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# Supporting information

# Living cationic polymerization and polyhomologation: an ideal combination to synthesize functionalized polyethylene-polyisobutylene block copolymers

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## Experiments

### Chemicals

Trimethylsulfoxonium iodide (98 %, Alfa Aesar), benzyltri-*n*-butylammonium chloride (98%, Alfa Aesar) and trimethylamine *N*-oxide dihydrate (TAO·2$H_2O$) (>99%, Fluka) were used as received. Sodium hydride (NaH) (60% in mineral oil, Aldrich) was washed by hexane before use. Celite 545® (Aldrich) was dried at 150 °C for 48h before use. Tetrahydrofuran (THF) (99%, Fisher) and toluene (99.7%, Fluka) were distilled from sodium/benzophenone before use. $BH_3$·THF solution (1.0M in THF, Aldrich) was used as received. The dimethylsulfoxonium methylide solution (0.80 M in toluene) was prepared according to our previous work.[1]
Isobutylene (IB, Matheson Tri Gas) and methyl chloride (MeCl, Airgas) were dried in their gaseous state by passing them through in-line gas-purifier columns packed with BaO/Drierite and then condensed in a receiver flask at -80 °C before use. Titanium (IV) chloride ($TiCl_4$, 99.9%, Sigma-Aldrich), 2,6-di-*tert*-butylpyridine (DTBP, 97%, Aldrich) and allyltrimethylsilane (ATMS, 98%, Aldrich) were used as received.

Hexane, mixture of isomers (Hex ≥ 98.5%, Sigma-Aldrich, ACS reagent) was purified by refluxing over concentrated sulfuric acid for 48 h. It was then washed with aqueous solution of KOH three times followed by washing with distilled water until neutral to pH paper. Then it was kept over anhydrous $Na_2SO_4$ overnight at room temperature and finally distilled over $CaH_2$ under a nitrogen atmosphere twice before use in the polymerization. 2-chloro-2,4,4-trimethylpentane (TMPCl) was synthesized according to the literature.[2]

### Instruments

High temperature gel permeation chromatography (HT-GPC) measurements were carried out on a Viscoteck HT-GPC module 350 instrument with two PLgel 10 μm MIXED-B columns equipped with a reflective index detector (RI), a two-angle light scattering detector (λ = 670 nm) (LS) and a viscometer. 1,2,4-Trichlorobenzene (TCB) was the eluent (0.8 mL/min) at 150 ºC. RI detector was calibrated by using PS standards with molecular weights ($M_p$) from 1050 g/mol to 1.9 × $10^6$ g/mol (PDIs < 1.15). Proton nuclear magnetic resonance spectra ($^1$H NMR) were recorded on a Bruker AVANCE III-600 spectrometer. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC1/TC100 system with an inert nitrogen atmosphere. The samples were heated

from room temperature to 160 ºC, cooled to -110 ºC and finally heated again to 160 ºC at a heating/cooling rate of 10 ºC/min. The second heating curve was used to determine the glass transition temperature ($T_g$), melting point ($T_m$) and crystallinity degree ($X_c$).

**Synthesis of allyl-terminated polyisobutylene (PIB-allyl)**

Allyl-terminated PIB (PIB-allyl) of three different molecular weights of 1070, 2660 and 3640 g/mol were synthesized by living cationic polymerization of IB in Hex/MeCl 60/40 (*v*/*v*) at -80 °C using TMPCl as the initiator followed by end-functionalization using ATMS following a previously reported procedure by Kennedy and coworkers.[3] Living cationic polymerization of IB was performed in an MBraun MB200MOD stainless steel glove box (Innovative Technology Inc.) equipped with a gas purification system (molecular sieves and cupper catalyst) under dry $N_2$ atmosphere. In a typical experiment, living cationic polymerization of IB was carried out in Hex/MeCl 60/40 (v/v) at -80 ºC using these following initial concentrations of reactants: [TMPCl] = 0.015 M, [DTBP] = 0.004 M, [IB] = 0.24 M and [$TiCl_4$] = 0.036 M. In a 1000 mL round bottomed flask equipped with an overhead mechanical stirrer, 9.4 mL of IB (0.12 mol), 450 µL DTBP (0.002 mol), 1.3 mL TMPCl (0.0075 mol), 290.6 mL of Hex and 192.0 mL of MeCl were added, and the mixture was cooled to -80 ºC. 10.0 mL $TiCl_4$ was added to 40 mL MeCl to prepare a stock solution of $TiCl_4$ in MeCl. 10 mL of this solution was added to the round bottomed flask to initiate the polymerization. After 60 min of IB polymerization, 10 mL of the reaction mixture was taken out using a dry syringe and quenched with 1.0 mL of prechilled methanol for the characterization of precursory PIB, and to the rest of the reaction solution, appropriate amount of ATMS (0.015 mmol at −80 °C) was added under stirring. The reaction was continued for another 4 h and then terminated by the addition of 5.0 mL of prechilled methanol at −80 °C. The solvent was evaporated and the crude product was dissolved in hexane. It was then precipitated by dropwise addition to methanol under stirring condition. This dissolution/ precipitation step was repeated twice more. After that, methanol was decanted out, and the polymer was vacuum-dried for 12 h in a vacuum oven at room temperature to remove any residual methanol.

