

## Supporting Information

### Facile polyisobutylene functionalization via thiol-ene Click chemistry

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### Experimental

**Materials.** All materials were purchased from Aldrich at the highest available purity and used as received unless otherwise stated. Free radical photoinitiator, dimethoxy-2-phenylacetophenone (DMPA), was purchased from CIBA and used as received.

**Synthesis of *exo*-olefin-terminated PIB.** Mono- and difunctional *exo*-olefin-terminated PIBs were prepared and characterized according to literature using 2-chloro-2,4,4-trimethylpentane (TMPCl) or 1,3-di(1-chloro-1-methylethyl)-5-*tert*-butylbenzene, respectively, as initiators and 1,2,2,6,6-pentamethylpiperidine (PMP) as a hindered-amine quencher ((a) K. L. Simison, C. D. Stokes, J. J. Harrison and R. F. Storey, *Macromolecules*, 2006, **39**, 2481 (b) A. J. D. Magenau, N. Martinez-Castro and R. F. Storey, *Macromolecules*, 2009, **42**, 2353-2359).

A representative procedure to prepare monofunctional *exo*-olefin-terminated PIB was as follows: Quasiliving polymerization of isobutylene (IB) with TMPCl as an initiator was carried out within a N<sub>2</sub> atmosphere glovebox, equipped with an integral cryostated hexane/heptanes bath. Into a round bottom flask with a mechanical stirrer, infrared probe, and thermocouple were added 572 mL CH<sub>3</sub>Cl, 860 mL hexane, 2.50 mL (2.19 g, 0.0147 mol) TMPCl, and 0.86 mL (0.79 g, 0.0074 mol) of 2,6-lutidine. The mixture was allowed to equilibrate to -60 °C, and then 29.0 mL (19.9 g, 0.354 mol) of IB was added to the reactor and allowed to reach thermal equilibrium. To begin the polymerization, 4.8 mL (8.3 g, 0.044 mol) of TiCl<sub>4</sub> was charged to the reactor. Full monomer conversion (≥ 98 %) was achieved in 90 min, after which time 8.0 mL (6.9 g, 0.044 mol) PMP and an additional 4.8 mL TiCl<sub>4</sub> (8.3 g, 0.044 mol) were added to the polymerization. PMP was allowed to react with the living chain ends for 90 min. Finally, the reaction was terminated by addition of excess prechilled methanol. The contents of the reaction flask were allowed to warm to room temperature, and the polymer in hexane was immediately washed with methanol and then precipitated into methanol from hexane. The precipitate was collected by dissolution in hexane; the solvent was washed with water, dried over MgSO<sub>4</sub>, and concentrated on a rotary evaporator. Residual solvent was removed under vacuum at 40 °C.

**Synthesis of mono-functional primary chloride-terminated PIB.** A representative procedure was as follows: *exo*-olefin-terminated PIB (0.251 g, 0.20 mmol), DMPA (0.006 g, 1 wt%), and 0.22 mL dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) were charged to a 20 mL glass scintillation vial. After dissolution, 3-chloro-1-propanethiol (29.2 μL, 0.30 mmol) was added, and the contents were shaken for 20 min. The sample was then irradiated using a medium pressure Hg lamp (light intensity ~6.68 mW/cm<sup>2</sup>) for approximately 3.5 min. CH<sub>2</sub>Cl<sub>2</sub> was removed under reduced pressure, and the crude reaction mixture was twice precipitated into methanol from hexane. The final precipitate was collected and put under reduced pressure until a constant weight was achieved.

