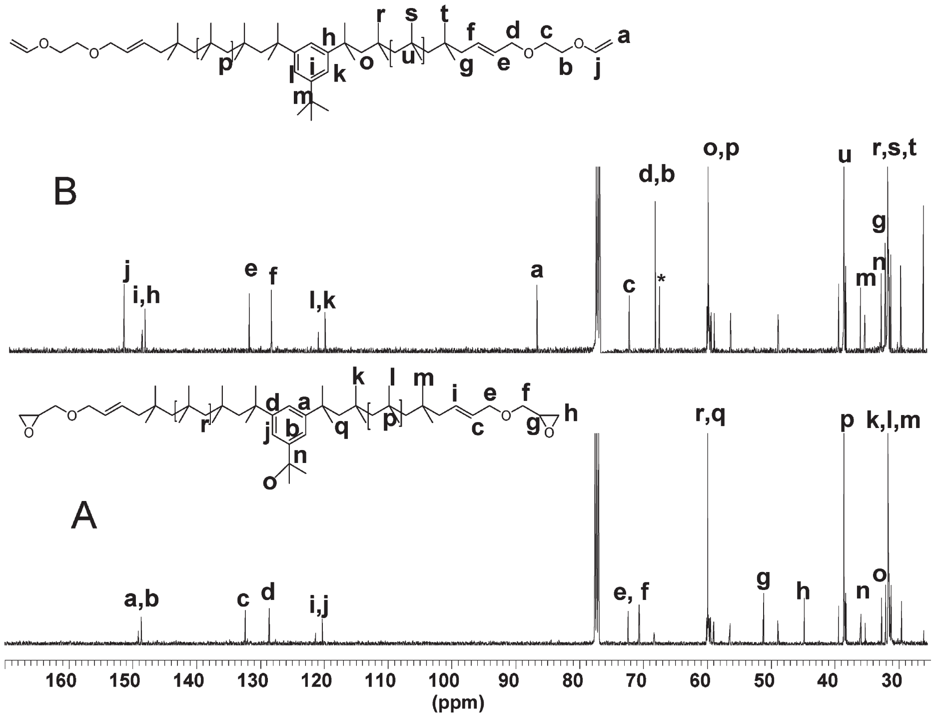


Figure 2. ^{13}C NMR spectra of (A) EP−PIB−EP and (B) VE−PIB−VE. The peak marked with an asterisk is designated as solvent (tetrahydrofuran) peak.

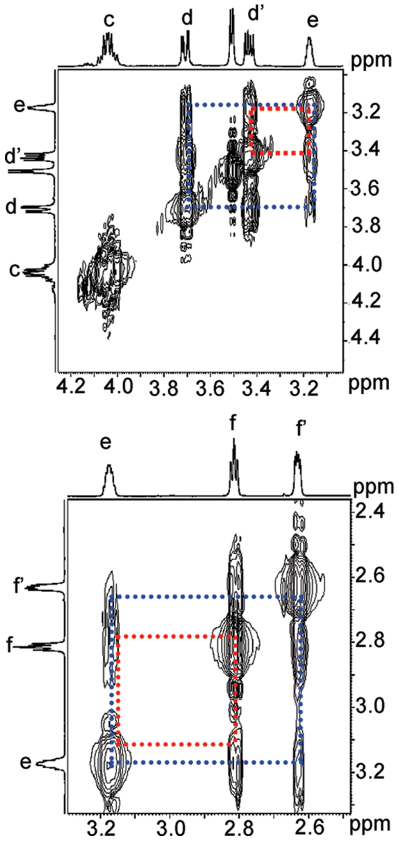


Figure 3. 2D gradient COSY-NMR spectrum of EP−PIB−EP showing the cross-peaks for d, d′ (−OCH_2−epoxy) with e (−CH(CH$_2$)O) and f, f′ (−CH(CH_2)O) with e.