**Synthesis and titration of macroinitiator $PIB_3B$**

Taking the synthesis and titration of ($PIB_{3.6k}$)B as an example, in a 50 mL Schlenk flask, 5.0 g of dry $PIB_{3.6k}$-allyl (1.39 mmol) was dissolved in 30 mL of freshly distilled toluene. After cooled down to 0 °C, 0.4 mL of $BH_3$·THF solution in THF (1.0 M) was added for hydroboration leading to the macroinitiator for polyhomologation, $PIB_3B$. The mixture was kept in a glove box with argon atmosphere at room temperature for 10 days.

Because of the unavoidable existence of impurities, the real concentration of initiator ($PIB_3B$) should be determined by titration before use. For this purpose a small-scale polyhomologation process was performed. 5 mL of $PIB_3B$ solution was added into 15 mL of dimethylsulfoxonium methylide solution in toluene (0.80 M) at 80 °C. The polyhomologation was finished in 20 min followed by addition of 0.3 g of TAO. After 4 h,

the resultant solution was precipitated in excess methanol to give a white solid product, which is a mixture of PIB-*b*-PE-OH and unreacted PIB-allyl. To separate the PIB homopolymer from the copolymer of PIB-*b*-PE-OH, the crude product was dissolved in hot toluene (80 °C) and then cooled down to room temperature leading to a cloudy solution. After centrifugation, the cloudy solution was separated into two phases, one was gel-like (PIB-*b*-PE-OH) and the other was clear and transparent solution (PIB homopolymer in toluene). HT-GPC traces indicated a high purity PIB-*b*-PE-OH (Figure S1). From the $^1$H NMR spectrum (Figure S2), the molecular weight $M_n$ = 4 570 g/mol of PE block was calculated according to $M_{n,\,PE}$ = 63 × 14 × (area of the peaks at δ=1.3 ppm)/(area of the peaks at δ=1.5 ppm) (g/mol), where 63 is the average DP of isobutene units in the PIB chain, 14 is molecular weight of -$CH_2$- unit in PE block (g/mol). The peak at δ=1.60 ppm (peak **1** in Figure S2, right image**)** corresponds to the methylene group (-C***H***$_2$-) of PIB block and the peak at δ=1.25 ppm (peak **6** in Figure S2, right image) to the -C***H***$_2$- of PE block. By using this molecular weight ($M_n$ = 4 570 g/mol), the real concentration of $PIB_3B$ of 0.0025 mmol/mL was calculated according to c = 12.0/(326×3×5) (mmol/mL), where 12.0 is the amount of dimethylsulfoxonium methylide in mmole, 316 is the average number of -$CH_2$- unit in PE block, 3 is the functionality of the macroinitiator and 5 is the volume of macroinitiator (mL). The lower concentration than the expected one of 0.013 mmol/mL is a consequence of impurities existing either in the PIB-allyl samples or introduced during the operation.