**One-pot synthesis of mono-functional primary amine-terminated PIB.** A representative procedure was as follows: *exo*-olefin-terminated PIB (0.251 g, 0.20 mmol), DMPA (0.006 g, 1 wt. %), and 0.26 mL CH<sub>2</sub>Cl<sub>2</sub> were charged to a 20 mL glass scintillation vial. After dissolution, 2-(*tert*-

butoxycarbonylamino)ethanethiol (50.7  $\mu\text{L}$ , 0.30 mmol) was added, and the contents were shaken for 20 min. The sample was then irradiated using a medium pressure Hg lamp (light intensity  $\sim 6.68 \text{ mW/cm}^2$ ) for approximately 3.5 min. For deprotection, 4.28 mL of a trifluoroacetic acid and  $\text{CH}_2\text{Cl}_2$  mixture (50:50 v/v) was injected into the scintillation vial and agitated for 30 min.  $\text{CH}_2\text{Cl}_2$  was then removed under reduced pressure, and the crude reaction mixture was dissolved in hexane. The resulting solution was washed twice with brine and then twice with deionized water, neutralized with sodium bicarbonate, filtered, and put under reduced pressure until a constant weight was achieved.

**Synthesis of mono-functional carboxylic acid-terminated PIB.** A representative procedure was as follows: *exo*-olefin-terminated PIB (0.126 g, 0.10 mmol), DMPA (0.005 g, 1 wt%), and 0.23 mL chloroform ( $\text{CHCl}_3$ ) were charged to a 20 mL glass scintillation vial. After dissolution, thiol glycolic acid (20.8  $\mu\text{L}$ , 0.30 mmol) was added, and the contents were shaken for 20 min. The sample was then irradiated using a medium pressure Hg lamp (light intensity  $\sim 6.68 \text{ mW/cm}^2$ ) for approximately 8 min.  $\text{CHCl}_3$  was removed under reduced pressure, and the crude reaction mixture was dissolved in hexane. The resulting solution was washed three times with water and put under reduced pressure until a constant weight was achieved.

**Synthesis of mono-functional primary alcohol-terminated PIB.** A representative procedure was as follows: *exo*-olefin-terminated PIB (0.157 g, 1.25 mmol), DMPA (0.061 g, 1 wt%), and 0.26 mL  $\text{CHCl}_3$  were charged to a 20 mL glass scintillation vial. After dissolution, 1-mercapto-6-hexanol (68.4  $\mu\text{L}$ , 5.00 mmol) was added, and the contents were shaken for 20 min. The sample was then irradiated using a medium pressure Hg lamp (light intensity  $\sim 6.68 \text{ mW/cm}^2$ ) for approximately 6 min.  $\text{CHCl}_3$  was removed under reduced pressure, and the crude reaction mixture was dissolved in hexane. The resulting solution was washed three times with methanol and put under reduced pressure until a constant weight was achieved.

**Instrumentation.** FTIR spectra were recorded using a Bruker Equinox 55 spectrometer. Samples were sandwiched between two sodium chloride plates. Each spectrum was collected as an average of 64 scans. The data were analyzed using the Bruker OPUS/IR Version 4.0 software.

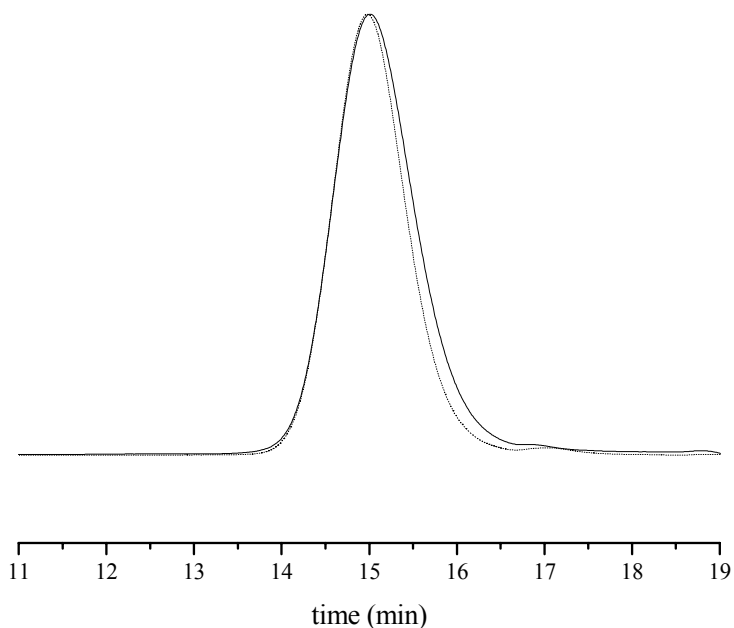
**Real-time FTIR.** Real-time FTIR was used to monitor *exo*-olefin conversion kinetics ( $1640 \text{ cm}^{-1}$ ). *Exo*-olefin-terminated PIB (0.501 g, 0.40 mmol), DMPA (0.012 g, 1 wt%), and 0.40 mL  $\text{CH}_2\text{Cl}_2$  were charged to a 20 mL glass scintillation vial. After dissolution, 2-(*tert*-butoxycarbonylamino)ethanethiol (100.9  $\mu\text{L}$ , 0.60 mmol) was added, and the contents were shaken for 20 min. The resulting reaction mixture was sandwiched between sodium chloride plates resulting in a sample thickness of approximately 250 microns. The light intensity of the high pressure mercury lamp delivered to the sample *via* a light pipe was  $\sim 28.3 \text{ mW/cm}^2$ .

