A New General Methodology for the Syntheses of End-Functional Polyisobutylenes by Nucleophilic Substitution Reactions

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ABSTRACT: The syntheses of end-functional polyisobutylenes (PIBs) including hydroxy, amino, carboxy, azide, propargyl, methoxy, and thymine end groups have been accomplished using nucleophilic substitution reactions. S_N2 reactions on PIB-Allyl-X (X = Cl or Br), the trans-1,4 addition product of the capping reaction of living PIB with 1,3-butadiene, with different nucleophiles successfully yielded the corresponding PIB-Allyl-OH, PIB-Allyl-OMe, PIB-Allyl-NH_2, PIB-Allyl-$OCH_2C{\equiv}CH$, PIB-Allyl-N_3, and PIB-Allyl-CH_2COOH with quantitative functionalization as determined by ^1H and ^{13}C NMR, FT-IR, and matrix-assisted time-of-flight mass spectroscopy. As expected, the rate of substitution was faster with PIB-Allyl-Br compared to PIB-Allyl-Cl. GPC analysis of the precursor PIB-Allyl-X and the products indicated that the polymer chain is unaffected by the substitution reactions. The synthesis of hydroxy telechelic PIBs was also achieved using X-Allyl-PIB-Allyl-X at reaction conditions similar to that employed for the preparation of PIB-Allyl-OH. The methodology was extended to the synthesis of PIB block copolymers by employing polymeric nucleophiles. PIB-*b*-poly(ethylene oxide) (PEO) was synthesized by the nucleophilic substitution of PIB-Allyl-Cl with PEO-O^-Na^+.

Introduction

Functional polyisobutylenes (PIBs) are of great interest due to their potential applications in many important areas of technology such as surface modification, adhesion, drug delivery, compatibilization of polymer blends, and motor oil and fuel additives.[1] Living polymerizations provide the simplest and most convenient method for the preparation of functional polymers.[2] However, there are relatively few end-functional polymers synthesized by living cationic polymerization of vinyl monomers. The two basic methods to prepare functional polymers by cationic polymerization are (a) initiation from functional initiators or (b) termination by functional terminators.[3] Although the second approach appears to be more attractive than the first one, in-situ end functionalization of the living ends is limited to nucleophiles that do not react with the Lewis acid co-initiator. Because the ionization equilibrium between the dormant halogen-terminated and ionic active species is shifted to the covalent species, the concentration of the ionic active species is very low.[4] Quantitative functionalization can only be accomplished, therefore, when ionization takes place continuously in the presence of a nucleophile, which must not react with the Lewis acid. There are few examples for functional PIBs prepared by this method. For instance, allyl telechelic PIBs were obtained by end-quenching with allyltrimethylsilane.[5] Kaneka Corp. (Japan) commercialized this method in 1998 for the preparation of PIB RTV sealant.

When all dormant chain ends are converted to active ionic species, as in the capping reaction with diarylethylenes,[6] many other nucleophiles, such as NH_3, CH_3OH, etc., which also quench the Lewis acid, could be used.[7] The obtained functional PIBs, however, may possess low reactivity due to steric hindrance, and for low molecular weight polymers the high cost of diarylethylene limits commercial feasibility of this process. There is a similar limitation for the preparation of telechelic polymers by the coupling of α-functional living polymer chains using any of the recently discovered coupling agents,[8,9] which are expensive and commercially unavailable. Therefore, most functional PIBs reported to date have been prepared by the chemical modification of the chloro chain ends obtained by quenching the polymerization with methanol. Although a wide variety of functional groups can be incorporated this way,[10] the method generally involves several steps and is rather cumbersome.

Recently, we reported on the synthesis of haloallyl functional PIBs (PIB-Allyl-X, where X = Cl or Br) using the capping reaction of living PIB with 1,3-butadiene in hexanes (Hex)/methyl chloride (MeCl) 60/40 (v/v) solvent mixtures at −80 °C[11] with titanium tetrachloride ($TiCl_4$) or methylaluminum sesquibromide ($Me_{1.5}AlBr_{1.5}$) as a Lewis acid. Monoaddition of 1,3-butadiene followed by instantaneous halide transfer from the counteranion and selective formation of the trans-1,4-adduct (PIB-Allyl-X) was observed in Hex/MeCl 60/40 (v/v) solvent mixtures at −80 °C at $[1,3\text{-butadiene}] \leq 0.05$ mol L^{-1} ($[1,3\text{-butadiene}]/[\text{chain end}] \leq 12$).

The selective formation of the 1,4-trans-adduct is unexpected and intriguing. Theoretically, cis-1,4 and 1,2-addition of 1,3-butadiene to PIB^+ are also possible. For instance, mixtures (1:1) of 1,2- and 1,4-addition products were obtained in the reaction of *p*-methoxydiphenylcarbenium tetrachloroborate with 1,3-butadiene in CH_2Cl_2 at −70 °C.[12] The exclusive formation of the trans 1,4-addition product, demonstrated by ^{13}C NMR spectroscopy of the polymer and low molecular weight model compounds, could be attributed to the large difference in the stability of cis and trans adduct; for instance, the E isomer of 1-chloro-2-butene is 6.96 kJ/mol more stable than the Z isomer.[13] The selective formation of the 1,4-adduct was attributed to the formation and subsequent reionization and isomerization of the 1,2-addition product to the 1,4-addition product, which cannot be reionized with the $TiCl_4$ or $Me_{1.5}AlBr_{1.5}$.

The exclusive formation of the 1,4-trans-addition product (PIB-Allyl-Cl or PIB-Allyl-Br) in the capping reaction of living PIB with 1,3-butadiane offers a promising new avenue to functional PIBs by simple nucleophilic substitution reactions. In this report, synthetic routes to a range of functional PIBs have been elaborated. The synthetic Scheme 1 summarizes the different transformations reported in this paper.

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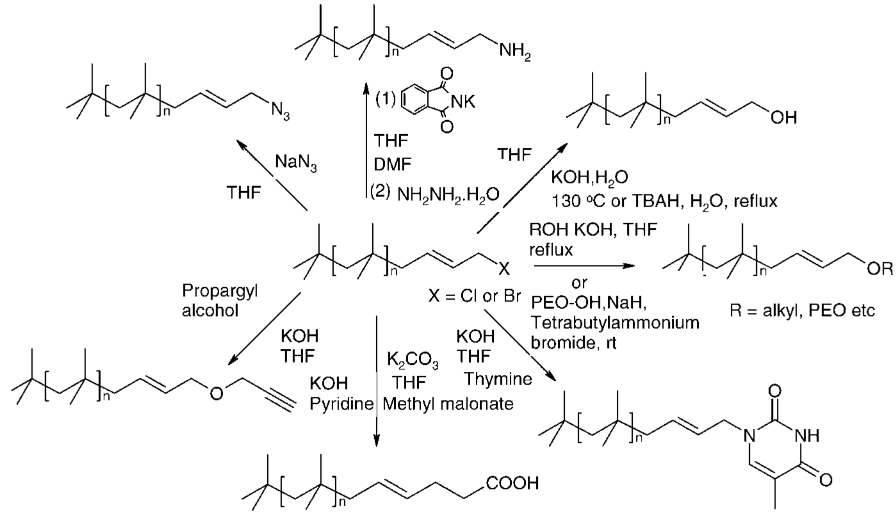
Scheme 1. Synthesis of Various End-Functional Polyisobutylenes Obtained by Reaction of Polyisobutylene-Allyl-Halide (Chloride or Bromide) with Different Nucleophiles Such as Sodium Azide, Propargyl Alcohol, Thymine, KOH (Potassium Hydroxide)/OH$^-$, PEO-OH (Hydroxy End-Capped Polyethylene Oxide), Phthalimide Potassium, TBAH (Tetrabutylammonium Hydroxide), or OR$^-$ in THF (Tetrahydrofuran) or THF:DMF (*N,N*-Dimethylformamide) Mixture



Experimental Section

Materials. Pyridine (Aldrich, 99.8%), $TiCl_4$ (Aldrich, 99.9%), propargyl alcohol (Aldrich, 99%), thymine (Aldrich, 99%), phthalimide potassium (Aldrich, 98%), 2,6-di-*tert*-butylpyridine (DTBP, Aldrich, 97+%), tetrabutylammonium hydroxide (TBAH, Alfa Aesar, 55% w/w aqueous solution), *N,N*-dimethylformamide anhydrous (DMF, Sigma-Aldrich, 99.8%), dimethyl malonate (Aldrich, 98%), tetrabutylammonium bromide (TBAB, Aldrich, 99%), sodium azide (Aldrich, ≥99.5%), sodium trifluoroacetate (NaTFA, Fluka, ≥99%), silver trifluoroacetate (AgTFA, Aldrich, 99.99+%), dithranol (1,8,9-anthracenetriol, Fluka, ≥99.0%), and 1,3-butadiene (BD, Aldrich, 99+%) were used as received. Potassium hydroxide (KOH), hydrazine hydrate, hydroxy-terminated polyethylene oxide (PEO-OH), and potassium carbonate (K_2CO_3) were purchased from Aldrich as reagent grade chemicals and were used without further purification. MeCl and isobutylene (IB) were dried in the gaseous state by passing them through in-line gas purifier columns packed with BaO/Drierite. They were condensed in the cold bath of a glovebox prior to polymerization. The initiators 2-chloro-2,4,4-trimethylpentane (TMPCl) and 5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene (*t*BuDicumylCl) were synthesized according to the procedure reported elsewhere.[14] Hexanes (Hex, Doe & Ingals, Technical grade), methanol (Doe & Ingals, Technical grade), etc., were purified as described previously.[15] Tetrahydrofuran (THF, Sigma-Aldrich, 99+%) was dried over sodium metal and benzophenone before use. Polymerizations were carried out under a dry nitrogen atmosphere or in an Mbraun 150-M glovebox (Innovative Technology Inc., Newburyport, MA). The polymers were purified by precipitation from hexanes/methanol. 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.