methylene group of the epoxy ring also showed two peaks at 2.8 and 2.6 ppm. In 2D COSY-NMR spectroscopic analysis, cross-peaks for 3.7 and 3.4 ppm were obtained with 3.2 ppm, indicating that both peaks belong to the methylene group attached to the epoxy moiety (Figure 3). These peak positions were further confirmed by 2D gradient HSQC NMR spectral analysis as both peaks (3.7 and 3.4 ppm) showed connectivity to $=$CH−CH$_2$−O*C*H$_2$− (70 ppm), and resonances at 2.8 and 2.6 ppm were correlated to −OCH$_2$(CHO*C*H$_2$) resonated at 45 ppm (Supporting Information). The ^{13}C NMR spectroscopy supported the conversion by displaying resonances at 132.5 and 121.5 ppm for the olefinic carbons. New signals at 51, 45, and 70 ppm also appeared for −CH$_2$(***C***HO***C***H$_2$) and −CH$_2$O***C***H$_2$(CHOCH$_2$), respectively (Figure 2A).

The end-functionality of EP−PIB−EP was further investigated by MALDI-TOF MS. The polymer showed a single set of peaks distributed at regular interval of 56 Da. Each peak was expressed by the following equation:

$$M_1 = M_{Ag+} + M_{init} + nM_{IB} + 2M_{EG}$$

where M_1 corresponds to the mass of each peak, M_{Ag+} represents the average atomic mass of silver ion, M_{IB} is mass of IB, and M_{init} is the mass of initiator (5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene) residue. The calculated M_{EG} = 253 (from MALDI-TOF analysis) is close to the average molecular mass (254.3, theoretical) of two end-units (Figure 4A). The average molecular mass of each end group was calculated using the following equation:

$$M_{EG} = (C_{AAM} \times 7 + H_{AAM} \times 11 + O_{AAM} \times 2)$$

whereas H_{AAM} = 1.00794 Da, C_{AAM} = 12.0107 Da, and O_{AAM} = 15.9994 Da.

The GPC-RI trace of EP−PIB−EP was similar to the precursor, indicating that the polymer backbone is unaffected during postpolymerization end-functionalization (Figure 8).

Synthesis of Vinyl Ether-Functional Polyisobutylene. SN$_2$ reaction of bromoallyl-telechelic PIB with ethylene glycol vinyl ether was carried out in THF using NaH as base to

