Electronic Supplementary Material (ESI) for Polymer Chemistry

Electronic Supporting Information for Copolymerization of Isoprene and Hydroxyl Containing Monomers by Controlled Radical and Emulsion Methods

William M. Gramlich,[‡] Grayce Theryo,[‡] Marc A. Hillmyer[†,*]

[†]Department of Chemistry, University of Minnesota, 207 Pleasant St SE, Minneapolis, MN 55455-0431. [‡]Department of Chemical Engineering and Material Science, University of Minnesota, 421 Washington Ave. SE, Minneapolis, MN 55455-0132.

* To whom correspondence should be addressed: hillmyer@umn.edu

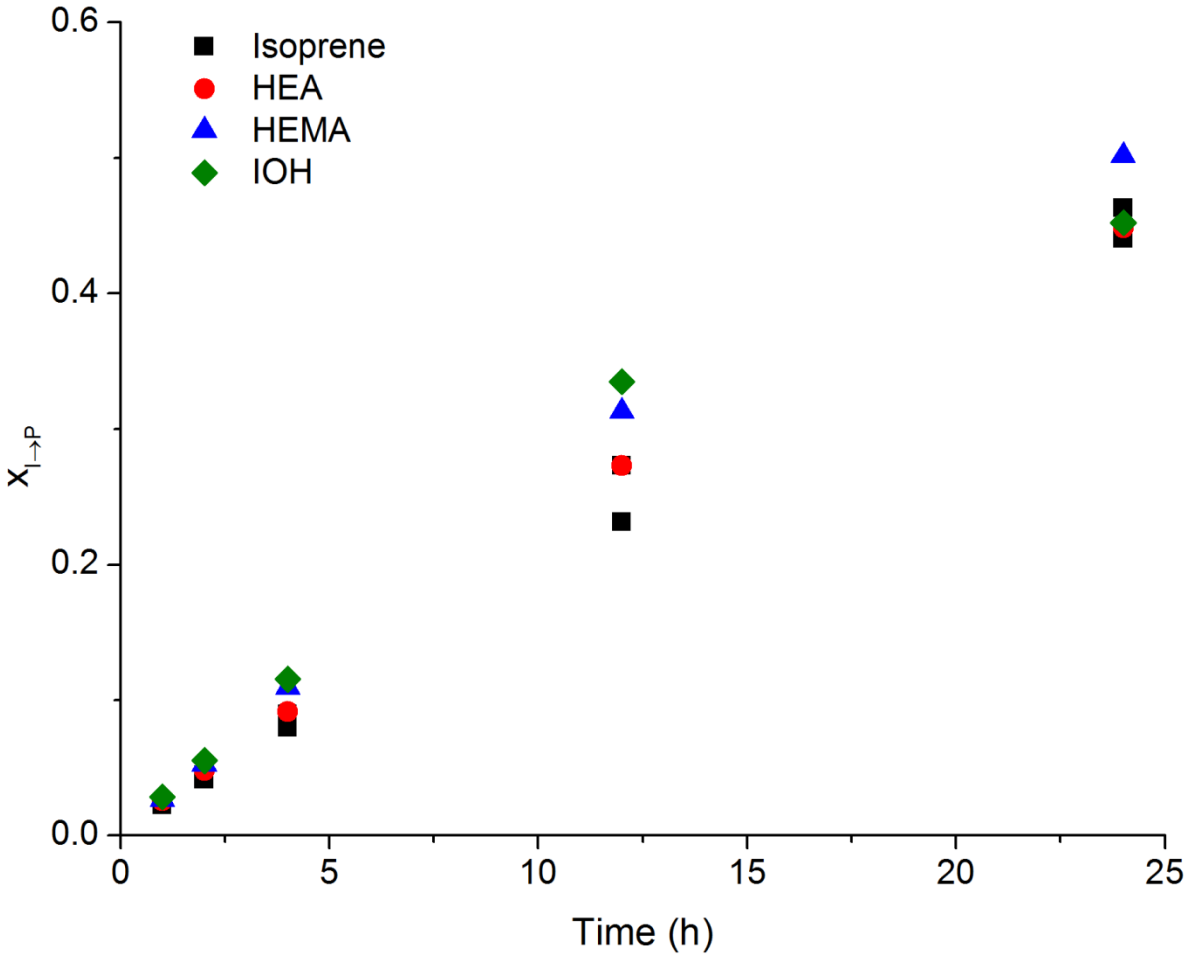

Figure S1. The conversion of isoprene to polymer ($x_{I \rightarrow P}$) plotted as a function of polymerization time for isoprene homopolymerizations and hydroxyl monomer copolymerizations. Points labeled isoprene (black squares) correspond to isoprene homopolymerizations. Conditions were [M]:[CTA] = 190, 125 °C reaction temperature, and initial hydroxyl monomer mole fraction (if used) (f_{OH}) of 0.03. The conversion of isoprene to polymer behaves similarly for both homopolymerizations and copolymerizations. Values were calculated by ^{1}H NMR spectroscopic end group analysis on dried aliquots from the polymerizing reaction mixture. Two separate runs of isoprene homopolymerization gave similar conversions over time, indicating that the polymerizations are repeatable.

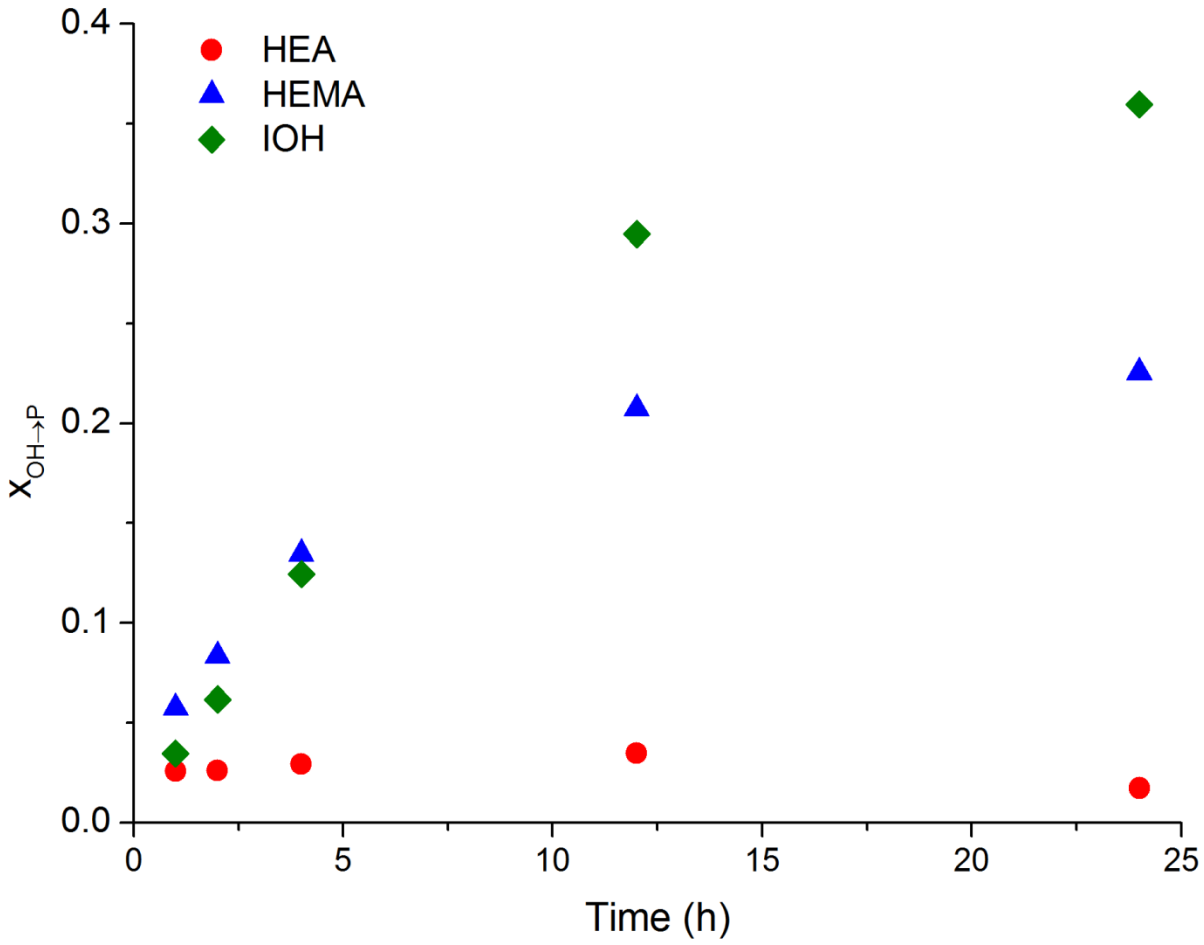

Figure S2. Hydroxyl monomer conversion to polymer ($x_{OH \rightarrow P}$) as a function of polymerization time for RAFT controlled radical copolymerizations. The $x_{OH \rightarrow P}$ values were calculated following the procedure described in the Experimental Details. Conditions were [M]:[CTA] = 190, 125 °C reaction temperature, and f_{OH} of 0.03. Of the hydroxyl comonomers, more IOH is converted into polymer.