Measurements. ^1H and ^{13}C NMR spectroscopy for structural analysis was carried out on a Bruker 500 MHz spectrometer using $CDCl_3$ (Cambridge Isotope Laboratories, Inc.) as a solvent. ^1H NMR spectra of solutions in $CDCl_3$ were calibrated to tetramethylsilane (TMS) as internal standard (δH 0.00). An AVATAR 370 FT-IR spectrometer was used to record the FT-IR spectra of the samples in either dry CCl_4 solutions or thin films on NaCl pellet. The absolute molecular weights were measured with a Waters HPLC system equipped with a model 510 HPLC pump, a model 410 differential refractometer, a model 441 absorbance detector, online multiangle laser light scattering (MALLS) detector (MiniDawn, Wyatt Technology Inc., three angles 45°, 90°, and 135°), a model 712 sample processor, and five Ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. THF was used as a carrier solvent with a flow rate of 1 mL/min at room temperature. 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 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 samples were 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 4000 Da, Polysciences, Inc.). The matrix solution was prepared by dissolving dithranol in THF at a concentration of 20 mg/mL. CF_3COOAg (AgTFA) or CF_3COONa (NaTFA) 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 or NaTFA solutions were mixed in 10:10:1 volume ratio, and 1 μL of the resulting solution was evaporated on the sample holder.

Synthesis of PIB-Allyl-X. A low molecular weight PIB-Allyl-Cl ($M_n = 3200$, PDI = 1.12) was synthesized by living cationic polymerization of IB followed by end-capping with 1,3-butadiene hexanes/methyl chloride 60/40 (v/v) mixture at −80 °C using the TMPCl/$TiCl_4$ initiating system as published elsewhere.[11] PIB-Allyl-Br was obtained by halogen exchange reaction between PIB-Allyl-Cl and LiBr as reported.[16] Difunctional Cl-Allyl-PIB-Allyl-Cl (M_n = 3400, PDI = 1.10) was obtained similarly, except using *t*-BuDicumylCl as an initiator for the polymer synthesis.

Synthesis of PIB-Allyl-Phthalimide. PIB-Allyl-Cl (272 mg, 0.085 mmol) was dissolved in dry THF (9 mL), and dry DMF (3 mL) was added followed by the addition of phthalimide potassium (278 mg, 1.5 mmol); the mixture was refluxed under a dry nitrogen atmosphere for 12 h. The reaction mixture was cooled to room temperature, and THF was evaporated. Methanol was added to the sticky mass left over, and the precipitate was separated and 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. Yield: 83%. ^1H NMR ($CDCl_3$, ppm, δ): 7.9 (q, 2H, Ar), 7.7 (q, 2H, Ar), 5.85 (p, 1H, $C(CH_3)_2CH_2\boldsymbol{CH}{=}$), 5.5 (p, 1H, $={\boldsymbol{CH}}CH_2N(CO)_2$), 4.3 (d, 2H, $=CH\boldsymbol{CH_2}N(CO)_2$), 2.0 (d, 2H, $C(CH_3)_2\boldsymbol{CH_2}CH{=}$), 1.5−14 (br, 120H, $-\boldsymbol{CH_2}C(CH_3)_2-$), 1.2−1.1 (br, 366H, $-CH_2C(\boldsymbol{CH_3})_2-$). FT-IR (thin film, cm^{-1}): 2980

($-C-H_{str,}CH_2$ and CH_3), 1719 ($-C{=}O_{str}$, phthalimide), 1595 ($C{=}C_{str}$, aromatic), 1475 ($-C-H_{def}$, CH_2), 1361 ($-C-H_{def}$, CH_3), 1227 ($C({=}O)-N_{str}$), 759 ($=C-H_{def}$, out-of-plane, Ar), 719 ($C{=}C_{def}$, out-of-plane). ^{13}C NMR ($CDCl_3$, ppm, δ): 168.3 ($=CHCH_2N(\boldsymbol{C}O)_2$), 134.2 ($C(CH_3)_2CH_2\boldsymbol{C}H=$), 133.1 ($=\boldsymbol{C}H$, Ar), 132.7 ($=\boldsymbol{C}-CO$, Ar), 125.9 ($=\boldsymbol{C}HCH_2N(CO)_2$), 123.6 ($=\boldsymbol{C}H$, Ar), 60.0 ($-\boldsymbol{C}H_2C(CH_3)_2-$), 59.3 ($-\boldsymbol{C}H_2C(CH_3)_3$), 58.6 ($(CH_3)_3\boldsymbol{C}H_2C(CH_3)_2CH_2-$), 56.3 ($C(CH_3)_2\boldsymbol{C}H_2C(CH_3)_2CH_2CH=$), 49.0 ($C(CH_3)_2\boldsymbol{C}H_2CH=$), 40.1 ($=CH\boldsymbol{C}H_2N$), 38.6−38.2 ($CH_2\boldsymbol{C}(CH_3)_2$), 36.0 ($C(\boldsymbol{C}H_3)_3CH_2-$), 32.9 ($C(\boldsymbol{C}H_3)_2CH_2CH=$), 31.7 ($-CH_2C(\boldsymbol{C}H_3)_2-$), 31.2 ($C(\boldsymbol{C}H_3)_2CH_2C(CH_3)_2CH_2CH=$).

Deprotection of Phthalimide to PIB-Allyl-Amine. PIB-Allyl-phthalimide (210 mg, 0.061 mmol) was dissolved in THF (10 mL), and hydrazine hydrate (190 mg, 3.8 mmol) was added. The mixture was refluxed for 24 h. The reaction was stopped and cooled to room temperature. A solution of KOH (320 mg, 5.7 mmol) in water (2 mL) was added and stirred for 30 min. THF was evaporated under reduced pressure, and methanol was added. The precipitate obtained was purified by dissolving in hexanes and reprecipitating in methanol. Yield: 82%. ^1H NMR ($CDCl_3$, ppm, δ): 5.6 (m, 2H, $CH_2\boldsymbol{CH}{=}\boldsymbol{CH}CH_2$), 3.3 (d, 2H, $=CH\boldsymbol{CH}_2NH_2$), 2.7 (br, 2H, $=CHCH_2\boldsymbol{NH}_2$), 2.0 (d, 2H, $C(CH_3)_2\boldsymbol{CH}_2CH=$), 1.5−1.4 (br, 118H, $-\boldsymbol{CH}_2C(CH_3)_2-$), 1.2−1.1 (br, 362H, $-CH_2C(\boldsymbol{CH}_3)_2$). FT-IR (thin film, cm^{-1}): 3379 ($-N-H_{str}$, $-CH_2NH_2$), 2951 ($-C-H_{str}$, CH_2 and CH_3), 1600 ($-N-H_{def}$, CH_2NH_2), 1468 ($-C-H_{def}$, CH_2), 1385 ($-C-H_{def}$, CH_3), 1114 ($C-N_{str}$, CH_2NH_2), 772 ($N-H_{wag}$, CH_2NH_2). ^{13}C NMR ($CDCl_3$, ppm, δ): 134.4 ($=\boldsymbol{C}HCH_2NH_2$), 128.0 ($C(CH_3)_2CH_2\boldsymbol{C}H=$), 60.0 ($-\boldsymbol{C}H_2C(CH_3)_2-$), 59.3 ($-\boldsymbol{C}H_2C(CH_3)_3$), 58.6 ($(CH_3)_3CH_2C(CH_3)_2\boldsymbol{C}H_2-$), 56.3 ($C(CH_3)_2\boldsymbol{C}H_2C\ (CH_3)_2CH_2CH=$), 49.0 ($C(CH_3)_2\boldsymbol{C}H_2CH=$), 44.7 ($=CH\boldsymbol{C}H_2NH_2$), 38.6−38.2 ($CH_2\boldsymbol{C}(CH_3)_2$), 36.0 ($C(\boldsymbol{C}H_3)_3CH_2-$), 32.9 ($C(\boldsymbol{C}H_3)_2CH_2CH=$), 31.7 ($-CH_2C(\boldsymbol{C}H_3)_2-$), 31.2 ($C(\boldsymbol{C}H_3)_2CH_2C(CH_3)_2-CH_2CH=$).

Synthesis of PIB-Allyl-Alcohol. In a typical reaction, PIB-Allyl-Cl (100 mg, 0.031 mmol) dissolved in 10 mL of THF was placed in a pressure reactor (capacity 125 mL, Parr Instruments), and 1% KOH solution (10 mL) was added. The reaction was then heated at 130 °C for 24 h. The reactor was cooled to room temperature, and the solvent was evaporated on the rotavap. The polymer was dissolved in hexanes and washed with distilled water. The organic layer was dried with anhydrous sodium sulfate, and hexanes were evaporated to yield the crude product. The crude product was purified by reprecipitation in hexanes/methanol, and the polymer was dried under vacuum.

In a typical reaction, PIB-Allyl-Br (100 mg, 0.031 mmol) dissolved in 10 mL of THF was placed in a pressure reactor, and 1% KOH aqueous solution (10 mL) was added. The reaction was then heated at 120 °C for 3 h. At the end of the reaction, excess solvent was removed under reduced pressure. The polymer was dissolved in hexanes and washed with distilled water. The organic layer was dried on anhydrous sodium sulfate and concentrated under reduced pressure to yield the crude product. Purification was carried out by reprecipitation in hexanes/methanol, and the polymer was dried under vacuum.