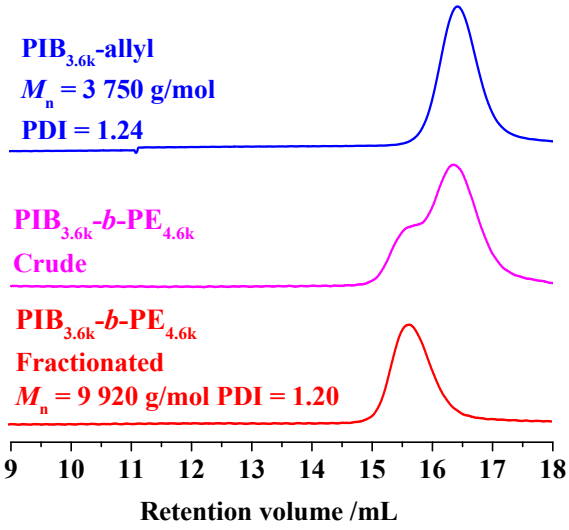


**Figure S1**. Monitoring the synthesis of $PIB_{3.6k}$-*b*-$PE_{4.6k}$ by HT-GPC in TCB at 150 °C. All peaks are negative and shown in positive style for better presentation

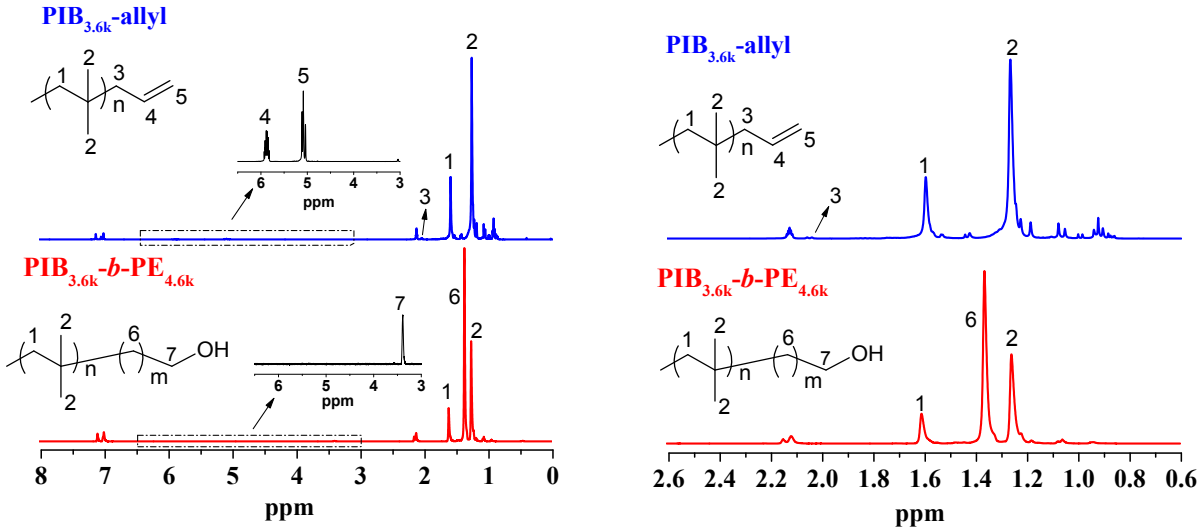


**Figure S2**. $^1$H NMR spectra of $PIB_{3.6k}$-*b*-$PE_{4.6k}$ synthesized for determining the real concentration of $PIB_3B$ (left: full spectra, right: after zooming)

**Synthesis of PIB-*b*-PE-OH**

All PIB-*b*-PE-OHs copolymers were synthesized following the same process used for titration. For example, $PIB_{3.6k}$-*b*-$PE_{9.3k}$ was synthesized using 10 mL of $PIB_3B$ solution and 55 mL of dimethylsulfoxonium methylide solution in toluene (0.80 M).

All the products were characterized by HT-GPC (Figure S3 and S4), $^1$H NMR (Figure S5 and S6) and DSC (Figure S7 and S8).