**NMR spectroscopy.** NMR spectra were acquired using a Varian Mercury<sup>plus</sup> 500 MHz NMR spectrometer. Samples were dissolved in chloroform-*d* (3–7%, w/v) and analyzed within 5 mm NMR tubes.

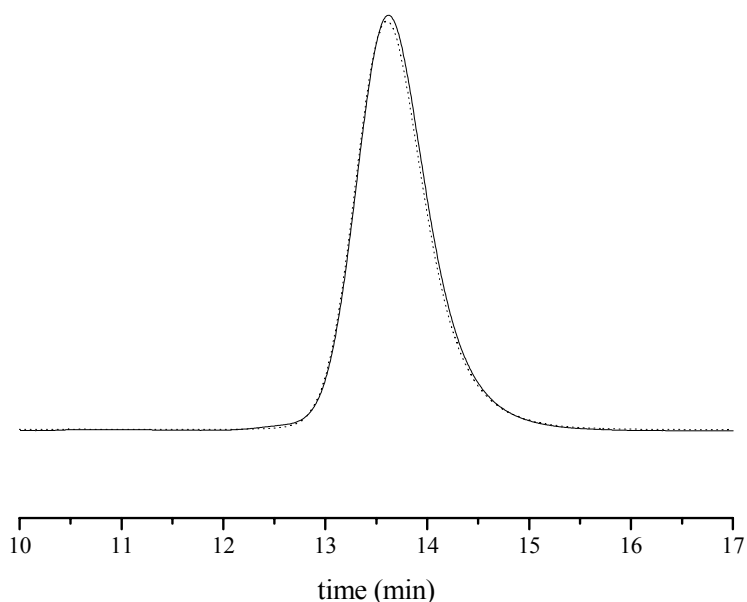
**Gel permeation chromatography.** The number-average molecular weight ( $M_n$ ) and polydispersity index (PDI) of the polymeric materials were measured using gel permeation chromatography (GPC). The GPC system, operating at 35  $^\circ\text{C}$ , consisted of a Waters Alliance 2695 separations module, an online multiangle laser light scattering (MALLS) detector (MiniDAWN, Wyatt Technology Inc.), an interferometric refractometer (Optilab rEX, Wyatt Technology Inc.), an online differential viscometer (ViscoStar, Wyatt Technology, Inc.), and two mixed E (3  $\mu\text{m}$  bead size) PL gel (Polymer Laboratories Inc.) GPC columns connected in series. Freshly distilled THF served as the mobile phase at a flow rate of 1.0 mL/min. Sample concentrations were 10–12 mg/mL, with an injection volume of 100  $\mu\text{L}$ . The detector signals

were recorded using ASTRA software (Wyatt Technology Inc.) and molecular weights were determined using  $dn/dc$  values calculated from an equation relating  $dn/dc$  of PIB in THF as a function of PIB molecular weight (N. Martinez-Castro, D. L. Morgan and R. F. Storey, *Macromolecules*, 2009, **42**, 4963-4971).