Hydrolysis Using TBAH. In a typical reaction, PIB-Allyl-Cl or PIB-Allyl-Br (150 mg, 0.05 mmol) was dissolved in THF (20 mL), TBAH 27% w/w aqueous solution (129 mg, 0.5 mmol) was added, and the mixture was refluxed for 14 h for PIB-Allyl-Cl or in the case of PIB-Allyl-Br stirred at room temperature for 1 h. The polymer product was purified by reprecipitation using hexanes/methanol and dried under vacuum. Yield: 99%. ^1H NMR ($CDCl_3$, ppm, δ): 5.75 (p, 1H, $C(CH_3)_2CH_2\boldsymbol{CH}=$), 5.65 (p, 1H, $=\boldsymbol{CH}CH_2OH$), 4.15 (t, 2H, $=CH\boldsymbol{CH}_2OH$), 2.05 (d, 2H, $C(CH_3)_2\boldsymbol{CH}_2CH=$), 1.5−1.4 (br, 119H, $-\boldsymbol{CH}_2(CH_3)_2-$), 1.2−1.1 (br, 365H, $-CH_2(CH_3)_2$). ^{13}C NMR ($CDCl_3$, ppm, δ): 131.8 ($=\boldsymbol{C}HCH_2OH$), 130.7 ($C(CH_3)_2CH_2\boldsymbol{C}H=$), 64.3 ($=CH\boldsymbol{C}H_2OH$), 60.0 ($-\boldsymbol{C}H_2C(CH_3)_2-$), 59.3 ($-\boldsymbol{C}H_2C(CH_3)_3$), 58.6 ($(CH_3)_3CH_2C(CH_3)_2\boldsymbol{C}H-$), 56.6 ($C(CH_3)_2\boldsymbol{C}H_2C(CH_3)_2CH_2CH=$), 48.8 ($C(CH_3)_2\boldsymbol{C}H_2CH=$), 38.6−38.2 ($CH_2\boldsymbol{C}(CH_3)_2$), 36.0 ($C(\boldsymbol{C}H_3)_3CH_2-$), 32.9 ($C(\boldsymbol{C}H_3)_2CH_2CH=$), 31.7 ($-CH_2C(\boldsymbol{C}H_3)_2-$), 31.2 ($C(\boldsymbol{C}H_3)_2CH_2C(CH_3)_2CH_2\ CH=$).

Synthesis of HO-Allyl-PIB-Allyl-OH. The hydrolysis of Cl-Allyl-PIB-Allyl-Cl was carried out similarly to above. Yield: 100%. ^1H NMR ($CDCl_3$, ppm, δ): 7.20 (s, 3H, Ar), 5.75 (p, 2H, $C(CH_3)_2CH_2\boldsymbol{CH}=$), 5.65 (p, 2H, $HOCH_2\boldsymbol{CH}=$), 4.15 (t, 4H, $=CH\boldsymbol{CH}_2OH$), 2.05 (d, 4H, $C(CH_3)_2\boldsymbol{CH}_2CH=$), 1.89 (s, 4H, $ArC(CH_3)_2\boldsymbol{CH}_2$), 1.5−1.4 (br, 116H, CH_2), 1.2−1.1 (br, 356H, CH_2). FT-IR (thin film, cm^{-1}): 3375 ($-O-H_{str}$), 2952 ($-C-H_{str}$, CH_2 and CH_3), 1470 ($-C-H_{def}$, CH_2), 1389 ($-O-H_{def}$, in-plane), 1366 ($-C-H_{def}$, CH_3), 1230 ($C-O_{str}$, CH_2-OH), 971 ($-O-H_{def}$, out-of-plane). ^{13}C NMR ($CDCl_3$, ppm, δ): 149.4 ($=\boldsymbol{C}(C(CH3)_3)$, Ar), 148.9 ($=\boldsymbol{C}(C(CH_3)-$, Ar), 131.9 ($=\boldsymbol{C}HCH_2OH$), 130.7 ($C(CH_3)_2CH_2\boldsymbol{C}H=$), 121.6 ($=\boldsymbol{C}H$, Ar), 120.5 ($=\boldsymbol{C}H$, Ar), 64.3 ($=CH\boldsymbol{C}H_2OH$), 60.0 ($-\boldsymbol{C}H_2C(CH_3)_2-$), 59.7 ($-\boldsymbol{CH}_2C(CH_3)_2-$), 59.5 ($-\boldsymbol{C}(CH_3)_3$), 59.0 ($-\boldsymbol{C}H_2C(CH_3)_2Ar$), 56.4 ($C(CH_3)_2\boldsymbol{C}H_2C(CH_3)_2CH_2CH=$), 49.0 ($C(CH_3)_2\boldsymbol{C}H_2CH=$), 39.4 ($-\boldsymbol{C}(CH_3)_2Ar$), 38.6−38.2 ($CH_2\boldsymbol{C}(CH_3)_2$), 36.0 ($C(\boldsymbol{C}H_3)_3CH_2-$), 32.9 ($C(\boldsymbol{C}H_3)_2CH_2CH=$), 31.7 ($-CH_2C(\boldsymbol{C}H_3)_2-$), 31.2 ($C(\boldsymbol{C}H_3)_2CH_2C(CH_3)_2CH_2CH=$).

Synthesis of PIB-Allyl-Malonic Ester. PIB-Allyl-Br (406 mg, 0.127 mmol) was dissolved in THF (20 mL), and dry acetonitrile (6 mL) was added, followed by the addition of a mixture of dimethyl malonate (788 mg, 6.0 mmol) and K_2CO_3 (832 mg, 6.0 mmol). After refluxing for 20 h it was cooled to room temperature. The mixture was filtered, and the filtrate was concentrated under reduced pressure. The product was purified by reprecipitation from hexanes solution into methanol. Yield: 91%. ^1H NMR ($CDCl_3$, ppm, δ): 5.6 (p, 1H, $C(CH_3)_2CH_2\boldsymbol{CH}=$), 5.35 (p, 1H, $=\boldsymbol{CH}CH_2-CH(COOCH_3)_2$), 3.75 (s, 6H, $-COO\boldsymbol{CH_3}$), 3.45 (t, 1H, $\boldsymbol{CH}(COOCH_3)_2$), 2.65 (t, 2H, $=CH\boldsymbol{CH}_2CH(COOCH_3)_2$), 1.95 (d, 2H, $C(CH_3)_2\boldsymbol{CH}_2CH=$), 1.5−1.4 (br, 122H, $-\boldsymbol{CH}_2C(CH_3)_2$), 1.2−1.1.(br, 372H, $-CH_2C(\boldsymbol{CH}_3)_2$). FT-IR (thin film, cm^{-1}): 2953 ($-C-H_{str}$, CH_2 and CH_3), 1717 ($-C{=}O_{str}$, $-COOCH_3$), 1471 ($-C-H_{def}$, CH_2), 1399 ($C{=}O_{str}$, symmetric), 1366 ($-C-H_{def}$, CH_3), 1231 ($-C-O_{str}$, $-COOCH_3$), 1215 ($-O-C_{str}$, OCH_3), 762 ($=C-H_{def}$, out-of-plane). ^{13}C NMR ($CDCl_3$, ppm, δ): 169.7 ($-CH(\boldsymbol{C}OOCH_3)_2$), 131.5 ($C(CH_3)_2CH_2\boldsymbol{C}H=$), 128.0 ($=\boldsymbol{C}HCH_2C(COOMe)_2$), 60.0 ($-\boldsymbol{C}H_2C(CH_3)_2-$), 59.3 ($-\boldsymbol{C}H_2C(CH_3)_3$), 56.6 ($C(CH_3)_2\boldsymbol{C}H_2C(CH_3)_2\ -CH_2CH=$), 52.8 ($-\boldsymbol{C}H(COOCH_3)_2$), 52.4 ($-COO\boldsymbol{C}H_3$), 49.0 ($C(CH_3)_2\boldsymbol{C}H_2CH=$), 38.6−38.2 ($CH_2\boldsymbol{C}(CH_3)_2$), 36.0 ($C(\boldsymbol{C}H_3)_3CH_2-$), 32.9 ($C(\boldsymbol{C}H_3)_2CH_2CH=$), 31.7 ($-CH_2C(\boldsymbol{C}H_3)_2-$), 31.2 ($C(\boldsymbol{C}H_3)_2CH_2C(CH_3)_2CH_2\ CH=$).

Synthesis of PIB-Allyl-$\boldsymbol{CH_2COOH}$. PIB-Allyl-malonic ester (232 mg, 0.07 mmol) was dissolved in THF (15 mL), and H_2O (2 mL) was added followed by KOH (432 mg, 7.66 mmol). The mixture was set to reflux for 24 h. The mixture was acidified with concentrated HCl until pH 3, and the excess THF was evaporated under reduced pressure. The product was washed with 10 mL of methanol and then dissolved in 4 mL of pyridine. Water (0.6 mL) was added, and the solution was stirred under reflux for 40 h. The reaction was stopped, and the mixture was added to aqueous HCl solution. The residue was separated and dissolved in hexanes, and the solution was filtered. The polymer was purified by reprecipitation from hexanes into methanol. Yield: 81%. ^1H NMR ($CDCl_3$, ppm, δ): 5.55 (p, 1H, $C(CH_3)_2CH_2\boldsymbol{CH}=$), 5.43 (p, 1H, $=\boldsymbol{CH}CH_2OCH_2$), 2.45 (t, 2H, $-\boldsymbol{CH}_2COOH$), 2.4 (m, 2H, $-\boldsymbol{CH}_2CH_2COOH$), 1.95 (d, 2H, $C(CH_3)_2\boldsymbol{CH}_2CH=$), 1.5−1.4 (br, 120H, $-\boldsymbol{CH}_2C(CH_3)_2$), 1.2−1.1 (br, 370H, $\boldsymbol{CH}_3$). ^{13}C NMR ($CDCl_3$, ppm, δ): 182.2 ($-\boldsymbol{C}OOH$), 130.6 ($=\boldsymbol{C}HCH_2CH_2COOH$), 129.4 ($C(CH_3)_2CH_2\boldsymbol{C}H=$), 60.0 ($-\boldsymbol{C}H_2C(CH_3)_2-$), 59.3 ($-\boldsymbol{C}H_2C(CH_3)_3$), 58.6 ($\boldsymbol{C}H_2CH_2COOH$), 56.4 ($C(CH_3)_2\boldsymbol{C}H_2C(CH_3)_2CH_2CH=$), 49.0 ($C(CH_3)_2\boldsymbol{C}H_2CH=$), 38.6−38.2 ($CH_2\boldsymbol{C}(CH_3)_2$), 36.0 ($C(\boldsymbol{C}H_3)_3CH_2-$), 32.9 ($C(\boldsymbol{C}H_3)_2CH_2CH=$), 31.7 ($-CH_2C(\boldsymbol{C}H_3)_2-$), 31.2 ($C(\boldsymbol{C}H_3)_2CH_2C(CH_3)_2CH_2CH=$), 28.3 ($\boldsymbol{C}H_2CH_2COOH$).