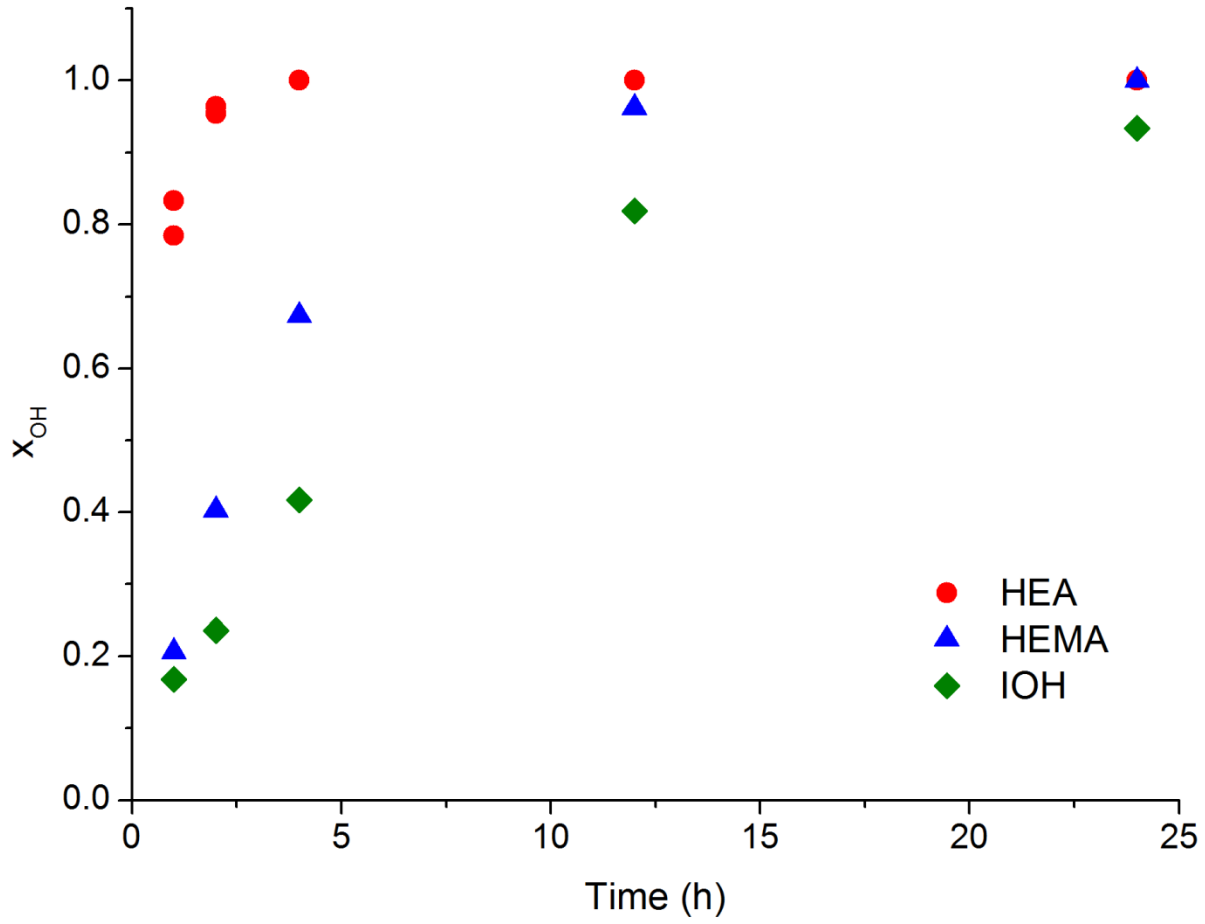

Figure S3. Total conversion of hydroxyl monomer (x_{OH}) plotted as a function of reaction time for RAFT controlled radical isoprene copolymerizations at 125 °C. The total conversion for the hydroxyl comonomers was calculated from the ^{1}H NMR spectra of the crude aliquots (before drying) as discussed in the Experimental Details. HEA is completely consumed by 4 h and HEMA is completely consumed by 24 h.

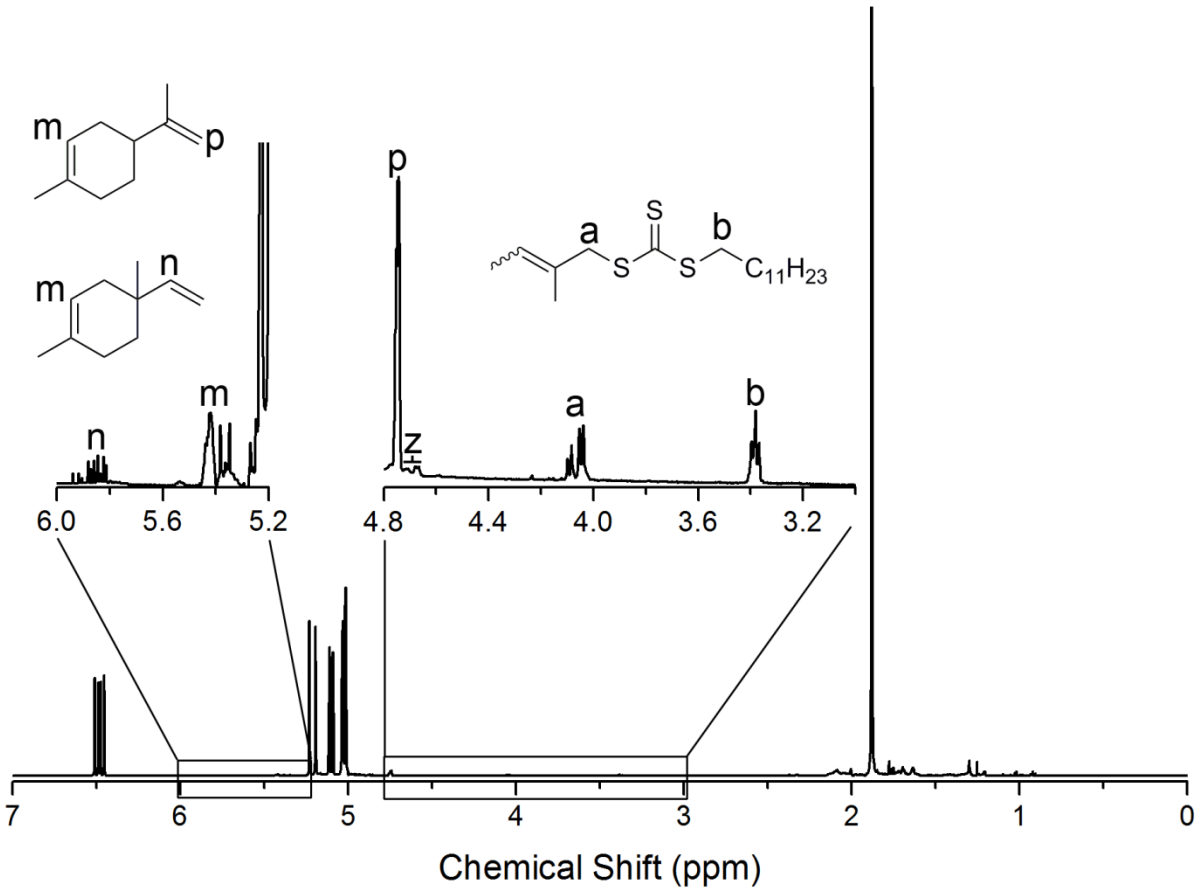

Figure S4. Representative ^{1}H NMR spectrum with magnified regions of the crude solution for the RAFT controlled radical homopolymerization of isoprene after 2 h at 125 °C. In the full axis spectrum, the prominent peaks belong to isoprene monomer. In the magnified regions, peaks that correspond to RAFT CTA end group region are labeled. The peak labeled "b" was used as an internal standard for all conversion calculations for all polymerizations. The peak labeled "p" corresponds with the isoprene Diels–Alder dimer limonene. It overlaps with a set of peaks that correspond to half of the vinyl protons of the 3,4-addition product (other half is labeled "z"). See Experimental Details for sample calculations for conversion of isoprene to limonene ($x_{I\rightarrow L}$). Limonene is not the only isoprene Diels–Alder dimer formed. Additionally, the dimer 1,4-dimethyl-4-vinylcyclohex-1-ene (DMVCH) is produced as a minor product. The representative peaks corresponding to the protons of DMVCH overlap with polymer proton peaks so the conversion of isoprene to DMVCH could not be calculated directly from the crude aliquot ^{1}H NMR spectra. Heating isoprene at 125 °C for 24 h without polymerization favored the formation of limonene 4 to 1 over DMVCH. Likely, a similar ratio exists in the system when polymerization occurs.