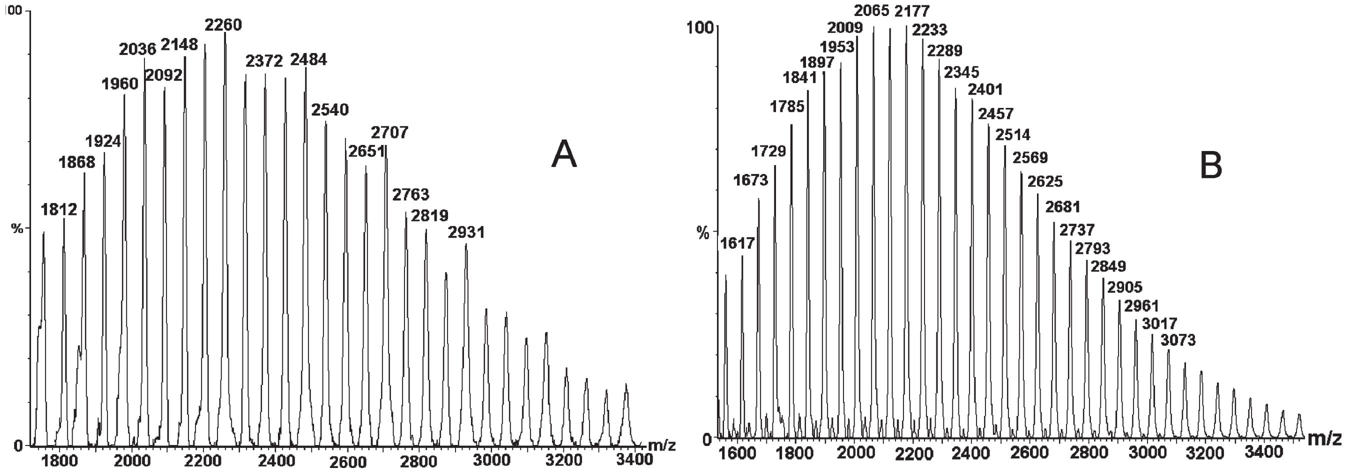


Figure 4. MALDI-TOF MS of (A) EP−PIB−EP and (B) VE−PIB−VE.

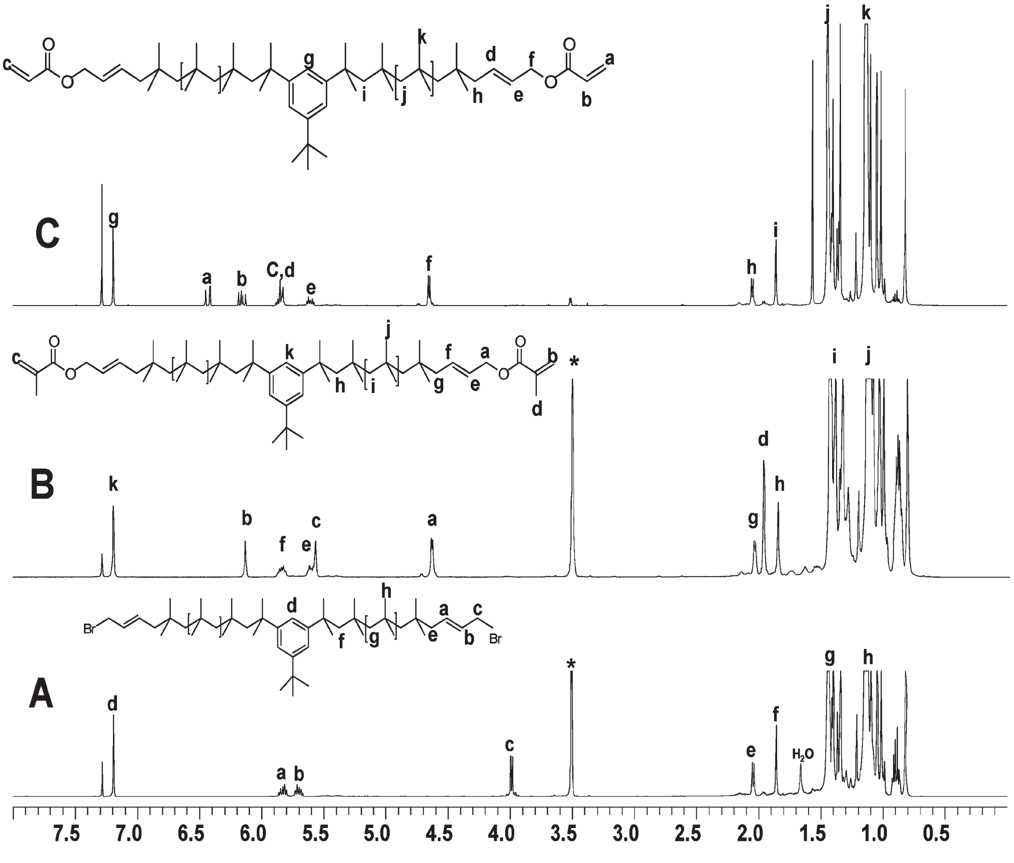


Figure 5. ^{1}H NMR spectra of (A) Br−PIB−Br, (B) MA−PIB−MA, and (C) Acr−PIB−Acr. The peak marked with an asterisk is designated as solvent (methanol) peak.