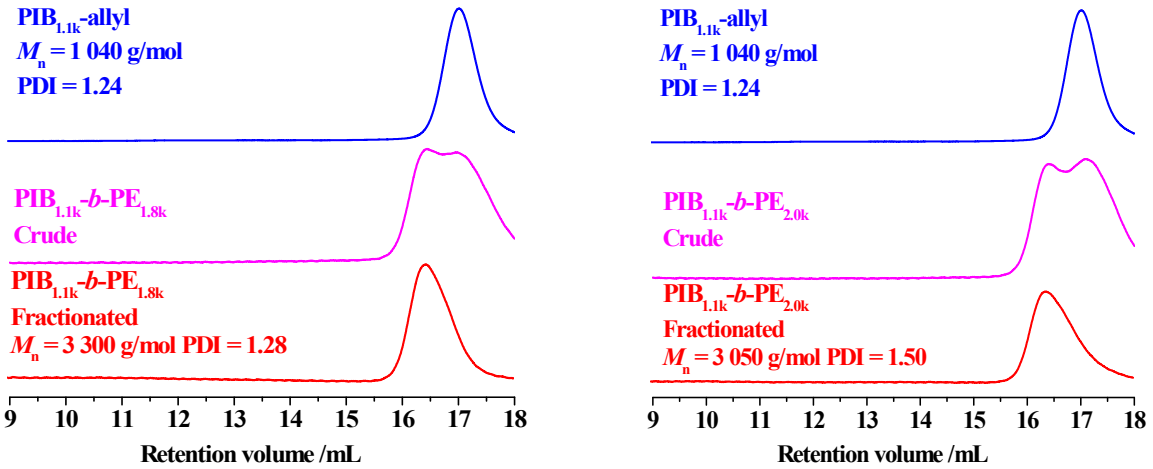


**Figure S3**. Monitoring the synthesis of $PIB_{1.1k}$-*b*-PEs by HT-GPC in TCB at 150 °C. All peaks are negative and shown in positive style for better presentation

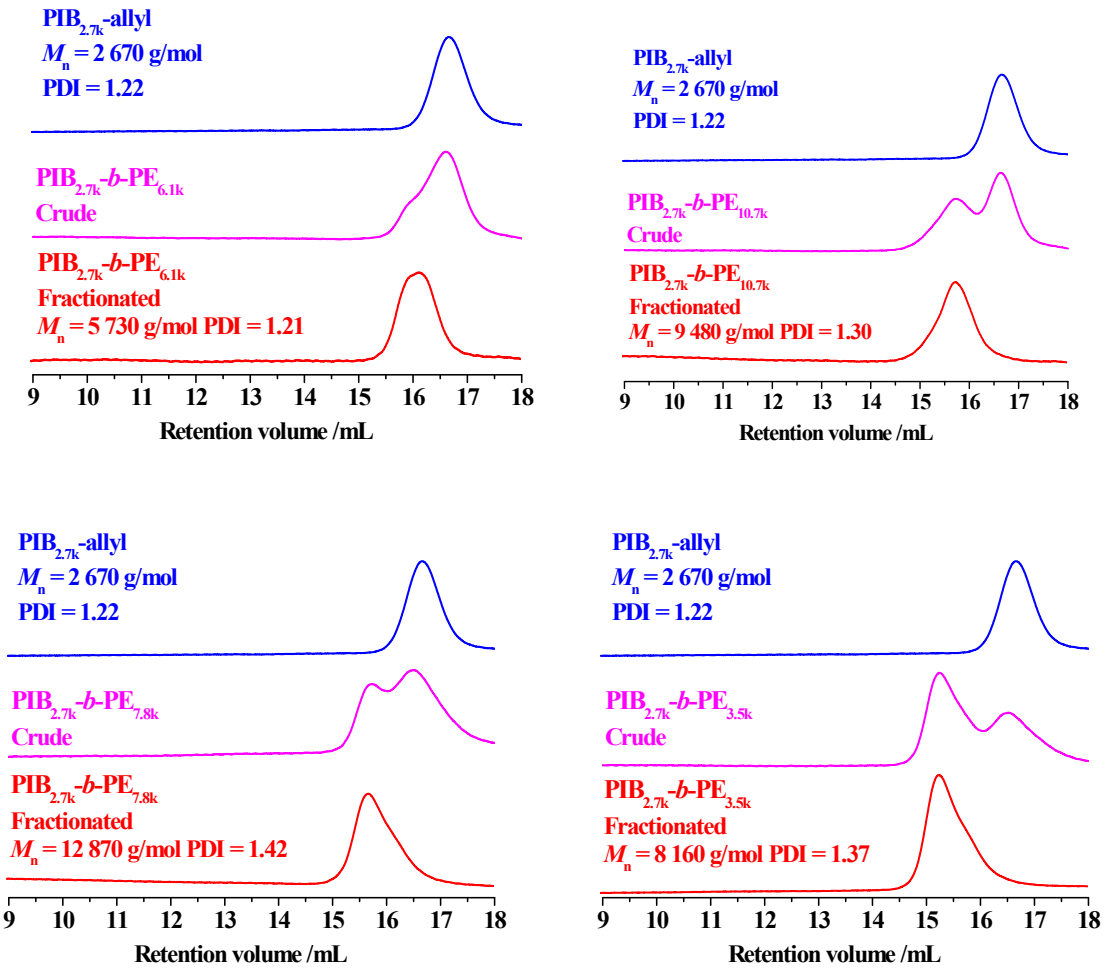


**Figure S4**. Monitoring the synthesis of $PIB_{2.7k}$-*b*-PEs by HT-GPC in TCB at150 °C. All peaks are negative and shown in positive style for better presentation