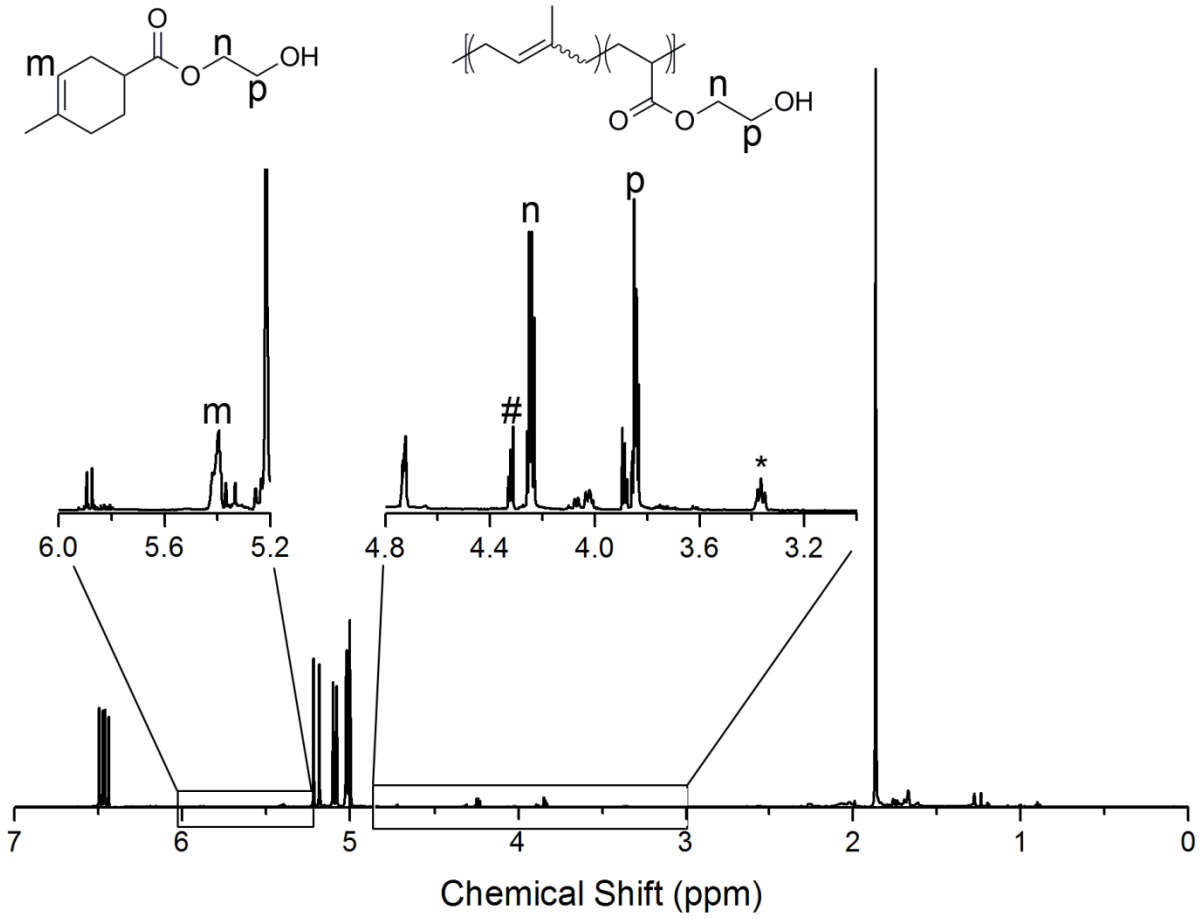

Figure S5. Representative ^{1}H NMR spectrum with magnified regions of the crude solution for the RAFT controlled radical copolymerization of isoprene and HEA after 1 h at 125 °C. The structure of HEA-isoprene Diels–Alder adduct is given with peak assignments. Protons associated with protons for both the Diels–Alder adduct and isoprene-HEA copolymer overlap as labeled on the magnified spectrum. The peak associated with residual HEA monomer is labeled with a pound sign (#) and the peak corresponding to the RAFT CTA end-group is labeled by an asterisk (*). Total HEA monomer conversion was calculated as described in the Experimental Details.

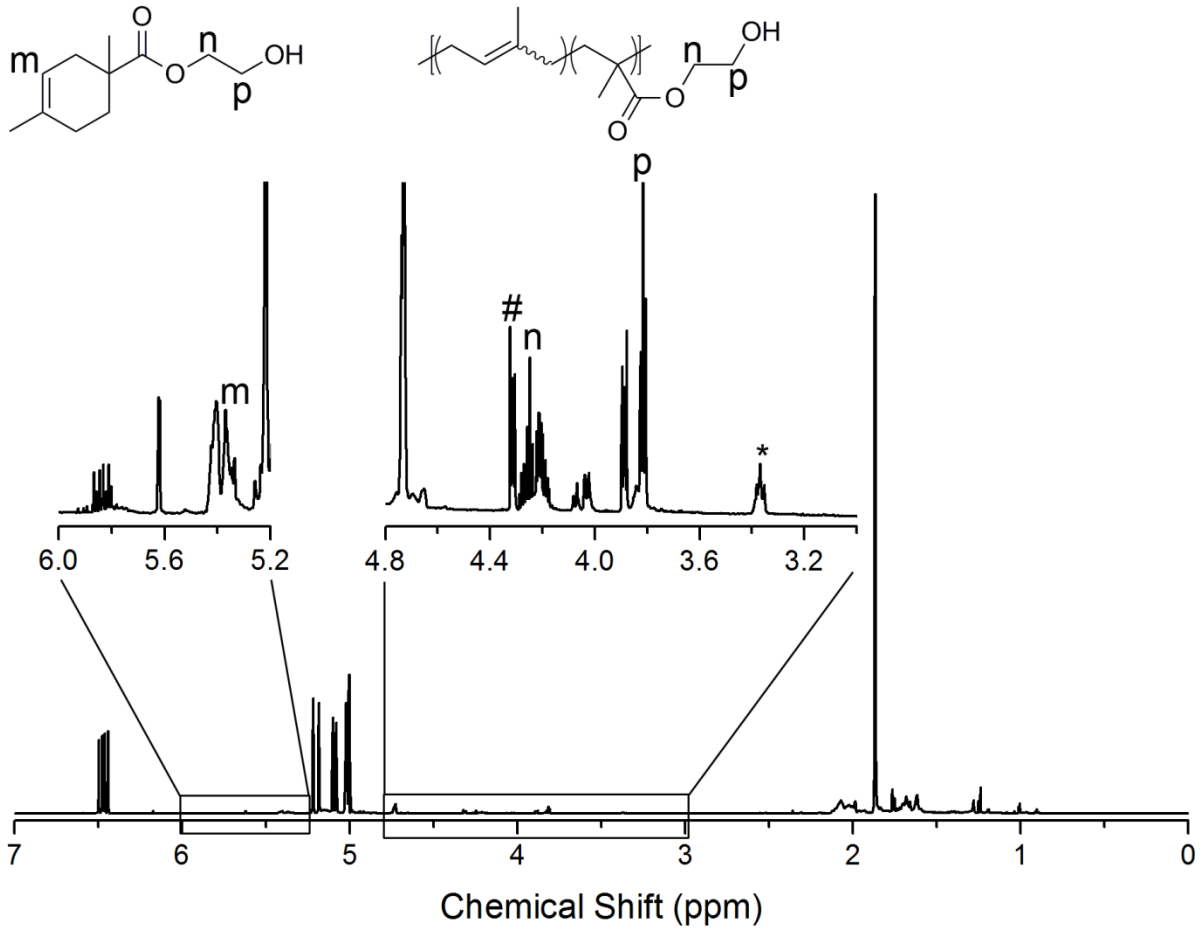

Figure S6. Representative ^{1}H NMR spectrum with magnified regions of the crude solution for the RAFT controlled radical copolymerization of isoprene and HEMA after 4 h at 125 °C. The structure of HEMA-isoprene Diels–Alder adduct is given with peak assignments. Protons associated with protons for both the Diels–Alder adduct and isoprene-HEMA copolymer overlap as labeled on the magnified spectrum. The peak associated with residual HEMA monomer is labeled with a pound sign (#) and the peak corresponding to the RAFT CTA end-group is labeled by an asterisk (*). Total HEMA monomer conversion was calculated as described in the Experimental Details.