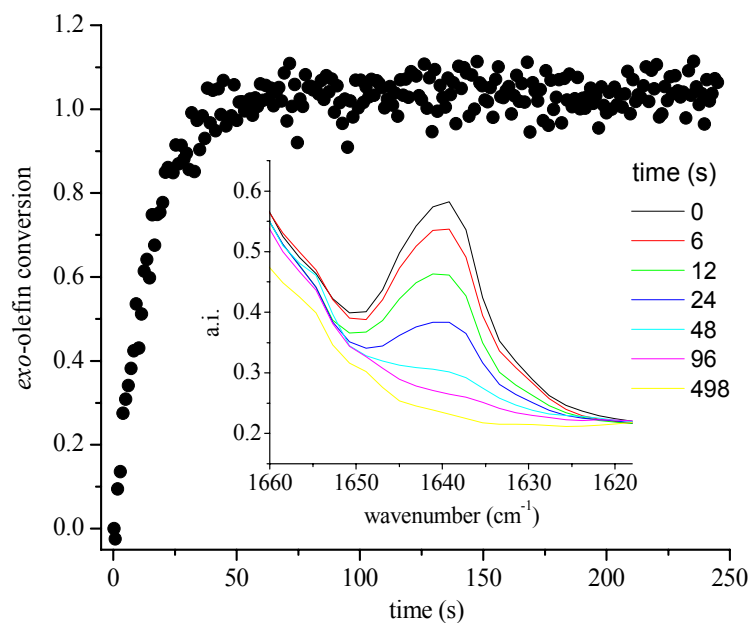
## Results



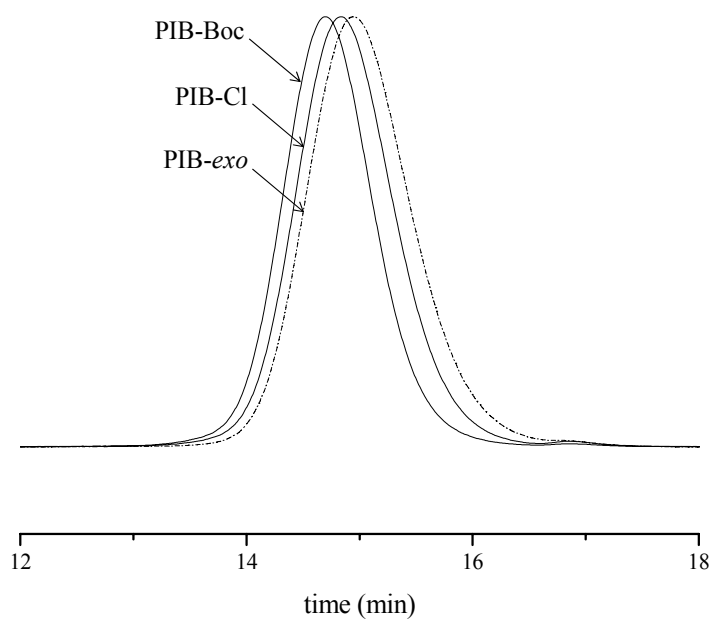
**Figure S1.** GPC traces of mono-functional PIB before (solid line, *tert*-chloride-terminated PIB) and after quenching with PMP (dashed line, *exo*-olefin-terminated PIB).