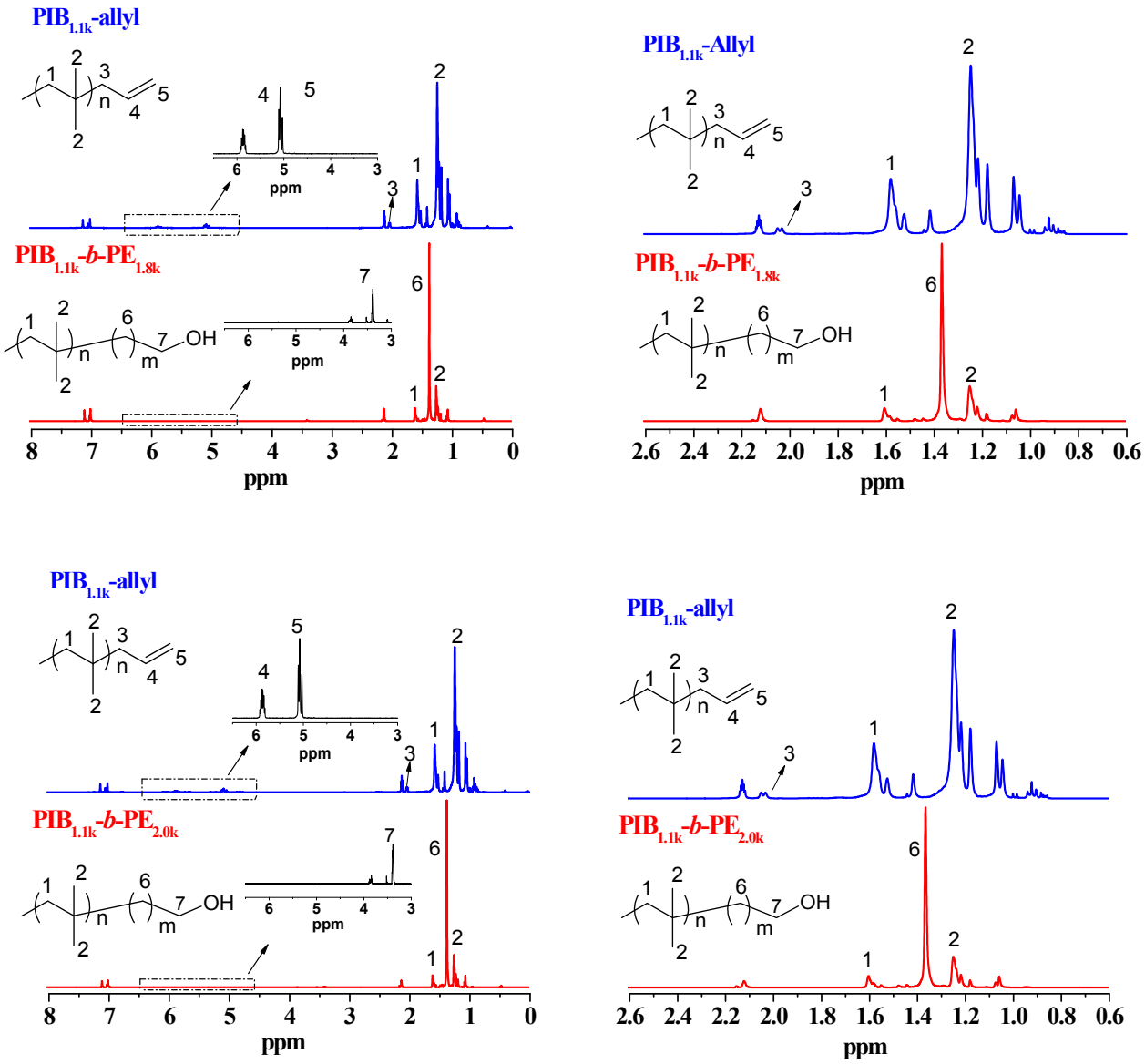


**Figure S5**. Monitoring the synthesis of $PIB_{1.1k}$-*b*-PEs and by $^1H$ NMR (left: full spectra, right: after zooming) (toluene-$d_8$, 80 °C)