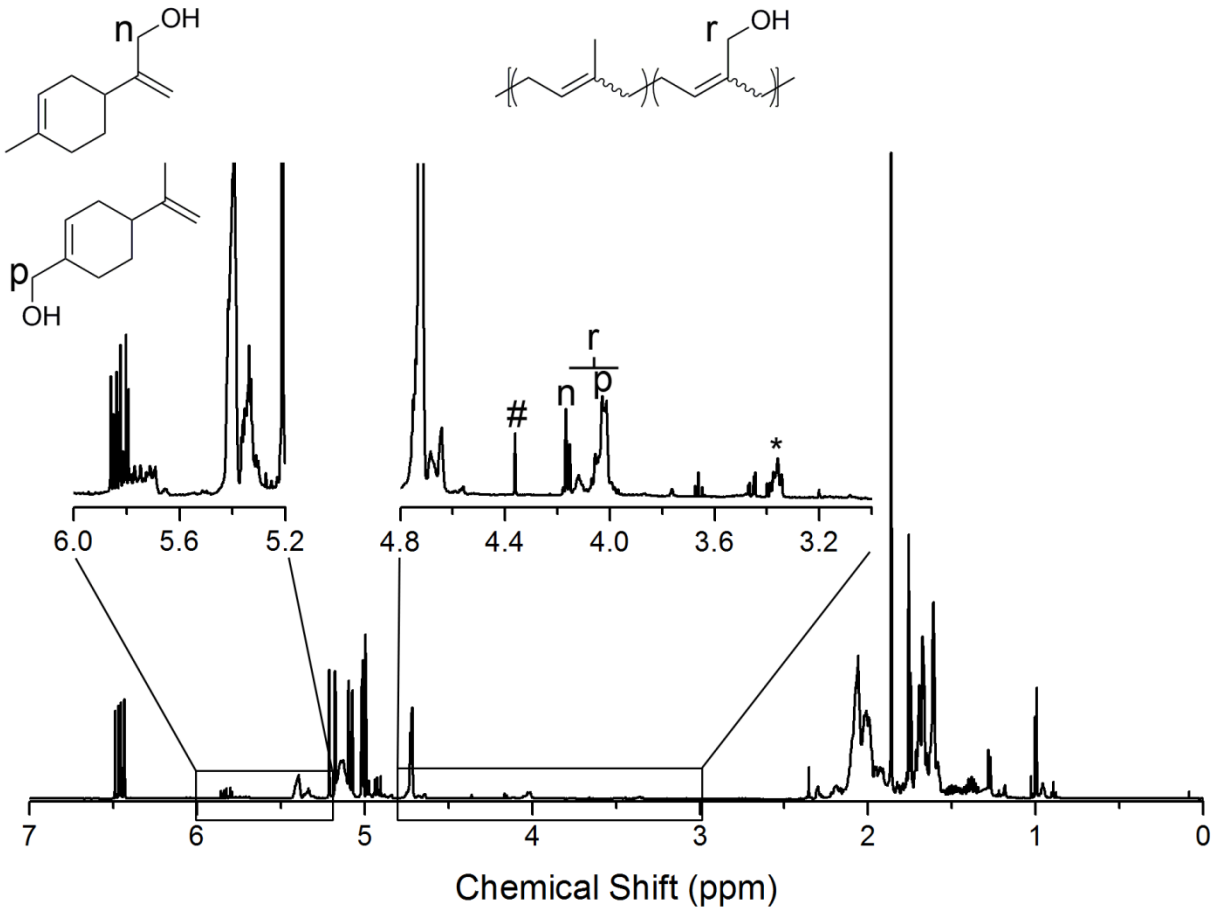

Figure S7. Representative ^{1}H NMR spectrum with magnified regions of the crude solution for the RAFT controlled radical copolymerization of isoprene and IOH after 24 h at 125 °C. Peaks are assigned for the Diels–Alder adducts of isoprene and IOH. The peak labeled "n" corresponds with the Diels–Alder adduct where IOH is the dienophile. The peak labeled "p" not only corresponds to protons on the Diels–Alder adduct where IOH is the diene, but it also corresponds to protons present on the IOH repeat units in the polymer and those that belong to the polymer end group (see Figure S4). The region labeled "r" contains peaks that correspond with the IOH repeat units in the polymer. The peak associated with residual IOH monomer is labeled with a pound sign (#) and the peak corresponding to the RAFT CTA end-group is labeled by an asterisk. Total IOH monomer conversion was calculated as described in the Experimental Details.

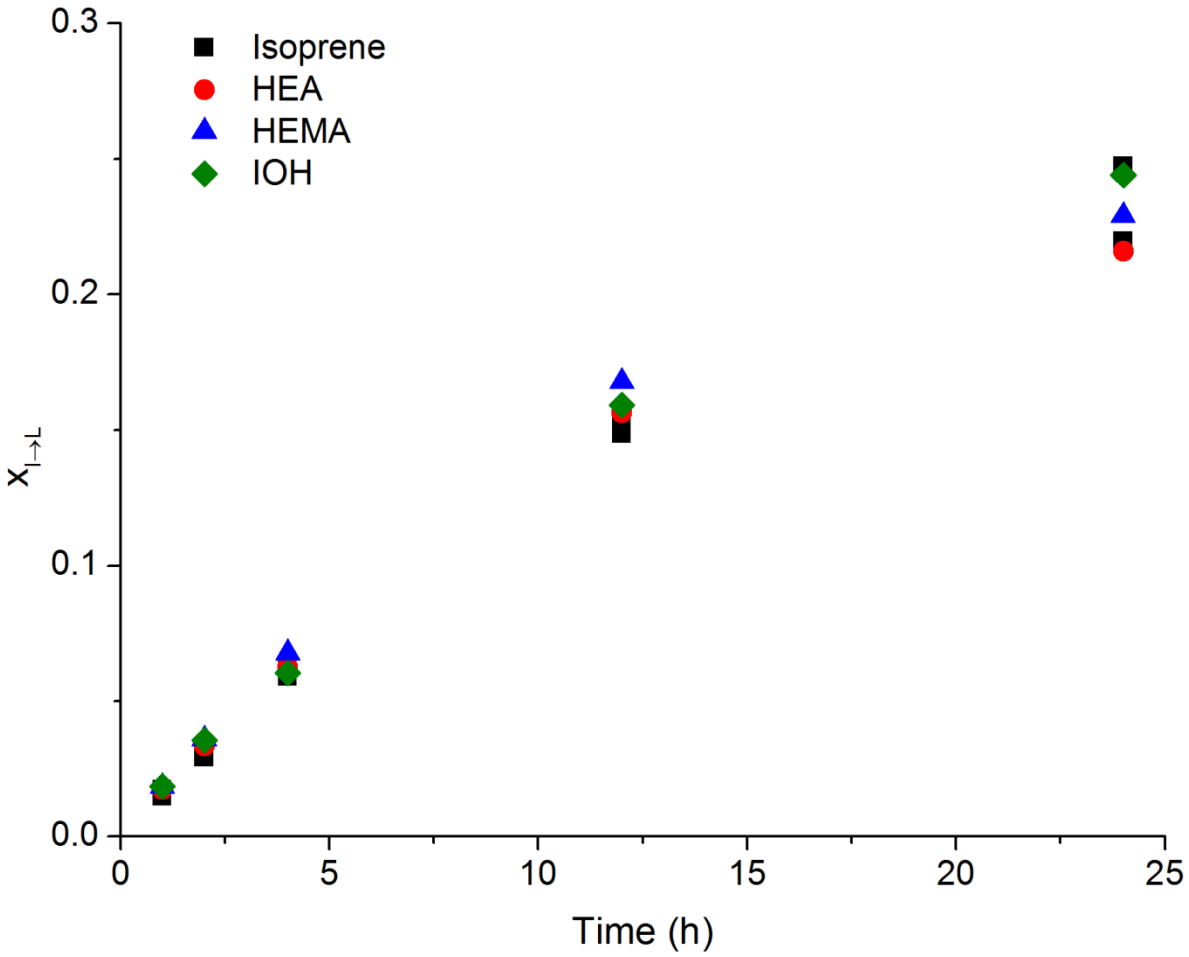

Figure S8. Conversion of isoprene to limonene ($x_{I\rightarrow L}$) plotted as function of the polymerization time for isoprene homopolymerizations (black squares) and hydroxyl monomer copolymerizations. Both homopolymerizations and copolymerizations exhibit similar trends in limonene production. Values are determined from ^{1}H NMR spectroscopic analysis of crude reaction solution aliquots taken during polymerization following the procedure discussed in Experimental Details.

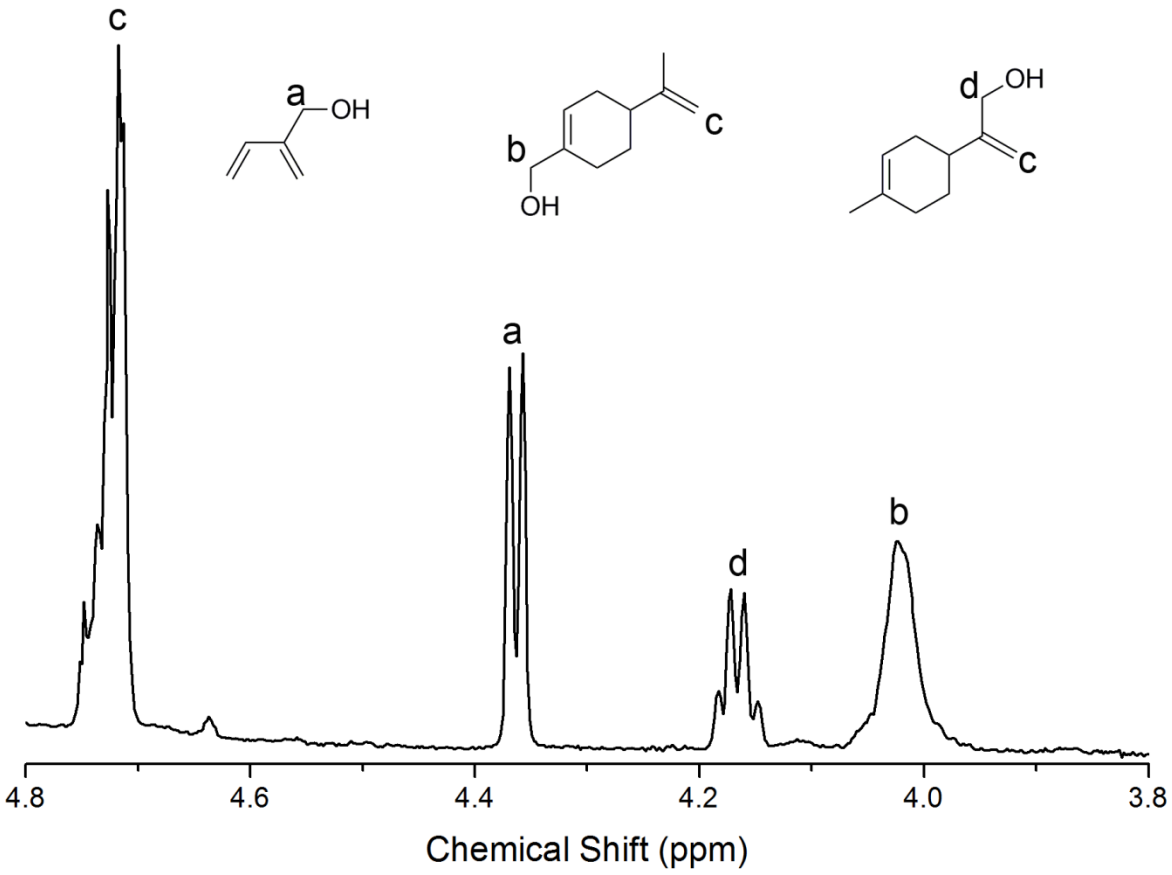

Figure S9. Magnified ^{1}H NMR spectrum of crude reaction solution of isoprene and IOH (3 mol % IOH) heated for 24 h at 125 °C. Peak assignments are given for the Diels–Alder adducts of isoprene and IOH where IOH is either the diene or dienophile. Other regioisomers are possible, but their structures are not shown. The peak corresponding to the remaining IOH monomer is labeled "a" and is split into a doublet by the alcohol proton. The peak labeled "c" corresponds to not only the Diels–Alder adduct of IOH and isoprene, but also the isoprene-isoprene Diels–Alder adduct. Total IOH conversion was 68% after 24 h. IOH is preferentially reacts as the diene (2.2 to 1).