Synthesis of PIB-Allyl-Azide. Dry THF (10 mL) was taken in a 100 mL three-necked round-bottomed flask fitted to a reflux condenser under dry nitrogen. PIB-Allyl-Cl (200 mg, 0.062 mmol) was added, and the mixture was stirred until a homogeneous solution was obtained. Dry DMF was then added dropwise until precipitation was observed. Further dry THF was added to the mixture to obtain a clear solution. Next NaN_3 (200 mg, 3.08 mmol) was added, and the mixture was held at 50 °C for 3 h and room temperature for 8 h. The excess THF was evaporated, and the polymer obtained was dissolved in hexanes and reprecipitated in methanol. The process was repeated three times to remove the inorganic impurities, and the product was dried under vacuum at room temperature. Yield: 91%. ^{1}H NMR ($CDCl_3$, ppm, δ): 5.82 (p, 1H, $C(CH_3)_2CH_2\boldsymbol{CH}{=}$), 5.55 (p, 1H, $=\boldsymbol{CH}CH_2N_3$), 3.74 (d, 2H, $=CH\boldsymbol{CH_2}N_3$), 2.08 (d, 2H, $C(CH_3)_2\boldsymbol{CH_2}CH{=}$), 1.5−1.4 (br, 122H, $\boldsymbol{CH_2}$), 1.2−1.1 (br, 370H, $\boldsymbol{CH_3}$). FT-IR (thin film, cm^{-1}): 2952 ($-C-H_{str}$), 2097 ($-N{=}N_{str}$, $-N_3$), 1472 ($-C-H_{def}$, CH_2), 1366 ($-C-H_{def}$, CH_3), 1231 ($C-N_{str}$, CH_2-N_3), 762 ($=C-H_{def}$, out-of-plane). ^{13}C NMR ($CDCl_3$, ppm, δ): 134.5 ($\boldsymbol{C}H{=}CHCH_2N_3$), 125.6 ($CH{=}\boldsymbol{C}HCH_2N_3$), 60.0 ($-\boldsymbol{C}H_2C(CH_3)_2-$), 59.3 ($-\boldsymbol{C}H_2C(CH_3)_3$), 58.6 ($\boldsymbol{C}H_2CH_2N_3$), 56.3 ($C(CH_3)_2\boldsymbol{C}H_2C(CH_3)_2CH_2CH{=}$), 53.4 ($=CH\boldsymbol{C}H_2N_3$), 49.0 ($C(CH_3)_2\boldsymbol{C}H_2CH{=}$), 38.6−38.2 ($CH_2\boldsymbol{C}(CH_3)_2$), 36.0 ($C(\boldsymbol{C}H_3)_3CH_2-$), 32.9 ($C(\boldsymbol{C}H_3)_2CH_2CH{=}$), 31.7 ($-CH_2C(\boldsymbol{C}H_3)_2-$), 31.2 ($C(\boldsymbol{C}H_3)_2CH_2C(CH_3)_2CH_2-CH{=}$).

Synthesis of PIB-Allyl-OC_3H_3. PIB-Allyl-Cl (212 mg, 0.066 mmol) was dissolved in dry THF (10 mL), and KOH (230 mg, 4.1 mmol) was added followed by propargyl alcohol (252 mg, 4.5 mmol). The reaction mixture was refluxed for 18 h. The progress of the reaction was monitored using ^{1}H NMR spectroscopy, which indicated 100% conversion after 18 h. The reaction was then stopped and cooled to room temperature. The excess THF was evaporated under reduced pressure. The product was dissolved in hexanes and precipitated into methanol three times and dried under vacuum.Yield: 92%. ^{1}H NMR ($CDCl_3$, ppm, δ): 5.80 (p, 1H, $=\boldsymbol{CH}CH_2O$), 5.55 (p, 1H, $C(CH_3)_2CH_2\boldsymbol{CH}{=}$), 4.2 (s, 2H, $O\boldsymbol{CH_2}C{\equiv}CH$), 4.1 (d, 2H, $=CH\boldsymbol{CH_2}O$), 2.45 (s, 1H, $-C{\equiv}\boldsymbol{CH}$), 2.0 (d, 2H, $C(CH_3)_2\boldsymbol{CH_2}CH{=}$), 1.5−1.4 (br, 118H, $\boldsymbol{CH_2}$), 1.2−1.1 (br, 372H, $\boldsymbol{CH_3}$). FT-IR (thin film, cm^{-1}): 3312 ($\equiv C-H_{str}$), 2117 ($C{\equiv}C_{str}$), 1472 ($-C-H_{def}$, CH_2), 1366 ($-C-H_{def}$, CH_3), 1389 ($C-H_{def}$, *tert*-butyl), 1263 ($\equiv C-H_{def}$, overtone), 1231 ($C-O_{str}$), 950 ($=C-H_{def}$, out-of-plane), 700−622 ($\equiv C-H_{def}$, fundamental). ^{13}C NMR ($CDCl_3$, ppm, δ): 133.4 ($=\boldsymbol{C}HCH_2O$), 128.2 ($C(CH_3)_2CH_2\boldsymbol{C}H{=}$), 80.3 ($-\boldsymbol{C}{\equiv}CH$), 74.6 ($-C{\equiv}\boldsymbol{C}H$), 70.7 ($=CH\boldsymbol{C}H_2O$), 60.0 ($-\boldsymbol{C}H_2C(CH_3)_2-$), 59.3 ($-\boldsymbol{C}H_2C(CH_3)_3$), 58.6 ($\boldsymbol{C}H_2CH_2COOH$), 57.0 ($O\boldsymbol{C}H_2C{\equiv}CH$), 56.5 ($C(CH_3)_2\boldsymbol{C}H_2C(CH_3)_2-CH_2CH{=}$), 49.0 ($C(CH_3)_2\boldsymbol{C}H_2CH{=}$), 38.6−38.2 ($CH_2\boldsymbol{C}(CH_3)_2$), 36.0 ($C(\boldsymbol{C}H_3)_3CH_2-$), 32.9 ($C(\boldsymbol{C}H_3)_2CH_2CH{=}$), 31.7 ($-CH_2C(\boldsymbol{C}H_3)_2-$), 31.2 ($C(\boldsymbol{C}H_3)_2CH_2C(CH_3)_2CH_2CH{=}$).

Synthesis of PIB-Allyl-Thymine. Thymine (250 mg, 1.98 mmol) and KOH (111 mg, 1.96 mmol) were dissolved in distilled water (2 mL). The solution was stirred at room temperature for 30 min, and a solution of PIB-Allyl-Br (212 mg, 0.066 mmol) in THF (30 mL) was added. The solution was refluxed for 6 h. The reaction was stopped, and THF (30 mL) was evaporated under reduced pressure. The residue was dissolved in hexanes, and the solution was filtered. The product was purified by reprecipitation from hexanes into methanol three times and dried under vacuum. Yield: 84%. ^{1}H NMR ($CDCl_3$, ppm, δ): 8.30 (s, 1H, $CO\boldsymbol{NH}CO$), 7.0 (s, 1H, $N\boldsymbol{CH}{=}CCH_3$), 5.80 (p, 1H, $C(CH_3)_2CH_2\boldsymbol{CH}{=}$), 5.45 (p, 1H, $=\boldsymbol{CH}CH_2N$), 4.30 (d, 2H, $=CH\boldsymbol{CH_2}N$), 2.05 (d, 2H, $C(CH_3)_2\boldsymbol{CH_2}CH{=}$), 1.96 (s, 3H, $=C(\boldsymbol{CH_3})CO$), 1.5−1.4 (br, 118H, $\boldsymbol{CH_2}$), 1.2−1.1 (br, 371H, $\boldsymbol{CH_3}$). FT-IR (thin film, cm^{-1}): 3400 ($N-H_{str}$, CONHCO), 3187 ($=C-H_{str}$), 2929 ($-C-H_{str}$), 1686 ($C{=}O_{str}$), 1475 ($-C-H_{def}$, CH_2), 1389 ($C-N_{str}$, CONHCO), 1366 ($-C-H_{def}$, CH_3), 1231 ($C-N_{str}$, $CONHCH_2$), 950 ($=C-H_{def}$, out-of-plane), 735 ($C{=}C_{def}$, out-of-plane). ^{13}C NMR ($CDCl_3$, ppm, δ): 164.2 ($NH\boldsymbol{C}OC$), 151.0 ($N\boldsymbol{C}ONH$), 139.9 ($N\boldsymbol{C}H{=}C$), 134.7 ($C(CH_3)_2CH_2\boldsymbol{C}H{=}$), 126.0 ($=\boldsymbol{C}HCH_2N$), 111.1 ($CH{=}\boldsymbol{C}CH_3$), 60.0 ($-\boldsymbol{C}H_2C(CH_3)_2-$), 59.3 ($-\boldsymbol{C}H_2C(CH_3)_3$), 58.6 ($\boldsymbol{C}H_2CH_2NCO$), 56.6 ($C(CH_3)_2\boldsymbol{C}H_2C(CH_3)_2CH_2CH{=}$), 49.8 ($=CH\boldsymbol{C}H_2N$), 48.8 ($C(CH_3)_2\boldsymbol{C}H_2CH{=}$), 38.6−38.2 ($CH_2\boldsymbol{C}(CH_3)_2$), 36.0 ($C(\boldsymbol{C}H_3)_3CH_2-$), 32.9 ($C(\boldsymbol{C}H_3)_2CH_2CH{=}$), 31.7 ($-CH_2C(\boldsymbol{C}H_3)_2-$), 31.2 ($C(\boldsymbol{C}H_3)_2CH_2C(CH_3)_2CH_2CH{=}$).