synthesize vinyl ether end-functional PIB. The addition of TBAB increased the substitution rate considerably, and quantitative conversion was achieved in 4 h under reflux conditions. The GPC-RI trace of the macromer was similar to Br−Allyl−PIB−Allyl−Br. The ^{1}H NMR spectrum of the product showed new signals at 4.05 and 5.55 ppm accountable to $-C\mathit{H}_2OCH_2CH_2OC\mathit{H}{=}CH_2$, $CH{=}C\mathit{H}CH_2OCH_2CH_2OCH{=}CH_2$, and resonances at 4.0 and 5.7 ppm for the $=CHC\mathit{H}_2Br$ and $=C\mathit{H}CH_2Br$ disappeared, suggesting quantitative conversion (Figure 1C). New peaks at 3.7, 3.8, 4.2, and 6.5 ppm appeared for $-C\mathit{H}_2CH_2OCH{=}CH_2$, $-C\mathit{H}_2OCH{=}CH_2$, and $-CH_2OCH{=}C\mathit{H}_2$. In the ^{13}C NMR spectrum signals at 67.5 and 73 ppm for $-\mathit{C}H_2OCH_2\mathit{C}H_2OCH{=}CH_2$ and $-\mathit{C}H_2CH_2OCH{=}CH_2$ were observed, whereas $-CH_2O\mathit{C}H{=}CH_2$ and $-CH_2OCH{=}\mathit{C}H_2$ resonated at 152.5 and 86.5 ppm, respectively (Figure 2B).

The end-functionality of VE−PIB−VE was further investigated by MALDI-TOF MS. The calculated $M_{EG} = 282$ is identical to the average molecular mass ($C_{16}O_4H_{26} = 282.4$) of two end-units (Figure 4B).

Synthesis of Methacrylate and Acrylate End-Functional Polyisobutylene. Activated halides such as benzyl bromide are reported to react readily with sodium methacrylate in the presence of an inorganic base in a polar solvent at elevated temperature.[16] Similarly, bromoallyl-telechelic polyisobutylene