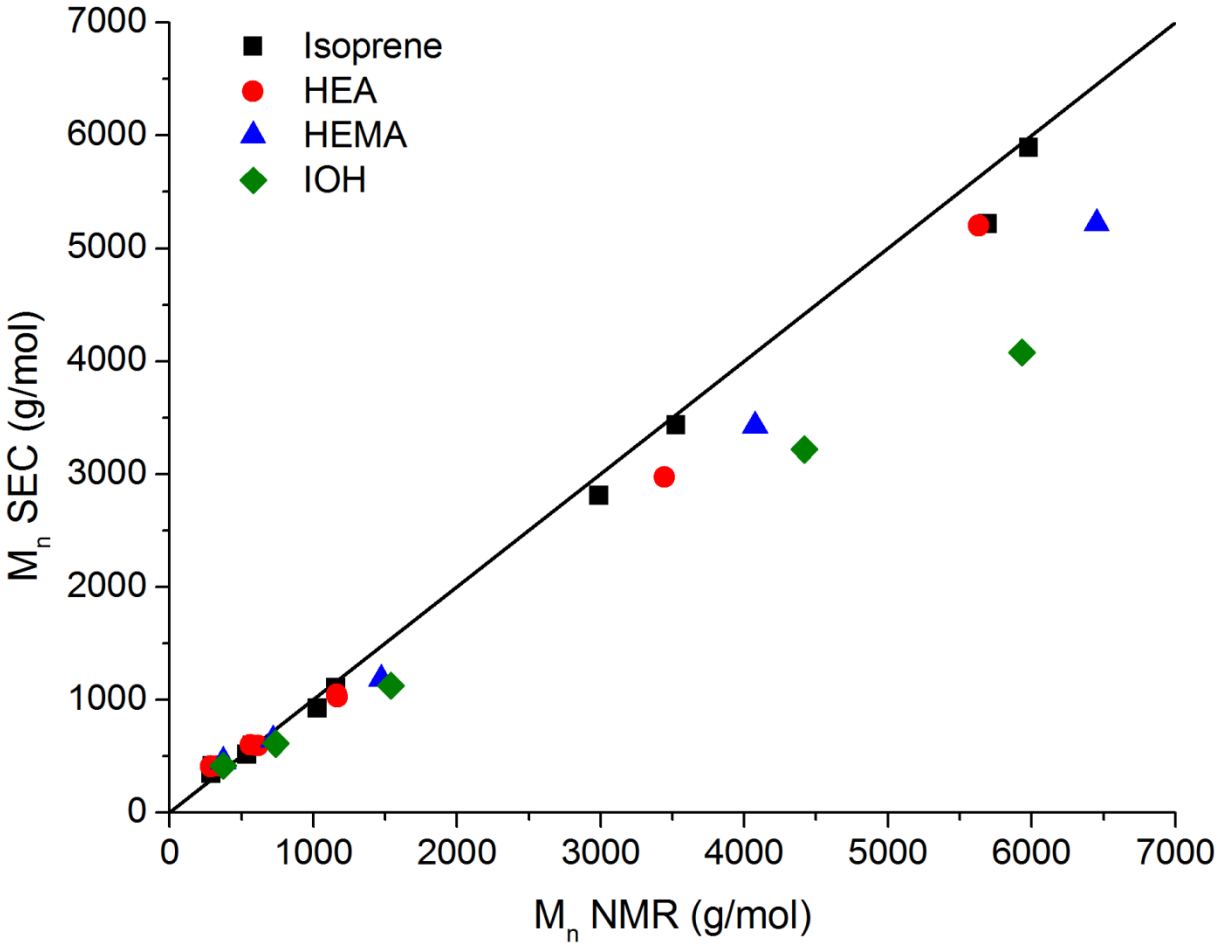

Figure S10. Comparison of M_n determined by SEC (M_n SEC) and ^{1}H NMR spectroscopy (M_n NMR) for isoprene homopolymerizations and hydroxyl monomer copolymerizations in the bulk at 125 °C. The solid line indicates where M_n SEC and M_n NMR are equal. Samples were taken as aliquots from the polymerizing reaction mixture. M_n NMR values were calculated by end group analysis and M_n SEC values were calculated by SEC calibrated with polyisoprene standards.

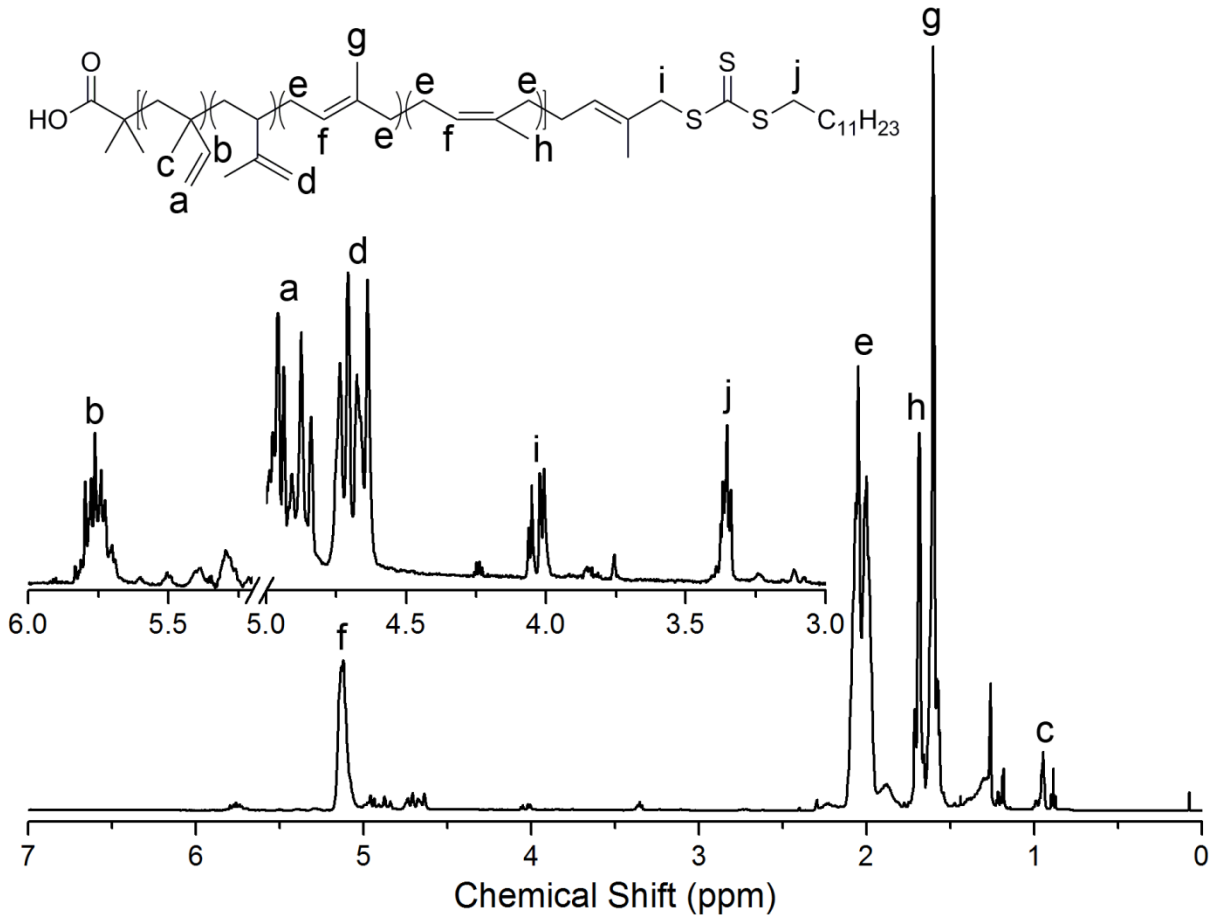

Figure S11. ^{1}H NMR spectrum with magnified region and peak assignments for RAFT controlled radical synthesized PI at [M]:[CTA] = 190 and 125 °C. The four possible isoprene repeat unit isomers are present in the polymer. Of the repeat units, 4.4 mol % are the 1,2-addition product; 6.0 mol % are the 3,4-addition product, and 89.6 mol % are the 1,4-addition product. Of the 1,4-addition product repeat units, 66% are of the *trans* configuration with the balance being the *cis* configuration. The isomeric composition of the PI is similar for all hydroxyl copolymers and the peaks assignments given are valid for the subsequent spectra of the hydroxyl copolymers.