Synthesis of PIB-Allyl-Methyl Ether. Dry THF (10 mL) was taken in a 100 mL three-necked round-bottomed flask fitted to a reflux condenser. To it PIB-Allyl-Cl (200 mg, 0.062 mmol) was added, and the mixture was stirred until a homogeneous solution was obtained. Dry MeOH was added to the solution dropwise until slight turbidity was observed. Then 3−4 drops of dry THF were added to obtain a clear solution. To the reaction mixture KOH (180 mg, 3.21 mmol) was added, and the mixture was refluxed for 5 h. The reaction mixture was cooled to room temperature. The excess THF was evaporated, and the product obtained was dissolved in hexanes and reprecipitated in methanol. The process was repeated three times to remove inorganic impurities followed by drying under vacuum. Yield: 87%. ^{1}H NMR ($CDCl_3$, ppm, δ): 5.75 (p, 1H, $C(CH_3)_2CH_2\boldsymbol{CH}{=}$), 5.55 (p, 1H, $=\boldsymbol{CH}CH_2O$), 3.90 ($=CH\boldsymbol{CH_2}O$), 3.35 (s, 3H, $O\boldsymbol{CH_3}$), 2.05 (d, 2H, $C(CH_3)_2\boldsymbol{CH_2}CH{=}$), 1.5−1.4 (br, 120H, $\boldsymbol{CH_2}$), 1.2−1.1 (br, 362H, $\boldsymbol{CH_3}$). FT-IR (thin film, cm^{-1}): 2936 ($-C-H_{str}$), 1598 ($C{=}C_{str}$), 1475 ($-C-H_{def}$, CH_2), 1368 ($-C-H_{def}$, CH_3), 1226 ($C-O_{str}$, CH_2OCH_3), 612. ^{13}C NMR ($CDCl_3$, ppm, δ): 132.2 ($=\boldsymbol{C}HCH_2O$), 129.1 ($C(CH_3)_2CH_2\boldsymbol{C}H{=}$), 73.7 ($CH\boldsymbol{C}H_2O$), 60.0 ($-\boldsymbol{C}H_2C(CH_3)_2-$), 59.3 ($-\boldsymbol{C}H_2C(CH_3)_3$), 57.8 ($O\boldsymbol{C}H_3$), 56.4 ($C(CH_3)_2\boldsymbol{C}H_2C\ (CH_3)_2CH_2CH{=}$), 49.0 ($C(CH_3)_2\boldsymbol{C}H_2CH{=}$), 38.6−38.2 ($CH_2\boldsymbol{C}(CH_3)_2$), 36.0 ($C(\boldsymbol{C}H_3)_3CH_2-$), 32.9 ($C(\boldsymbol{C}H_3)_2CH_2CH{=}$), 31.7 ($-CH_2C(\boldsymbol{C}H_3)_2-$), 31.2 ($C(\boldsymbol{C}H_3)_2CH_2C(CH_3)_2CH_2CH{=}$).

Synthesis of PIB-*b*-PEO. PIB-Allyl-Cl (200 mg, 0.07 mmol) was dissolved in dry THF (20 mL), and PEO-OH (420 mg, 0.21 mmol) was added, followed by the addition of KOH (960 mg, 17.5 mmol). The reaction mixture was refluxed for 48 h under a nitrogen atmosphere. The reaction was cooled to room temperature and filtered, and the solvent was evaporated. The residue was dissolved in chloroform and washed with distilled water to remove excess PEO-OH. The organic layer was passed through anhydrous sodium sulfate, and the solvent was evaporated.

PIB-Allyl-Cl (180 mg, 0.069 mmol) was dissolved in dry THF (20 mL), and PEO-OH (138 mg, 0.072 mmol) was added. Under a nitrogen atmosphere the temperature was decreased to 0 °C, and NaH (400 mg, 17.25 mmol) was added followed by TBAB (1.1 g, 3.45 mmol) with constant stirring. The temperature was slowly raised to room temperature, and stirring continued for 16 h. After 16 h water (1 mL) was added slowly to neutralize the unreacted NaH. The mixture was filtered and the solvent was evaporated. The residue was washed with acetone to remove excess TBAB, and then the crude product was dissolved in chloroform and washed with distilled water. The organic layer was dried on anhydrous sodium sulfate, and the solvent was evaporated. ^{1}H NMR ($CDCl_3$, ppm, δ): 5.72 (p, 1H, $C(CH_3)_2CH_2\boldsymbol{CH}{=}$), 5.55 (p, 1H, $=\boldsymbol{CH}CH_2O$), 3.9 (($=CH\boldsymbol{CH_2}O$), 3.65 (m, 134H, $O\boldsymbol{CH_2}CH_2O$), 2.0 (d, 2H, $C(CH_3)_2\boldsymbol{CH_2}CH{=}$), 1.5−1.4 (br, 118H, $\boldsymbol{CH_2}$), 1.2−1.1 (br, 353H, $\boldsymbol{CH_3}$). M_n (GPC) = 4500, PDI = 1.09.

Results and Discussion

Synthesis of Amino-Functional Polyisobutylene. Direct conversion of halides to corresponding amines may be achieved with ammonia.[17] However, it is usually more desirable to use an indirect method, since the reaction of ammonia with primary alkyl halides generally results in a mixture of primary, secondary, and tertiary amines. Facile alkylation of phthalimide followed by hydrazinolysis of the N-substituted derivatives provides a convenient synthesis for primary amines. Bergbreiter and co-workers have already reported the synthesis of amino functional PIB by a Gabriel synthesis.[18] However, the primary bromo-functional PIB precursor was obtained in four steps starting form the commercially available PIB exo-olefin. In a typical procedure, phthalimide potassium and a polar solvent such as DMF are used for the reaction. However, PIB is insoluble in DMF, therefore; a mixture of THF and DMF was used as solvent for the reaction of PIB-Allyl-Cl and potassium phthalimide. The ^{1}H NMR spectrum of the product obtained under reflux for 12 h showed new resonances at 5.5 and 4.3 ppm assigned to the olefinic and phthalimide methylene protons. Peaks at 5.82 and 5.64 ppm attributed to $C(CH_3)_2-CH_2-\boldsymbol{CH}{=}$ and $=\boldsymbol{CH}-CH_2-Cl$ disappeared, indicating complete substitution (Figure 1). The phenyl protons of PIB-Allyl-phthalimide were observed in the range of 7.5−8 ppm. In the ^{13}C NMR spectrum, the peak at 45.8 ppm assigned to the chloromethylene

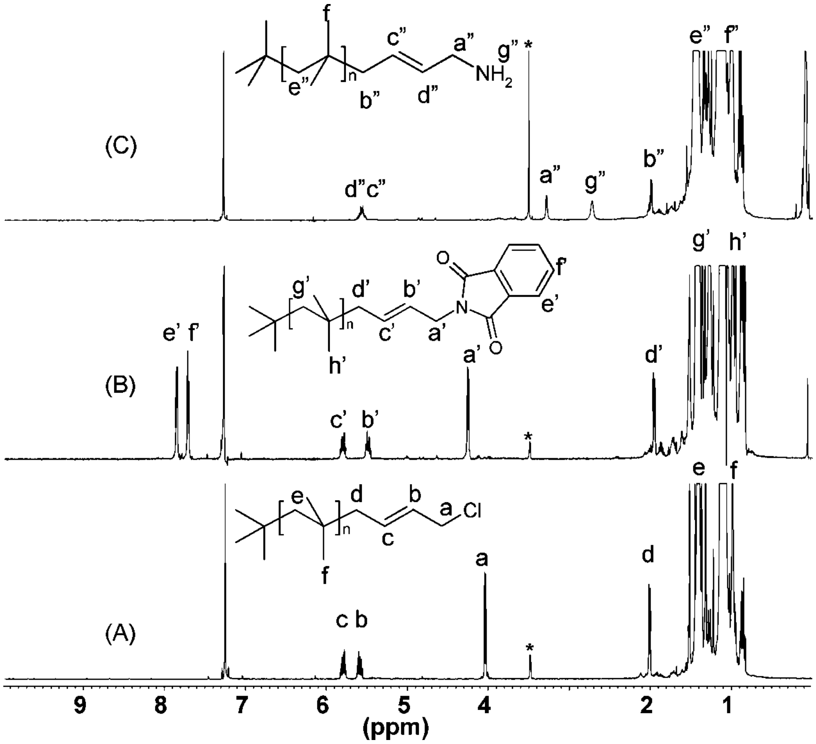


Figure 1. ${}^1H$ NMR spectra of (A) chloroallyl end-functional polyisobutylene and (B) allyl phthalimide functional polyisobutylene. Experimental conditions: PIB-Allyl-Cl = 0.085 mmol, potassium phthalimide = 1.5 mmol, THF (tetrahydrofuran) + *N,N*-dimethylformamide = 9 + 3 mL and 80 °C for 12 h. (C) Aminoallyl end-functional polyisobutylene. Experimental conditions: PIB-Allyl-phthalimide = 0.061 mmol, hydrazine hydrate = 3.5 mmol, THF 10 mL at 80 °C for 24 h. The peaks marked with * are identified as solvent (methanol) peaks.

unit disappeared, and a new signal at 40.1 ppm attributed to the $\boldsymbol{C}H_2$-phthalimide carbon appeared, indicating the formation of the phthalimide derivative (see Supporting Information, Figure 1.1). The resonance for the carbonyl carbon was observed at 168.3 ppm, whereas the signals at 134.2 and 123.6 ppm are attributed to the aromatic carbons. The presence of the allyl-phthalimide end group was further confirmed by MALDI-TOF MS analysis. The spectrum showed a uniform distribution of peaks at a regular interval of 56 amu, the molecular weight of the repeating unit (see Supporting Information, Figure 1.2). The *m/z* values of each signal corresponded to the pseudo-molecular ions that were expected due to the addition of AgTFA. Each peak were expressed according to the following equation:

$$M = Ag^{+} + M_{\mathrm{TMP}} + nM_{\mathrm{IB}} + M_{\mathrm{EG}} \tag{1}$$

where M is the mass of each peak, Ag^+ is the mass of silver ion, M_{TMP} is the mass of initiator fragment, M_{IB} is the mass of isobutylene unit with n repeating units, and M_{EG} is the mass of the end group. In case of PIB-Allyl-phthalimide, the M_{EG} is within 1.4 amu of allyl-phthalimide ($C_4H_6{-}NC_8H_4O_2$, average molecular mass = 200) end group in the polymer.