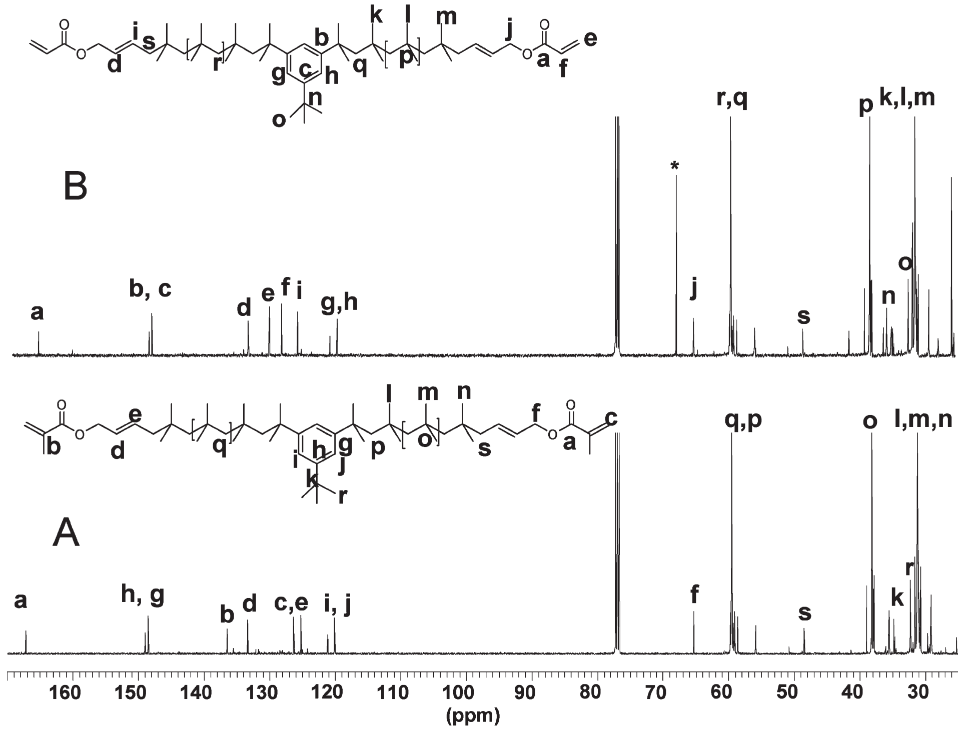


Figure 6. ^{13}C NMR spectra of (A) MA−PIB−MA and (B) Acr−PIB−Acr. The peak marked with an asterisk is designated as solvent (tetrahydrofuran) peak.

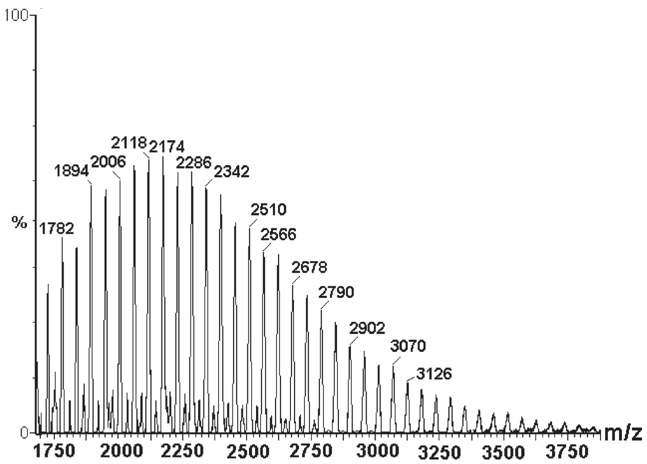


Figure 7. MALDI-TOF MS of MA−PIB−MA.

can be utilized for the synthesis of MA−PIB−MA by nucleophilic substitution reaction with sodium methacrylate. The substitution was carried out in the presence of DCC under reflux, and a small amount of 1,4-benzoquinone was added to the reaction mixture to prevent polymerization of the methacrylate end-group.

In the presence of TBAB quantitative conversion was achieved in 6 h under reflux and in 70 h at room temperature. The ^{1}H NMR spectrum of the product shows that the bromomethylene and bromoallylmethine protons peaks at 4.0, 5.7, and 5.75 ppm disappeared and new resonances at 4.6, 5.65, and 5.85 ppm accountable to $-\mathit{CH}_2\mathrm{OCOCH_3C{=}CH_2}$, $-\mathit{C}\mathrm{H{=}}\mathit{CH}\mathrm{CH_2OCOCH_3C{=}CH_2}$, and $-\mathit{CH}{=}\mathit{C}\mathrm{H}\mathit{C}\mathrm{H_2O}-$, and at 5.6, 6.15, and 2.0 ppm ($\mathrm{OCOCH_3C{=}C}\mathit{H}_2$ and $-\mathrm{C}\mathit{H}_3\mathrm{C{=}CH_2}$) appeared (Figure 5A). In the ^{13}C NMR spectrum the olefinic carbons resonated at 134 and 126 ppm and new signals for $-\mathrm{CH_2O}\mathit{C}\mathrm{OCH_3C{=}CH_2}$, $-\mathrm{CH_3}\mathit{C}\mathrm{{=}CH_2}$, and $-\mathrm{CH_3C{=}}\mathit{C}\mathrm{H_2}$ appeared at 167, 137, and 127 ppm, respectively (Figure 6A). MALDI-TOF MS of MA−PIB−MA verified the end-functionality as the calculated $M_{\mathrm{EG}} = 279$ is within 1 Da of the average molecular mass of two end-units ($\mathrm{C_{16}O_4H_{22}} = 278.3$) (Figure 7).