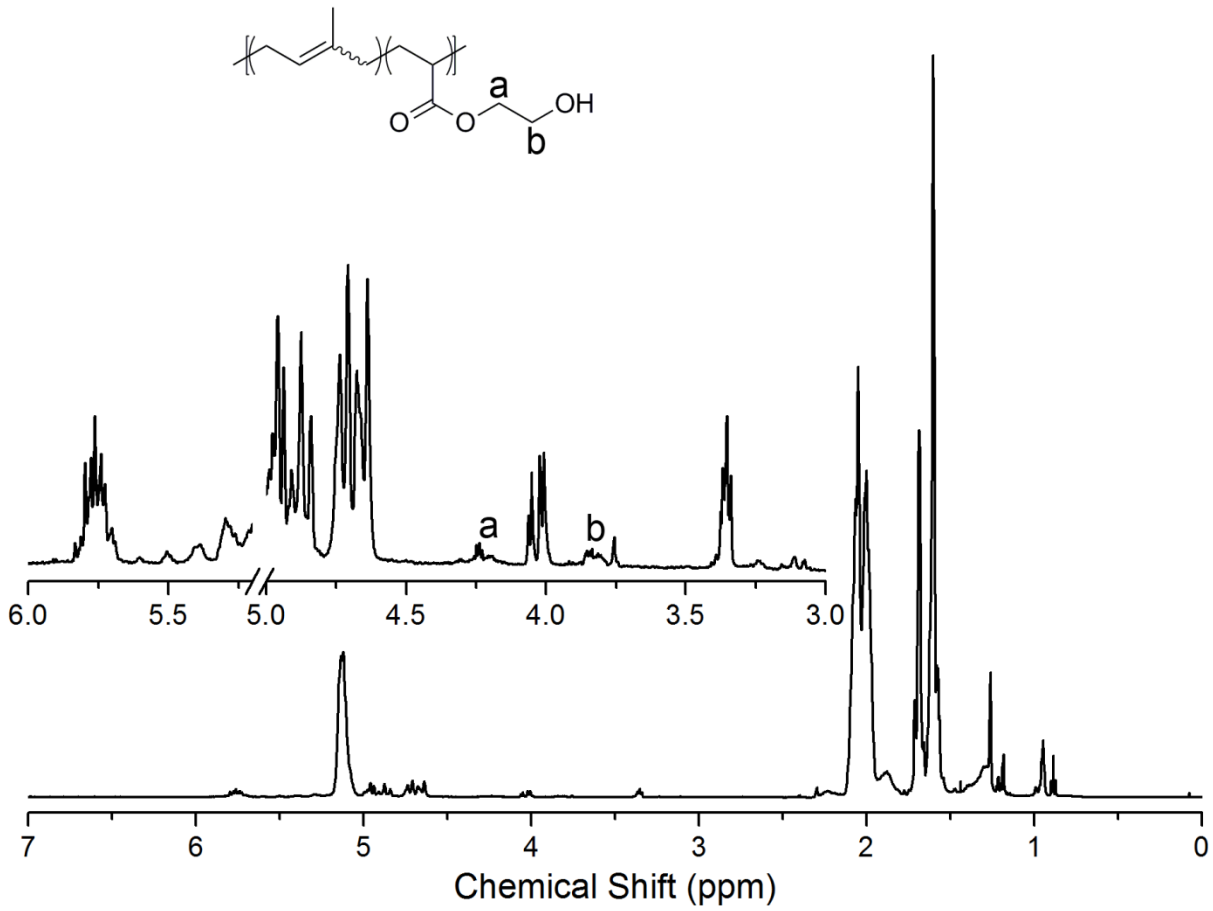

Figure S12. ^{1}H NMR spectrum with magnified region and peak assignments for RAFT controlled radical synthesized P(I-co-HEA) at [M]:[CTA] = 190, f_{OH} = 0.03, and 125 °C. PI peak assignments are given in Figure S11. The small labeled peaks are consistent with a limited amount of HEA copolymerized with isoprene.

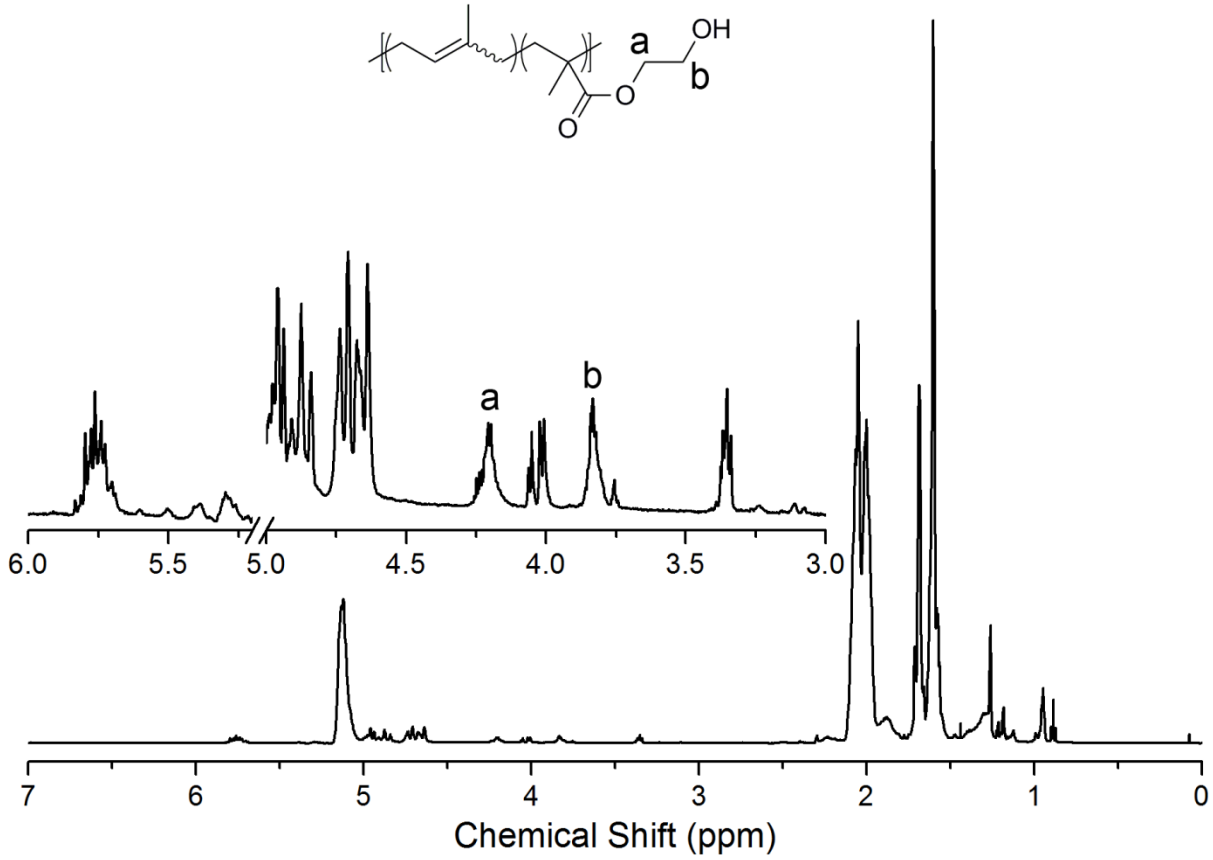

Figure S13. ^{1}H NMR spectrum with magnified region and peak assignments for RAFT controlled radical synthesized P(I-co-HEMA) at [M]:[CTA] = 190, f_{OH} = 0.03, and 125 °C. PI peak assignments are given in Figure S11. The small labeled peaks are consistent with the copolymerization of HEMA with isoprene.