The PIB-Allyl-phthalimide was hydrazinolyzed to yield PIB-Allyl-NH$_2$ quantitatively. The ${}^1H$ NMR spectrum (Figure 1) shows the complete disappearance of the $\boldsymbol{CH_2}$-phthalimide peak at 4.3 ppm and appearance of a new peak at 3.3 ppm assigned to the $-CH{=}CH{-}C\boldsymbol{H}_2{-}NH_2$ protons. The two olefinic protons were observed as a multiplet at 5.6 ppm. In the ${}^{13}C$ NMR spectrum (see Supporting Information, Figure 1.1), new peaks at 44.7 ($=CH{-}\boldsymbol{C}H_2{-}NH_2$) and 134.4 and 128.0 ppm ($-CH_2{-}\boldsymbol{C}H{=}\boldsymbol{C}H{-}CH_2{-}NH_2$) indicate the formation of PIB-Allyl-NH$_2$. The FT-IR spectrum showed a broad peak at 3379 cm^{-1} assigned to the $-NH$ stretching frequency of the corresponding amino end-functional PIB.

The MALDI-TOF MS figure (see Supporting Information, Figure 1.3) showed distribution of peaks at regular interval of 56 amu. Each peak can be expressed according to eq 1. The calculated M_{EG} = 71 amu is within 1.5 amu of the average molecular mass of the allyl-NH$_2$ moiety. The peak corresponding to the PIB-Allyl-phthalimide disappeared, indicating complete conversion to PIB-Allyl-NH$_2$. The M_n = 3300 and PDI = 1.11 values of PIB-Allyl-NH$_2$ obtained from GPC were virtually identical with those of the precursor PIB-Allyl-Cl.

Synthesis of Mono- and Dihydroxy Functional Polyisobutylene. It is well-known that allyl halides are readily hydrolyzed to olefinic alcohols in the presence of an inorganic base such as KOH or NaOH.[19] According to the ${}^1H$ NMR spectrum of the product of hydrolysis of PIB-Allyl-Cl with KOH in THF/water 1/1, v/v, hydrolysis is complete in 24 h. The disappearance of peaks at 5.82 and 5.64 ppm ($-C\boldsymbol{H}{=}C\boldsymbol{H}{-}CH_2{-}Cl$) and new resonances at 5.75 and 5.65 ppm ($C\boldsymbol{H}{=}C\boldsymbol{H}{-}CH_2{-}OH$) corroborate the formation of PIB-Allyl-OH (Figure 2). The peak at 4.05 ppm attributed to the chloromethylene protons disappeared, and a new peak at 4.15 ppm for hydroxymethylene protons appeared further supporting the complete conversion. In the ${}^{13}C$ NMR spectrum new peaks at 64.3, ($-\boldsymbol{C}H_2{-}OH$) and 130.7 and 131.8 ppm ($-CH_2{-}\boldsymbol{C}H{=}\boldsymbol{C}H{-}CH_2{-}OH$) were observed further confirming the formation of PIB-Allyl-OH (see Supporting Information, Figure 1.4). The FT-IR spectrum of the product was used to calculate functionality (see Supporting Information, Figure 1.5). On the basis of a calibration curve constructed using neopentyl alcohol as the reference compound and the absorbance of a 1.53 mM solution of PIB-Allyl-OH at 3640 cm^{-1} (A = 0.45), the hydroxy functionality $F_{n,\mathrm{OH}}$ = 0.98 was calculated.

Since the bromide anion is a better leaving group compared to the chloride, we expected the hydrolysis to be more facile with PIB-Allyl-Br. PIB-Allyl-Br was synthesized by the halogen exchange reaction according to the reported procedure.[16] As anticipated, the hydrolysis of PIB-Allyl-Br was much faster than the chloroallyl counterpart; complete conversion was observed

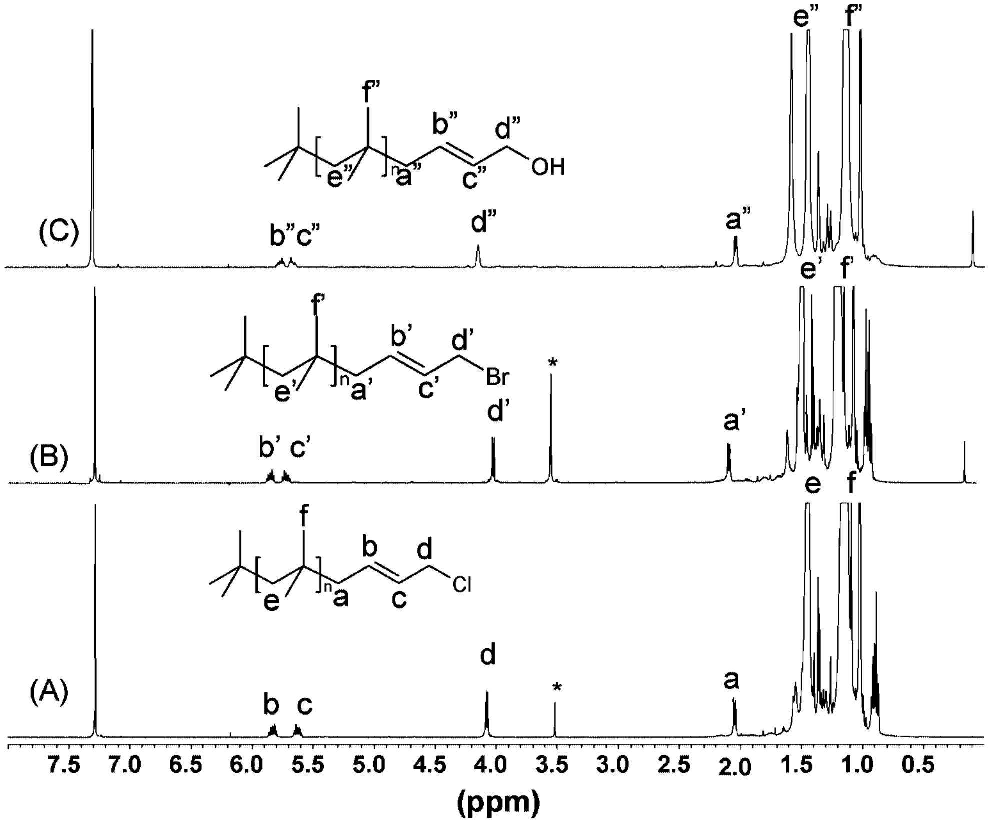


Figure 2. ^{1}H NMR spectra of (A) chloroallyl end-functional polyisobutylene, (B) bromoallyl end-functional polyisobutylene, and (C) hydroxyallyl end-functional polyisobutylene. The peaks marked with * are identified as solvent (methanol) peaks.

after 3 h under similar conditions. In the ^{1}H NMR spectrum, resonances at 4.0, 5.7, and 5.85 ppm assigned to the bromomethylene and bromoallylmethine protons disappeared, and new signals at 4.15, 5.65, and 5.75 ppm assigned to the hydroxymethylene and hydroxyallylmethine protons appeared, indicating the product formation (Figure 2).

Hydrolysis of both chloro- and bromoallyl telechelic PIB was also conducted at 130 °C using KOH as the base. Complete hydrolysis was accomplished in 3 h for Br-Allyl-PIB-Allyl-Br and 24 h for Cl-Allyl-PIB-Allyl-Cl. On the basis of quantitative FT-IR analysis, $F_{n,OH} = 1.96$ was derived.

The functionality of hydroxyl telechelic PIB was further investigated by MALDI-TOF MS. The spectra of completely and partially (60% determined by ^{1}H NMR spectroscopy) hydrolyzed Cl-Allyl-PIB-Allyl-Cl samples are shown in Figures 3 and 4. The completely hydrolyzed polymer showed a single set of peaks distributed at a regular interval of 56 amu. Each peak was expressed by the following equation:

$$M_1 = Ag^+ + M_{DCC} + nM_{IB} + M_{EG} \qquad (2)$$

where M_1 corresponded to the mass of each peak and M_{DCC} is the mass of initiator residue. The calculated $M_{EG} = 141$ amu is close to the average molecular mass of two units of $C_4H_6{-}OH$. The 60% hydrolyzed Cl-Allyl-PIB-Allyl-Cl showed two set of peaks distributed at a regular interval of 56 amu. This indicated the presence two different types of end groups: one set of peaks equivalent with the spectrum of hydroxy telechelic PIB, whereas the other set of peaks gave an end mass of 159 corresponding to the monohydrolyzed product (HO-Allyl-PIB-Allyl-Cl). The precursor Cl-Allyl-PIB-Allyl-Cl was not observed since even if it was present it does not ionize under the above conditions.

Although we have been unable to find literature references for the hydrolysis of activated halides by tetraalkylammonium hydroxide, we have carried out hydrolysis experiments with TBAH. TBAH is commercially available, inexpensive, and soluble in a wide range of organic solvents—including hydrocarbons, aromatics, alcohols, and halogenated organics. Perhaps most importantly the large organic cation enhances the reactivity due to looser ion pairing than is possible with metal hydroxides. Because of this increased reactivity, the rate of hydrolysis of PIB-Allyl-Cl or PIB-Allyl-Br in the presence of TBAH was much faster compared to KOH-mediated hydrolysis. Thus, the reaction was complete in 14 h under reflux with PIB-Allyl-Cl and in 1 h at room temperature with PIB-Allyl-Br. The NMR,

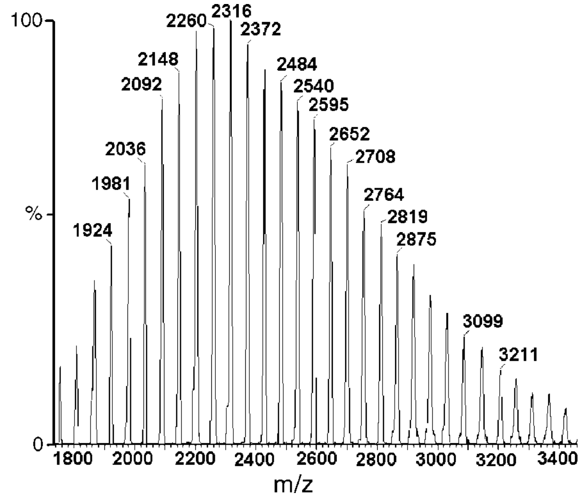


Figure 3. MALDI-TOF MS of the product obtained by the reaction of chloroallyl telechelic polyisobutylene with potassium hydroxide. Experimental conditions: Cl-Allyl-PIB-Allyl-Cl = 0.031 mmol in 10 mL of tetrahydrofuran, KOH = 1.78 mmol in 10 mL of H_2O, temperature of 130 °C in a pressure vessel, and time 24 h. The spectrum was recorded in linear mode using the dithranol/silver trifluoroacetate matrix system.