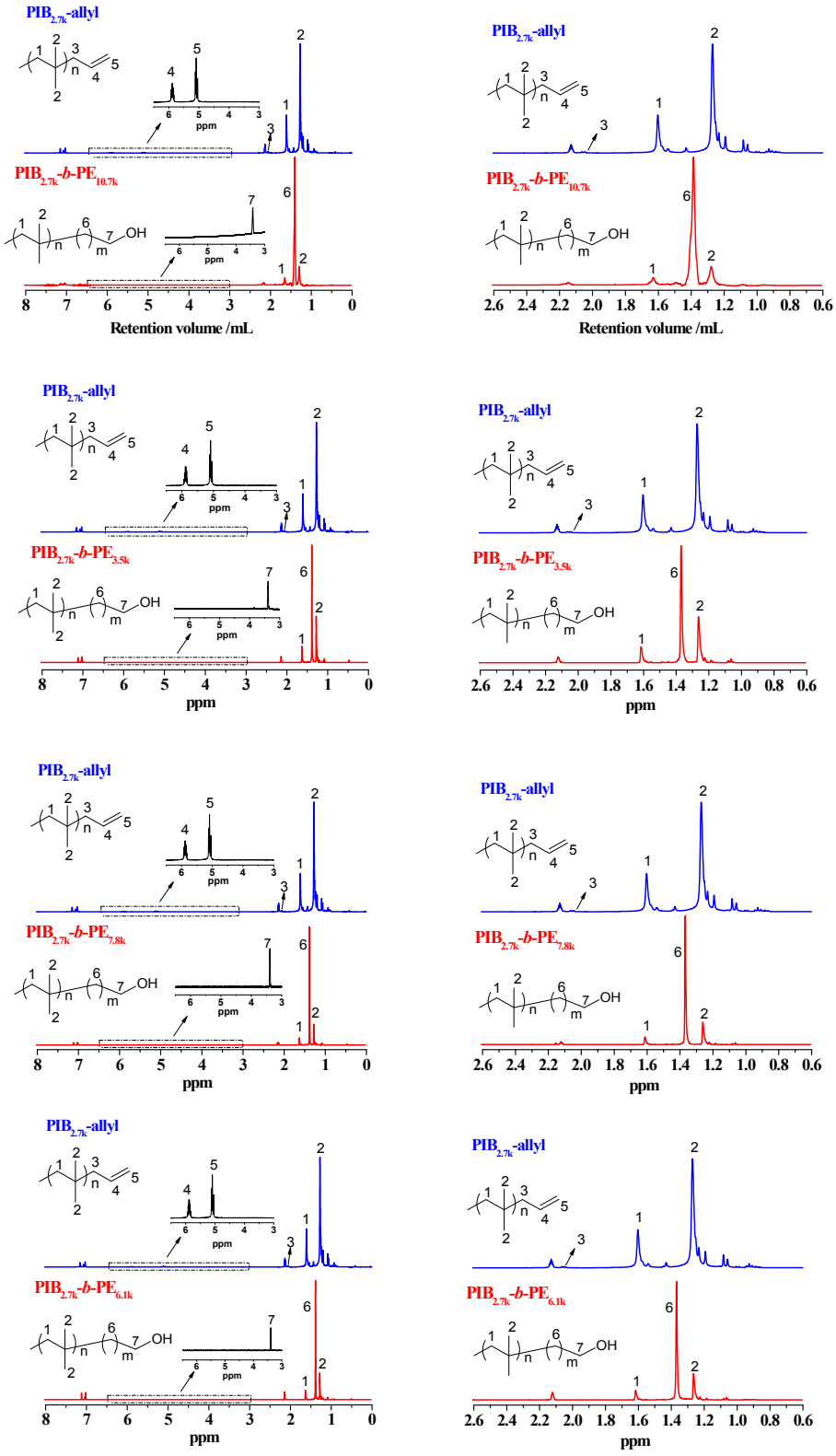


**Figure S6**. Monitoring the synthesis of $PIB_{2.7k}$-*b*-PEs by $^1H$ NMR (toluene-$d_8$, 80 °C) (left: full spectra, right: after zooming)