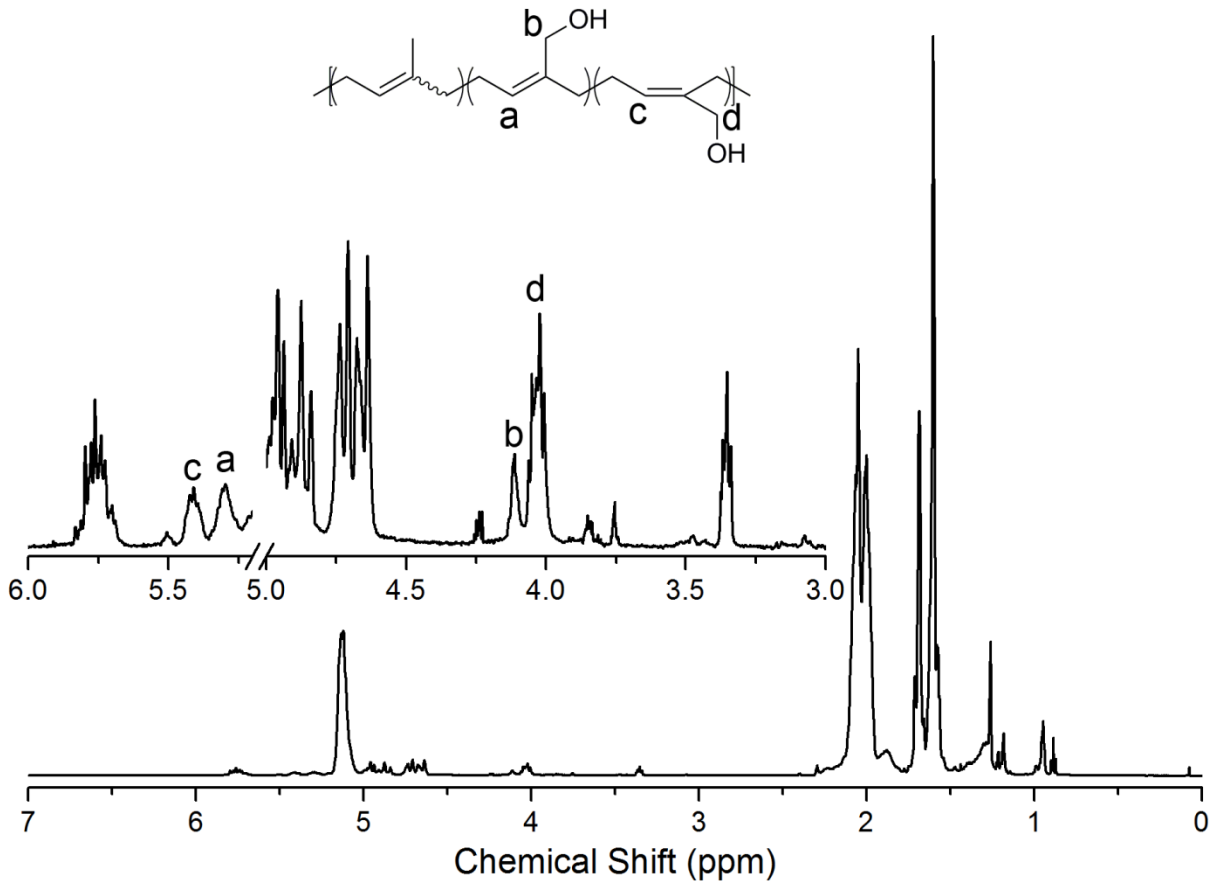

Figure S14. ^{1}H NMR spectrum with magnified region and peak assignments for RAFT controlled radical synthesized P(I-co-IOH) at [M]:[CTA] = 190, f_{OH} = 0.03, and 125 °C. PI peak assignments are given in Figure S11. Two of the possible isomers for the IOH repeat units are observed: *trans*-1,4-addition and *cis*-1,4-addition product. The production of the *cis* repeat units is preferred, accounting for 67% of the 1,4 isomers, with the *trans* isomers making up the balance. Significant production of the other two possible isomers of the IOH repeat unit (1,2 and 3,4) was not found. One of the peaks associated with the polymer end-group overlaps with the peak labeled "d," accounting for the multiplet observed.

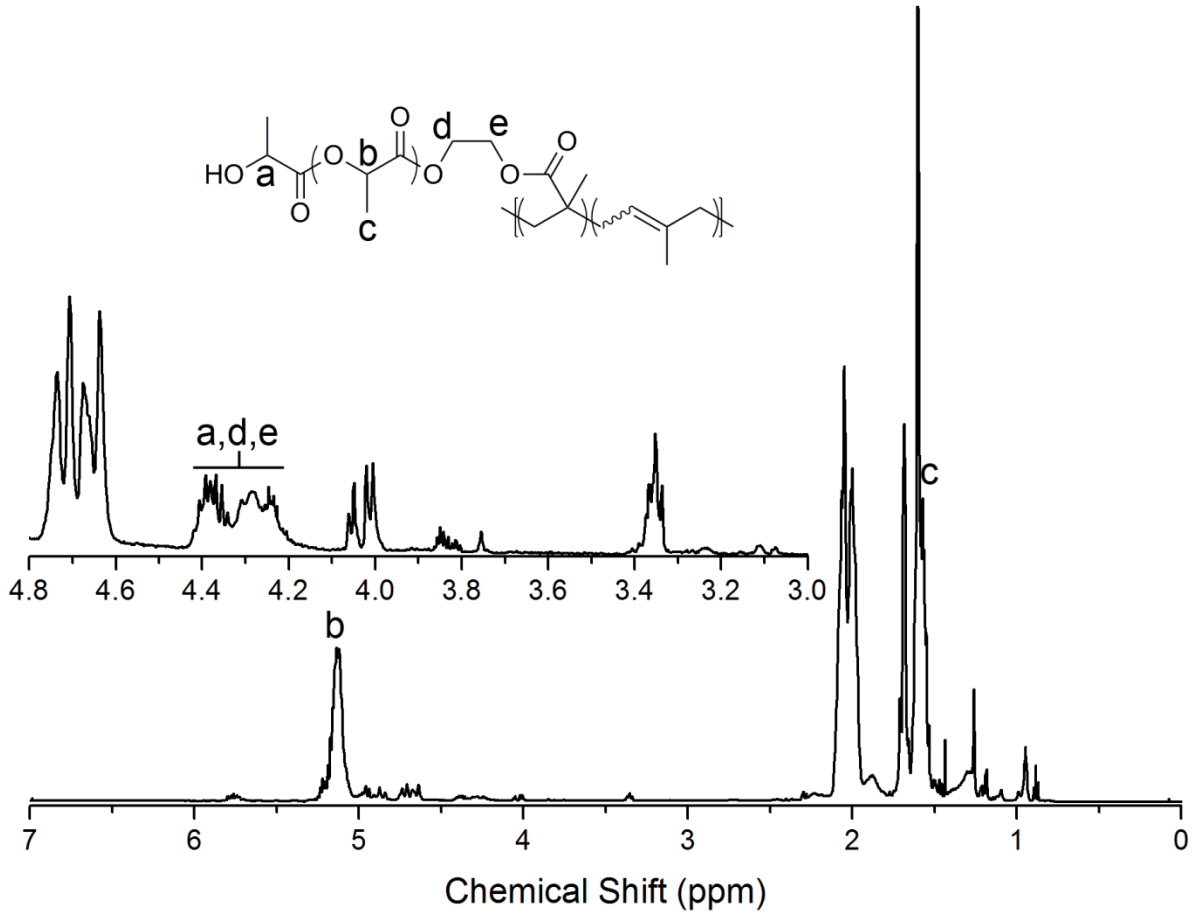

Figure S15. ^{1}H NMR spectrum and magnified spectrum region of P(I-co-HEMA)-g-PLA. P(I-co-HEMA) macroinitiator peaks assignments are given in Figure S13. Peaks that correspond to PLA repeat unit protons overlap with those corresponding to the macroinitiator. The peak associated with the PLA end-group proton overlaps with the peaks belonging to the initiating HEMA group. Consequently, the region indicated by "a,d,e" on the spectrum represents five protons per PLA arm.

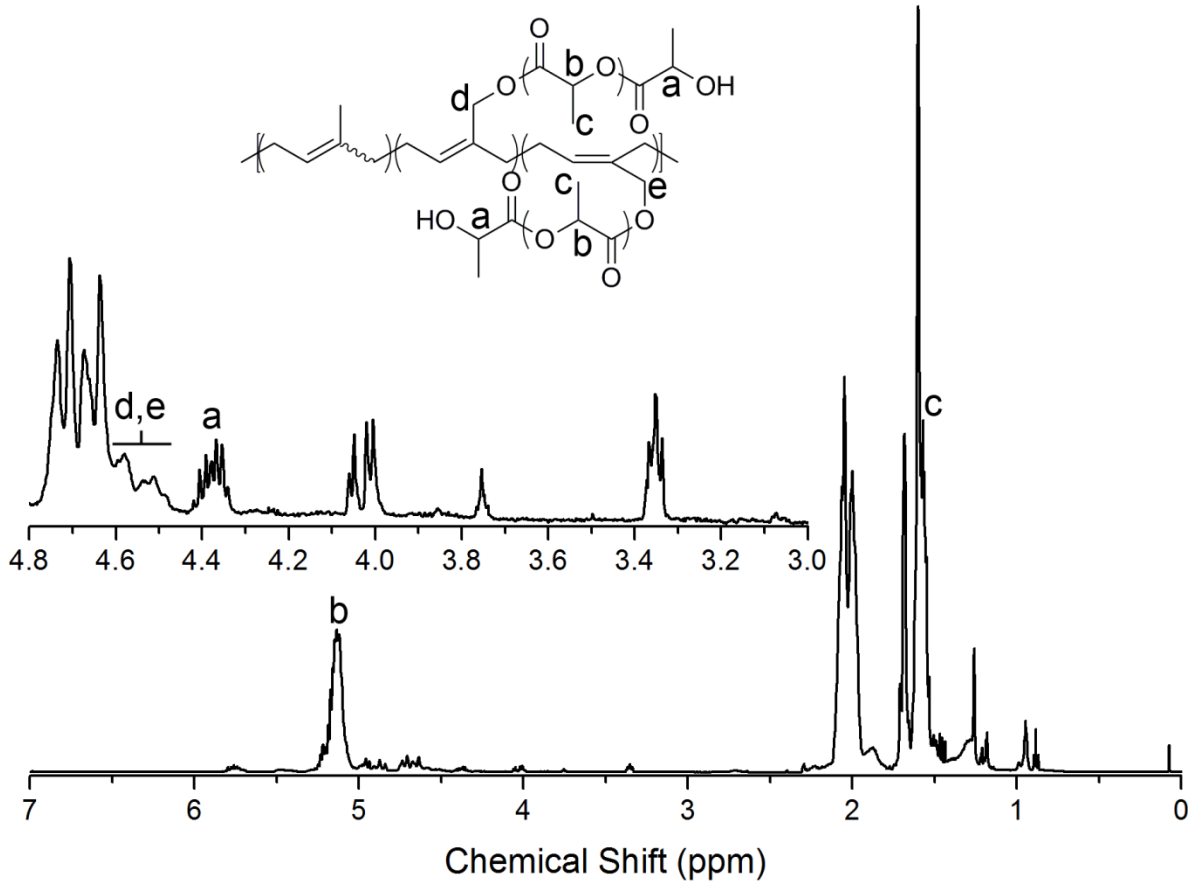

Figure S16. ^{1}H NMR spectrum and magnified region of P(I-co-IOH)-g-PLA. P(I-co-IOH) macroinitiator peaks assignments are given in Figure S14. Upon initiation of the PLA polymerization, peaks associated with the methylene protons of IOH repeat unit shift downfield and are labeled "d,e".