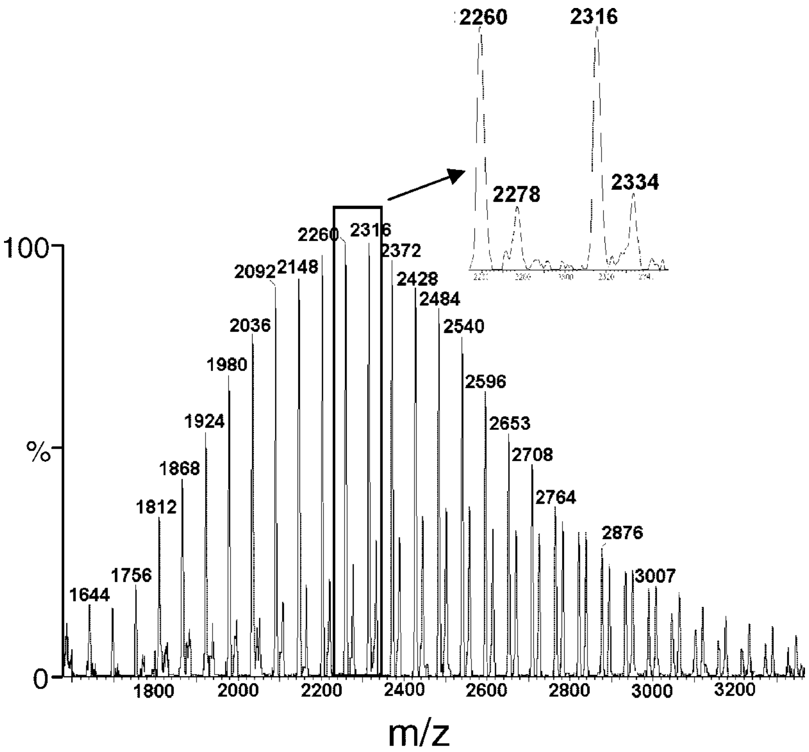


Figure 4. MALDI-TOF MS of the product obtained by the reaction of chloroallyl telechelic polyisobutylene with KOH after 5 h at 130 °C. The spectrum was recorded in linear mode using the dithranol/silver trifluoroacetate matrix system. The inset shows the magnified view where the large peaks correspond to the dihydroxy telechelic polyisobutylene, and the small peaks correspond to α-hydroxyallyl-*ω*-chloroallyl end-functional polyisobutylene.

MALDI-TOF MS, and FT-IR spectra were identical with that of the PIB-Allyl-OH shown earlier.

Synthesis of Carboxy-Functional Polyisobutylene. Decarboxylation of alkylated malonic esters readily yields carboxyl functionality. Generally alkylation of malonic ester is effected in good yields by primary bromides.[20] For instance, Dapporto et al. reported monosubstitution of benzyl bromide to malonic ester in the presence of K_2CO_3 with 92% yield.[21] Effective hydrolysis and decarboxylation of substituted malonic esters are also reported in literature.[22] Bergbreiter and co-workers[18] have already reported the synthesis of PIB carboxylic acid by this method starting with PIB-$CH_2OSO_2CH_3$. Using a similar approach, substitution of PIB-Allyl-Br with malonic ester followed by hydrolysis and decarboxylation was carried out. The ^{1}H NMR spectra of the starting PIB-Allyl-Cl (A), the PIB-Allyl-malonic ester (B), and the final PIB-Allyl-CH_2COOH (C) are shown in Figure 5. In spectrum B the peak at 3.95 ppm ($-C\boldsymbol{H}_2-Br$) is absent, and a new peak at 2.65 ppm ($-C\boldsymbol{H}-(COOMe)_2$) appeared, indicating successful alkylation. After decarboxylation this peak shifted to 2.3 ppm, indicating the formation of PIB-Allyl-CH_2COOH. In PIB-Allyl-malonic ester, the olefinic protons appear at 5.35 and 5.6 ppm, which shift to 5.55 and 5.43 ppm after decarboxylation, suggesting quantitative reaction. The end functionality was further investigated by MALDI-TOF MS (see Supporting Information, Figure 1.6). The calculated $M_{EG} = 113$ amu is identical to the average molecular weight of allyl-CH_2COOH moiety. This confirmed the quantitative conversion of PIB-Allyl-chloride to PIB-Allyl-CH_2COOH.

Synthesis of Azide and Propargyl-Functional Polyisobutylenes. Azide and propargyl end-functional PIBs can be employed as building blocks for different polymeric architectures using the Sharpless click reaction.[23] During the past several years the Sharpless click reaction,[24] an azide/alkyne 1,3-dipolar cycloaddition, has demonstrated wide utility in materials science. Click chemistry is especially attractive for the synthesis of block or graft copolymers when the second monomer cannot be polymerized by cationic polymerization. Opsteen et al. reported the synthesis of diblock and triblock copolymers based on PMMA (poly(methyl methacrylate)), PS (polystyrene), and PEO segments using click chemistry.[25] Binder et al. synthesized the azide-terminated triarm star PIB using a complicated procedure starting from allyl functional triarm star PIB.[26] Bergbreiter and co-workers also reported the synthesis of PIB-N_3.[18] This preparation involved five separate steps starting from the commercially available vinyl-terminated PIB. Acetylene functional PIB has not been reported so far. Click chemistry may be fully utilized for the synthesis of PIB-based polymer architectures if PIB azide and alkyne could be obtained in simple one-step functionalization reactions.

PIB-Allyl-X can be utilized for the syntheses of PIB-Allyl-azide and PIB-Allyl-alkyne by simple nucleophilic substitution with alkali metal azide and propargyl alcohol, respectively. Reactions of sodium azide with activated chlorides have been reported in the literature. The synthesis of PIB-Allyl-N_3 was carried out using reported procedures. [27] The ^{1}H NMR spectrum of PIB-Allyl-N_3 (see Supporting Information Figure 1.7) exhibited a new resonance at 3.75 ppm attributed to the $-C\boldsymbol{H}_2-N_3$ protons, the $-C\boldsymbol{H}_2-Cl$ peak at 4.05 ppm is completely absent, and the resonance of one of the olefinic proton shifted from 5.64 to 5.55 ppm, indicating complete substitution. The FT-IR spectrum showed a peak at 2097 cm^{-1} for the $N-N_{str}$ of the azide group (see Supporting Information Figure 1.8). The ^{13}C NMR spectrum showed disappearance of peaks at 132.2 and 129.1 ppm and appearance of new peaks at 134.5 and 125.6 ppm for the olefinic carbons. The resonance of chloromethylene carbon at 45.8 ppm disappeared, and a new peak at 53.4 ppm appeared for azidomethylene carbon (see Supporting Information Figure 1.9).

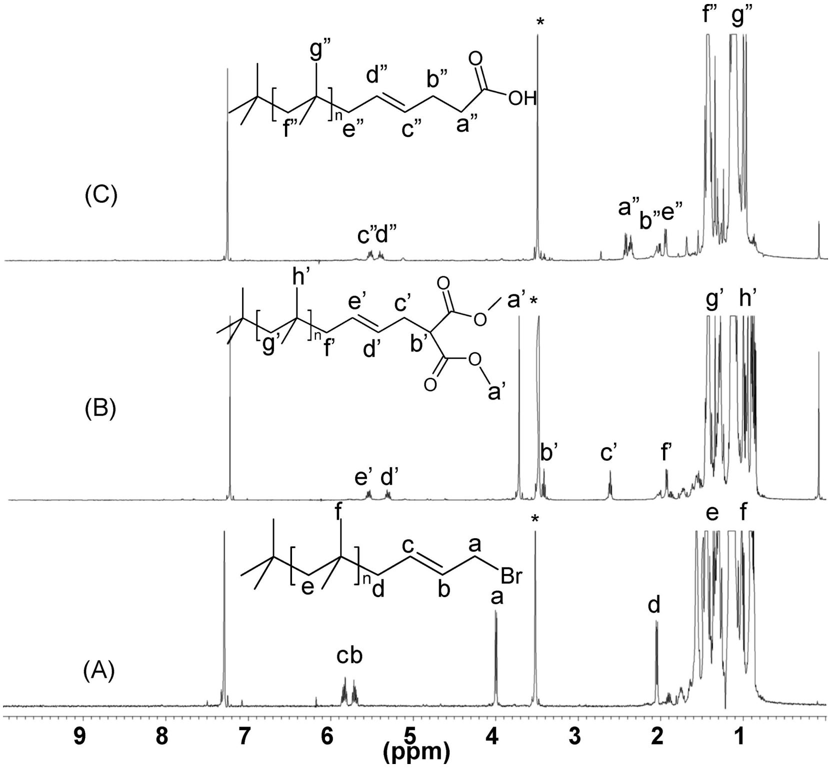


Figure 5. ^{1}H NMR spectra of (A) bromoallyl end-functional polyisobutylene, (B) allyl-malonic ester end-functional polyisobutylene, and (C) allyl-methanoic acid end-functional polyisobutylene. The peaks marked with * are identified as solvent (methanol) peaks.