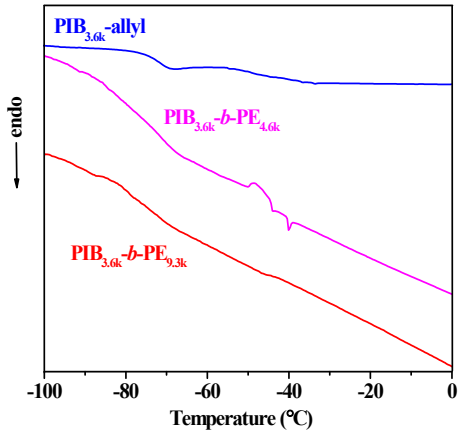


**Figure S7**. Zoomed DSC traces of $PIB_{3.6k}$-*b*-PEs ($N_2$, 10 °C/min, second heat cycle) (Figure 6 in the main text)

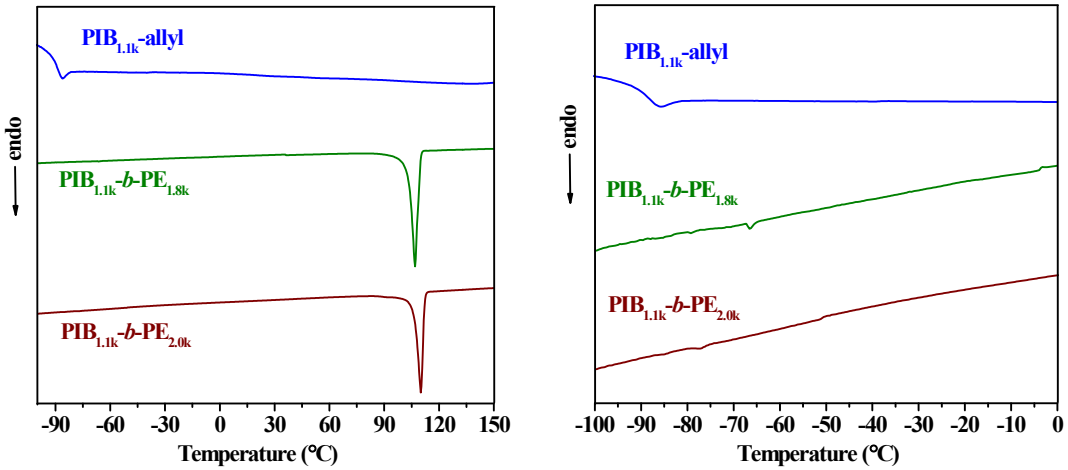


**Figure S8**. DSC traces of $PIB_{1.1k}$-*b*-PEs (left) and after zooming (right) ($N_2$, 10 °C/min, second heat cycle)

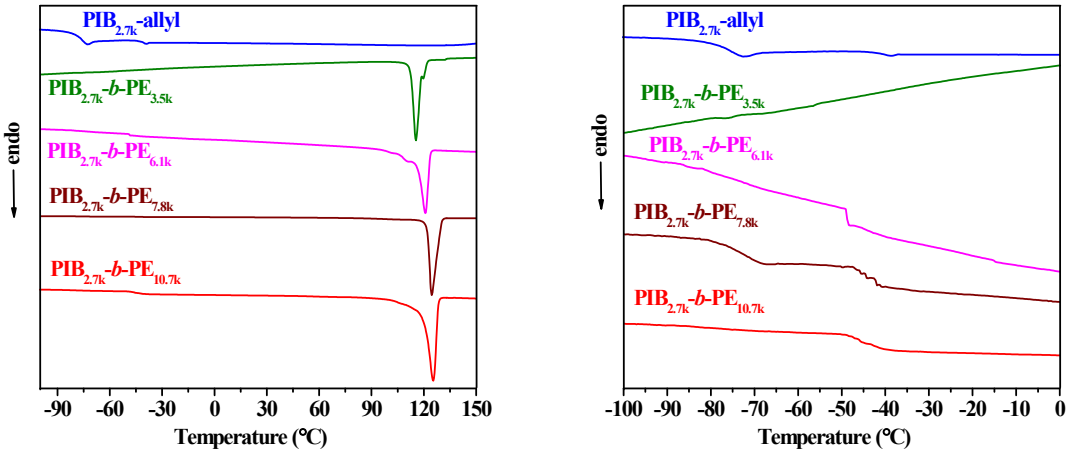


**Figure S9**. DSC traces of $PIB_{2.7k}$-*b*-PEs (left) and after zooming (right) ($N_2$, 10 °C/min, second heat cycle)

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3. Ivan, B.; Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 89-104.