Similarly, Acr−PIB−Acr was synthesized by $\mathrm{S_N2}$ reaction of sodium acrylate with Br−Allyl−PIB−Allyl−Br. Complete substitution was achieved in 6 h as indicated by the ^{1}H NMR spectrum that showed new peaks at 4.65, 5.65, and

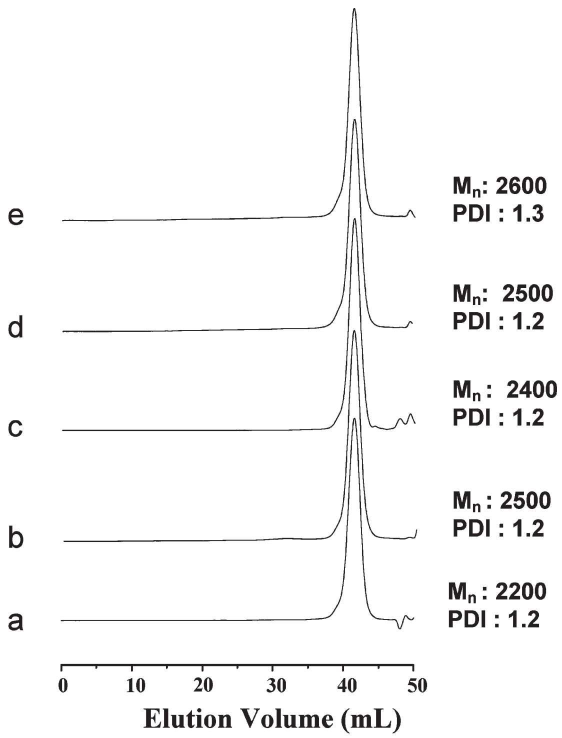


Figure 8. GPC-RI traces of (a) Br−PIB−Br, (b) MA−PIB−MA, (c) Acr−PIB−Acr, (d) EP−PIB−EP, and (e) VE−PIB−VE.

5.85 ppm accountable to $-C\boldsymbol{H}_2\mathrm{OCOCH{=}CH_2}$, $-\mathrm{CH{=}C}\boldsymbol{H}-\mathit{C}\mathrm{H_2OCOCH{=}CH_2}$, and $-\mathrm{C}\boldsymbol{H}\mathrm{{=}CH}\mathit{C}\mathrm{H_2OCOCH{=}CH_2}$ while peaks at 4.0, 5.7, and 5.75 ppm disappeared (Figure 5B). New signals at 6.4, 5.85, and 6.15 ppm also appeared for $-\mathit{C}\mathrm{H_2OCOCH{=}C}\boldsymbol{H}_2$ and $-\mathit{C}\mathrm{H_2OCOC}\boldsymbol{H}\mathrm{{=}CH_2}$. ^{13}C NMR spectroscopy showed the appearance of peaks at 166 and 65.5 ppm for $-\mathrm{O}\boldsymbol{C}\mathrm{OCH{=}CH_2}$ and $-\boldsymbol{C}\mathrm{H_2OCOCH{=}CH_2}$ (Figure 6B). However, we were unable to record the MALDI-TOF spectrum of the Acr−PIB−Acr.

The GPC-RI traces were similar to the precursor Br−Allyl−PIB−Allyl−Br, indicating the end-groups are unaffected during the synthesis and purification (Figure 8).

Conclusions

End-functional PIBs with polymerizable methacrylate, acrylate, vinyl ether, and epoxy end-functionalities could be synthesized in one-step $\mathrm{S_N2}$ reactions of bromoallyl end-functional PIB with quantitative functionalization. A small amount of the inhibitor hydroquinone prevents the polymerization of end-groups during synthesis. A phase transfer catalyst can be used to increase the rate of the substitution reaction. Applications of these macromers will be reported in the future.

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Supporting Information Available: ^{1}H NMR spectra of EP−PIB−EP, MA−PIB−MA, VE−PIB−VE, and Acr−PIB−Acr and HSQC-NMR spectrum of EP−PIB−EP. This material is available free of charge via the Internet at http://pubs.acs.org.

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