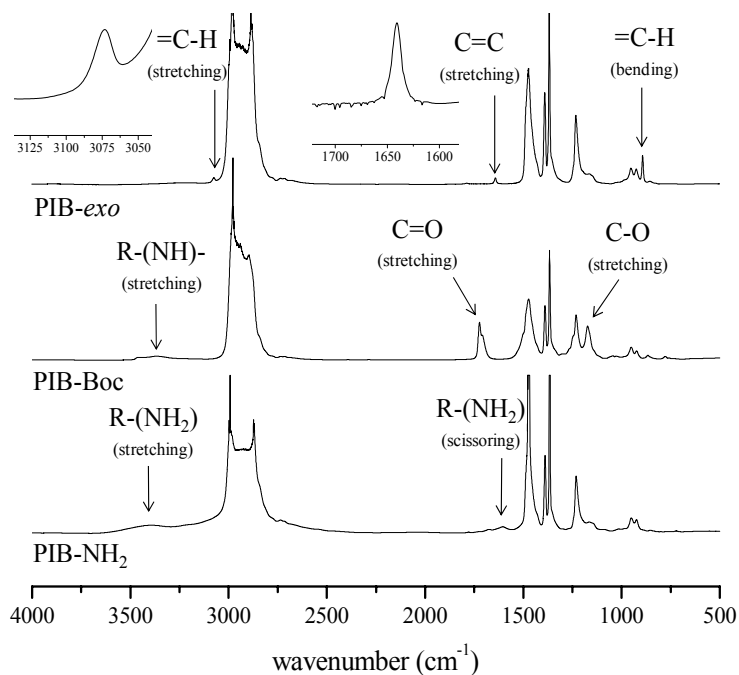
**Figure S2.** GPC traces of difunctional PIB before (solid line, *tert*-chloride-terminated PIB) and after quenching with PMP (dashed line, *exo*-olefin-terminated PIB).



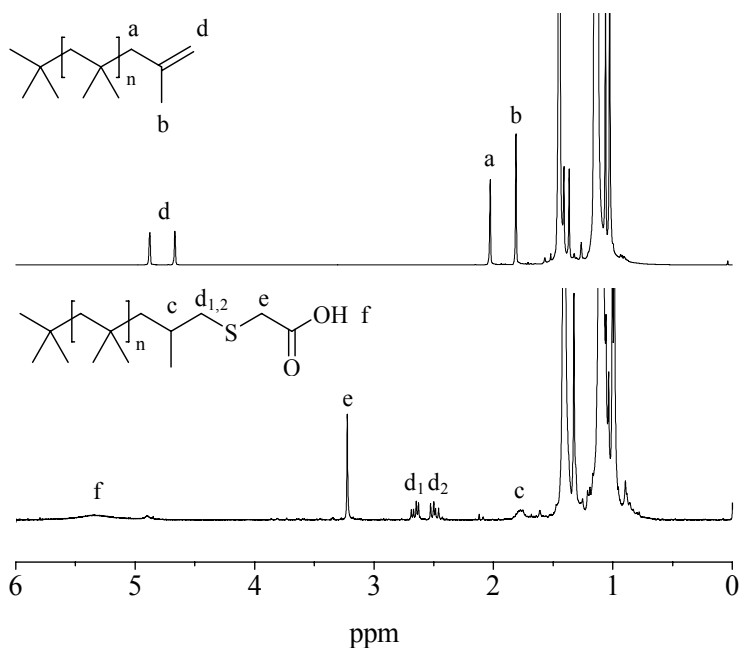
**Figure S3.** PIB *exo*-olefin conversion vs. time for reaction with 2-(*tert*-butoxycarbonylamino)ethanethiol, monitored by observing diminution of the C=C stretch at 1645 cm<sup>-1</sup> using real-time FTIR.



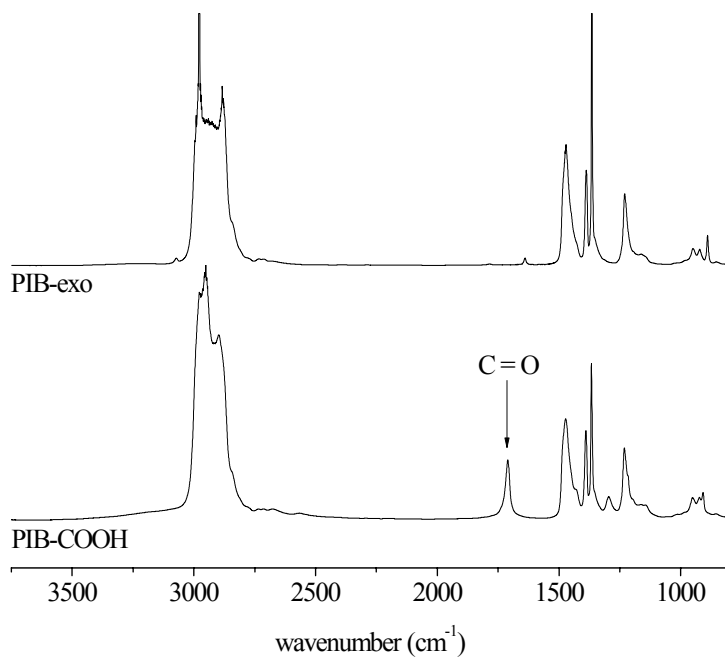
**Figure S4.** GPC traces of monofunctional PIB before (dashed line, *exo*-olefin-terminated PIB) and after thiol-ene reaction (solid line, Boc-protected and halogen-terminated PIB).