The propargyl end-functional PIB was synthesized by the reaction of PIB-Allyl-Cl with propargyl alcohol in the presence of KOH. The progress of the reaction was monitored by ^{1}H NMR spectroscopy following the disappearance of peak at 5.65 ppm. Complete substitution was observed after 18 h (see Supporting Information Figure 1.7). A new peak at 5.55 ppm appeared for the olefinic proton of propargyl terminal PIB. The methyne protons appeared at 2.4 ppm while the signals for $=CH-C\boldsymbol{H}_2-O-C\boldsymbol{H}_2-C\equiv CH$ protons were observed at 4.05 and 4.1 ppm. In the ^{13}C NMR spectrum the olefinic carbons showed two peaks at 133.4 and 128.3 ppm, the propargyl carbons showed the resonance at 80.3 and 74.6 ppm, and the $=CH-\boldsymbol{C}H_2-O-\boldsymbol{C}H_2-C\equiv CH$ carbons signals appeared at 70.7 and 57 ppm (see Supporting Information Figure 1.9).

Synthesis of Thymine-Functional Polyisobutylene. Nucleobase end-functionalized polymers are useful materials as they can form a variety of polymeric architectures by intermolecular hydrogen bonding.[28] Thymine end-functional materials are especially important, since they also readily undergo reversible UV-assisted photodimerization.[29] Binder and co-workers have reported nucleobase such as thymine, cytosine, and uracil functional PIBs and their pseudoblock copolymers with nucleobase end-capped PEK.[30] However, the synthetic route to these materials is rather inconvenient. Starting with allyl-terminated PIB, hydroxy functional PIB was prepared, which was transformed to chloromethyl ether end-functionalized PIB. The reaction of a silylated nucleobase with PIB-OCH$_2$Cl yielded the nucleobase end-functionality.

Previous reports show that thymine readily reacts with allyl and benzyl halides in the presence of a base in polar medium. 1,4-Dichloro-2-butene reacted with various nucleobases in the presence of K$_2$CO$_3$ in dimethyl sulfoxide or tetrabutylammonium fluoride in THF to form 40−60% N-substituted product.[31] Substituted benzyl chloride also reacted with thymine in presence of chlorotrimethylsilane to form 48% N-substituted product.[32] With allyl and benzyl bromides the extents of substitution were higher. The reaction of benzyl bromide with thymine yielded 95% substitution in the presence of bis(trimethylsilyl)amine.[33] With K$_2$CO$_3$ as a base in the presence of catalytic amounts of KI the yield decreased to 87%.[34]

PIB-Allyl-X is expected to readily react with nucleobases to form PIB-Allyl-nucleobase. Cheng et al. have showed that the thymine unit can be attached to chloromethylstyrene derivative in the presence of KOH.[35]

Our initial efforts to react thymine with PIB-Allyl-Cl in the presence of KOH were not successful due to the low reactivity of PIB-Allyl-Cl. With the more reactive PIB-Allyl-Br, however, the reaction readily proceeded and 94% thymine substituted PIB (determined by ^{1}H NMR spectroscopy) was obtained after 6 h. In PIB-Allyl-thymine resonances for both the olefinic and methylene protons attached to the thymine shifted compared to these proton in the precursor. A small peak, however, at 3.95 ppm (used to determine the conversion) due to an incomplete reaction is still visible (see Supporting Information Figure 2.0). The ^{13}C NMR spectrum also supported the product formation. MALDI-TOF MS of the product was also recorded (see Supporting Information Figure 2.1). The $M_{EG} = 179$ amu value is identical to the mass of the end group ($-C_4H_6-$thymine average $M_n = 179$). However, in the higher molecular weight region a marked deviation in the molecular mass of end group (M_{EG}) was observed.

Synthesis of PIB-Allyl-OR. In addition to nucleophilic substitution with OH$^-$ other O-nuclophiles perhaps most importantly small organic and polymeric alkoxides may be considered to obtain novel functional PIBs and PIB block copolymers. In a model experiment a reaction with methanol in the presence of KOH was carried out in refluxing THF for 5 h. In the ^{1}H NMR spectrum of the product the resonances at 4.05 ppm assigned to the $-\boldsymbol{CH_2}-Cl$ proton and at 5.82 and 5.64 ppm attributed to $-\boldsymbol{CH}=\boldsymbol{CH}-CH_2-Cl$ disappeared, and new peaks at 3.4 ppm ($-OC\boldsymbol{H}_3$), at 3.9 ppm ($-\boldsymbol{CH_2}-OCH_3$), and at 5.75 and 5.55 ppm ($-C\boldsymbol{H}=C\boldsymbol{H}-CH_2-OMe$) were

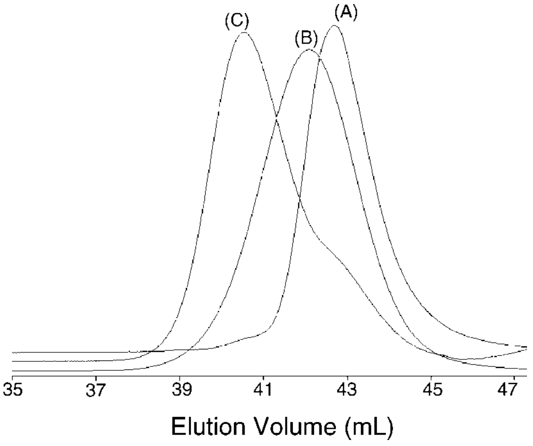


Figure 6. GPC traces of precursor (A) hydroxy-terminated polyethylene oxide (M_n = 1500, PDI = 1.06) (B) chloroallyl end-functional polyisobutylene (M_n = 3200, PDI = 1.12), and (C) polyisobutylene-*block*-polyethylene oxide diblock copolymer (M_n = 4500, PDI = 1.09).

observed. In the ^{13}C NMR spectrum (see Supporting Information Figure 2.2), the signals at 73.7, 133.7, and 128.7 ppm assigned to $-\boldsymbol{C}\mathrm{H_2}-\mathrm{OMe}$ and $-\boldsymbol{C}\mathrm{H}{=}\boldsymbol{C}\mathrm{H}-\mathrm{CH_2}-\mathrm{OMe}$ carbons appeared and peaks for $-\boldsymbol{C}\mathrm{H_2}-\mathrm{Cl}$ and $-\boldsymbol{C}\mathrm{H}{=}\boldsymbol{C}\mathrm{H}-\mathrm{CH_2}-\mathrm{Cl}$ carbons at 45.8, 132.2, and 129.1 ppm disappeared, also indicating quantitative methoxylation. This methodology was extended to prepare PIB-*b*-PEO. The synthesis of PIB-*b*-PEO has already been reported, but the methods were cumbersome and involved multiple steps.[36–38] Encouraged by the quantitative methoxylation of PIB-Allyl-Cl, PEO-OH (M_n = 1500) was reacted with PIB-Allyl-Cl. Replacing KOH with NaH and employing the phase transfer catalyst TBAB yielded 100% blocking efficiency in respect to PIB-Allyl-Cl by using a close to stoichiometric amount of PEO-OH ([PEO-OH]/[PIB-Allyl-Cl] = 1.05) (see Supporting Information Figure 2.3). The resonances at 5.64 and 5.82 ppm corresponding to the $-\boldsymbol{CH}{=}\boldsymbol{CH}-\mathrm{CH_2}-\mathrm{Cl}$ protons disappeared and new resonances at 5.55 and 5.72 ppm for the $-\boldsymbol{CH}{=}\boldsymbol{CH}-\mathrm{CH_2}-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_2}-$ protons appeared, confirming the formation of diblock copolymer. Compared to the precursors, the RI trace of the product shifted to higher molecular weights and only exhibits a small hump at the elution volume of PEO-OH due to the slight excess used (Figure 6).

Conclusions

A new general methodology has been developed for the efficient preparation of end-functional PIBs. The method involves the capping reaction of living PIB with 1,3-butadiene followed by simple nucleophilic substitution of the resulting trans-1,4-adduct to yield PIBs with $-\mathrm{OH}$, $-\mathrm{NH_2}$, $-\mathrm{COOH}$, $-\mathrm{N_3}$, and $-\mathrm{OCH{\equiv}CH}$ end groups. These reactions yield end-functional PIBs in simple, convenient, and quantitative reactions. The method can be extended to the synthesis of block copolymers by employing polymers with nucleophilic end groups. Although most of the reactions reported in here have not been optimized, the proposed methodology is by far the simplest and most efficient reported to date. Optimization of the above functionalization reactions and extending the scope to other nucleophiles as well as applications of functional PIBs in the synthesis of segmented block copolymer thermoplastic elastomers, amphiphilic block copolymers, and curable coatings, in click chemistry and reversible chain extension or cross-linking are ongoing in our laboratory.

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Supporting Information Available: Figures showing the ^{1}H NMR spectra of polymers PIB-Allyl-OMe, PIB-Allyl-$\mathrm{N_3}$, PIB-Allyl-$\mathrm{OCH_2C{\equiv}CH}$, PIB-*b*-PEO, and OH-Allyl-PIB-Cum-PIB-Allyl-OH, ^{13}C NMR spectra of PIB-Allyl-Cl, PIB-Allyl-phthalimide, PIB-Allyl-$\mathrm{NH_2}$, PIB-Allyl-OH, PIB-Allyl-OMe, PIB-Allyl-$\mathrm{N_3}$, PIB-Allyl-$\mathrm{OC_3H_3}$, OH-Allyl-PIB-Cum-PIB-Allyl-OH, PIB-Allyl-$\mathrm{CH_2COOH}$, and PIB-Allyl-thymine, MALDI-TOF MS of PIB-Allyl-phthalimide, PIB-Allyl-$\mathrm{NH_2}$, PIB-Allyl-$\mathrm{CH_2COOH}$, and PIB-Allyl-thymine, and FT-IR spectra of PIB-Allyl-$\mathrm{N_3}$, PIB-Allyl-$\mathrm{NH_2}$, PIB-Allyl-OH, and OH-Allyl-PIB-Cum-PIB-Allyl-OH. This material is available free of charge via the Internet at http://pubs.acs.org.

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