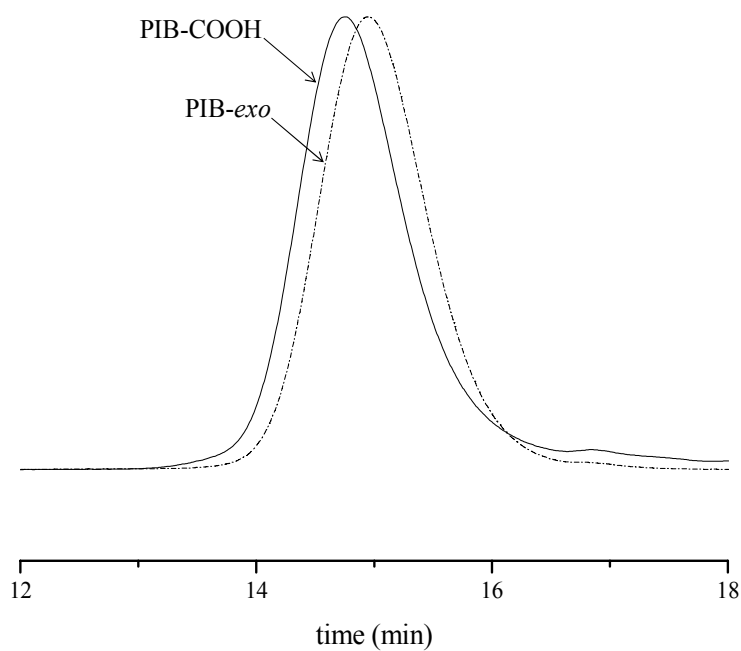
**Figure S5.** FTIR spectra of *exo*-olefin-terminated PIB (top), Boc-protected PIB (middle), and amine-terminated PIB (bottom).



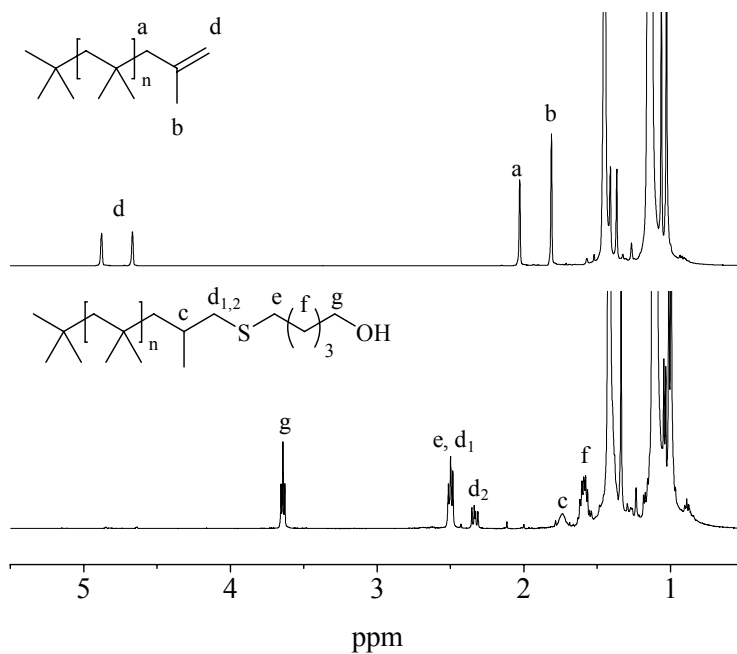
**Figure S6.** <sup>1</sup>H NMR spectra of *exo*-olefin-terminated PIB (top) and carboxylic acid-terminated PIB (bottom).



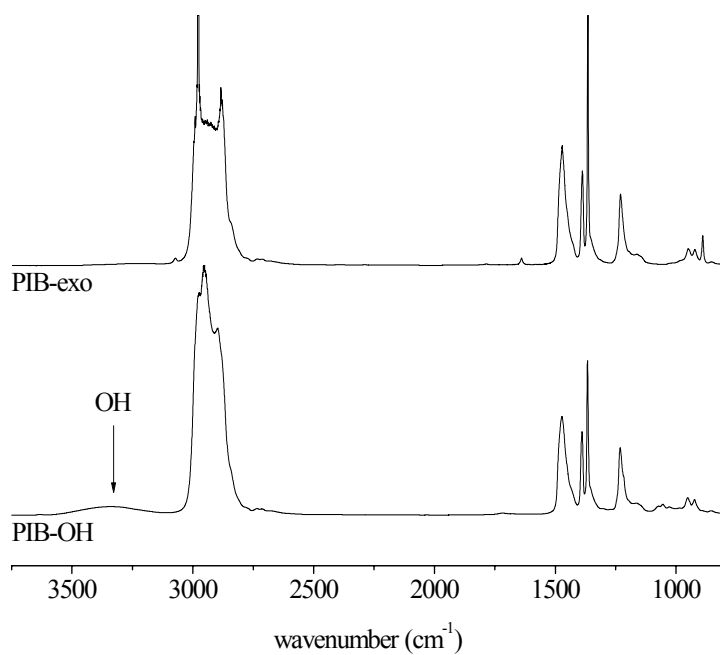
**Figure S7.** FTIR spectra of *exo*-olefin-terminated PIB (top) and carboxylic acid-terminated PIB (bottom).



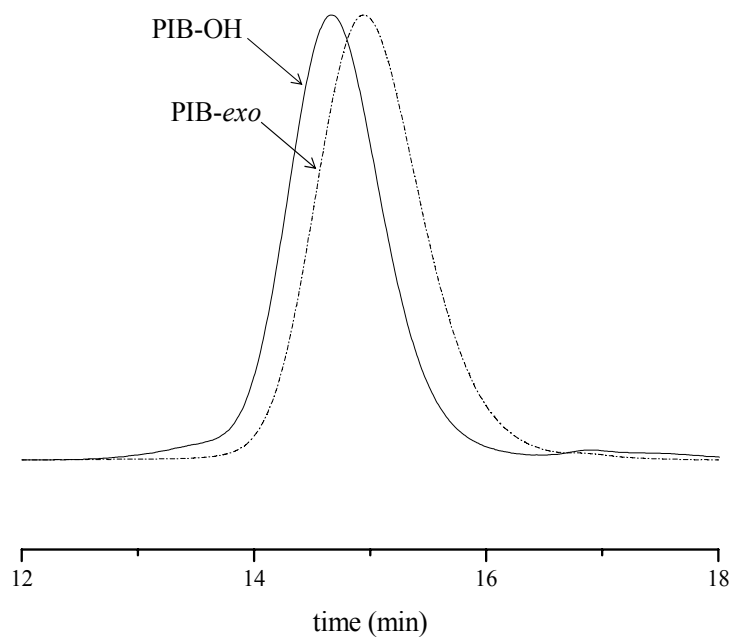
**Figure S8.** GPC traces of monofunctional PIB before (dashed line, *exo*-olefin-terminated PIB) and after thiol-ene reaction (solid line, acid-terminated PIB).



**Figure S9.** <sup>1</sup>H NMR spectra of *exo*-olefin-terminated PIB (top) and hydroxyl-terminated PIB (bottom).



**Figure S10.** FTIR spectra of *exo*-olefin-terminated PIB (top) and hydroxyl-terminated PIB (bottom).



**Figure S11.** GPC traces of monofunctional PIB before (dashed line, *exo*-olefin-terminated PIB) and after thiol-ene reaction (solid line, hydroxyl-terminated PIB).