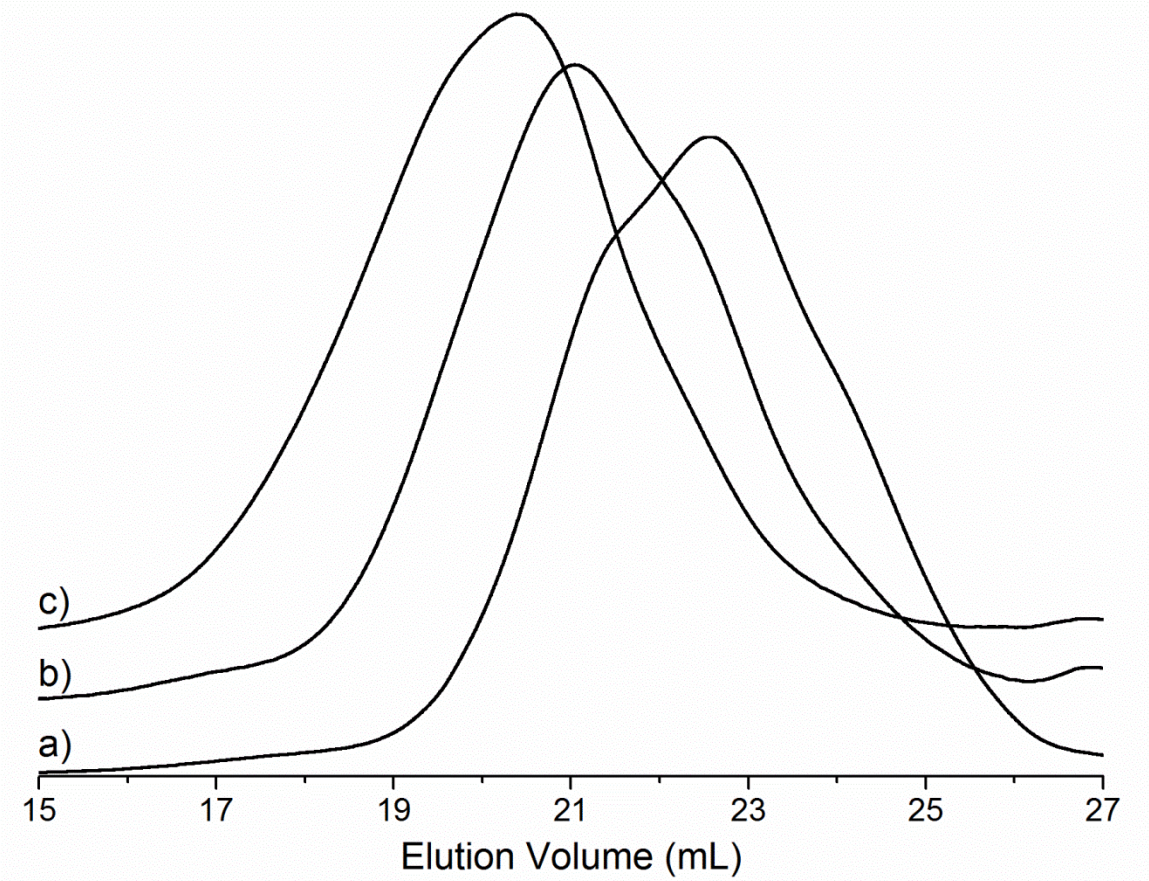

Figure S17. Representative SEC elution curves for emulsion copolymerizations of isoprene and IOH at [M]:[I] values of (a) 50, (b) 150, and (c) 430. As [M]:[I] increases the peak of each elution curve shifts to lower elution volume, indicative of a higher M_n. Distributions are broad ($Đ > 2$) and typically have a shoulder off the main peak.

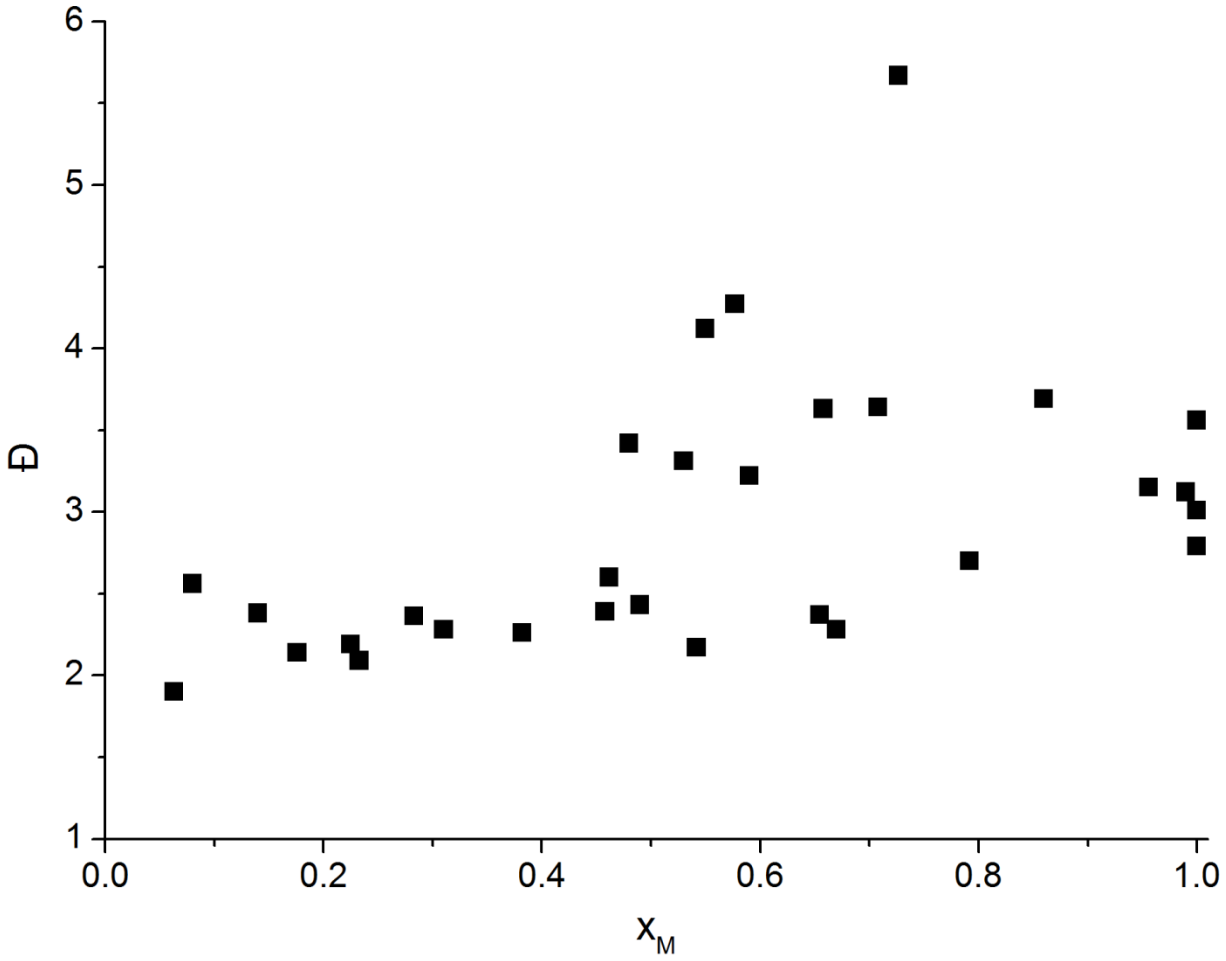

Figure S18. The dispersity (Đ) of emulsion isoprene/IOH (f_{IOH} range of 0.03 to 0.05) copolymers plotted as a function of total monomer conversion calculated gravimetrically (x_M). The SEC distributions of the P(I-co-IOH) copolymers (Figure S17) are broad with Đ values greater than 2 and tend to have a shoulder or some bimodal characteristics. If the average number radicals per emulsion particle is low (ca. 0.5) and the polymerization terminates primarily by disproportionation, the Đ of the resulting polymer will go to 4 as small oligomers and large polymers are formed.[1] The addition of a CTA such as the TDM used in these experiments should mitigate the disproportionation and lower the Đ.[1] Formation of branched polymers could also account for the broad distributions. P(I-co-IOH) has double bonds along its backbone that can react with radicals, providing a branch point for polymerization. At low conversions (0–40%), the Đ is close to that of the most probable distribution (Đ = 2), but as x_M increases the Đ generally goes up. Due to decreasing monomer concentration, the likelihood of branching events amplifies as polymeric double bonds become a significant fraction of the available radical reaction points. In cases of extreme branching, crosslinked networks would be formed. Such gel fractions have been observed in isoprene emulsion homopolymerizations run to high conversions.[2]

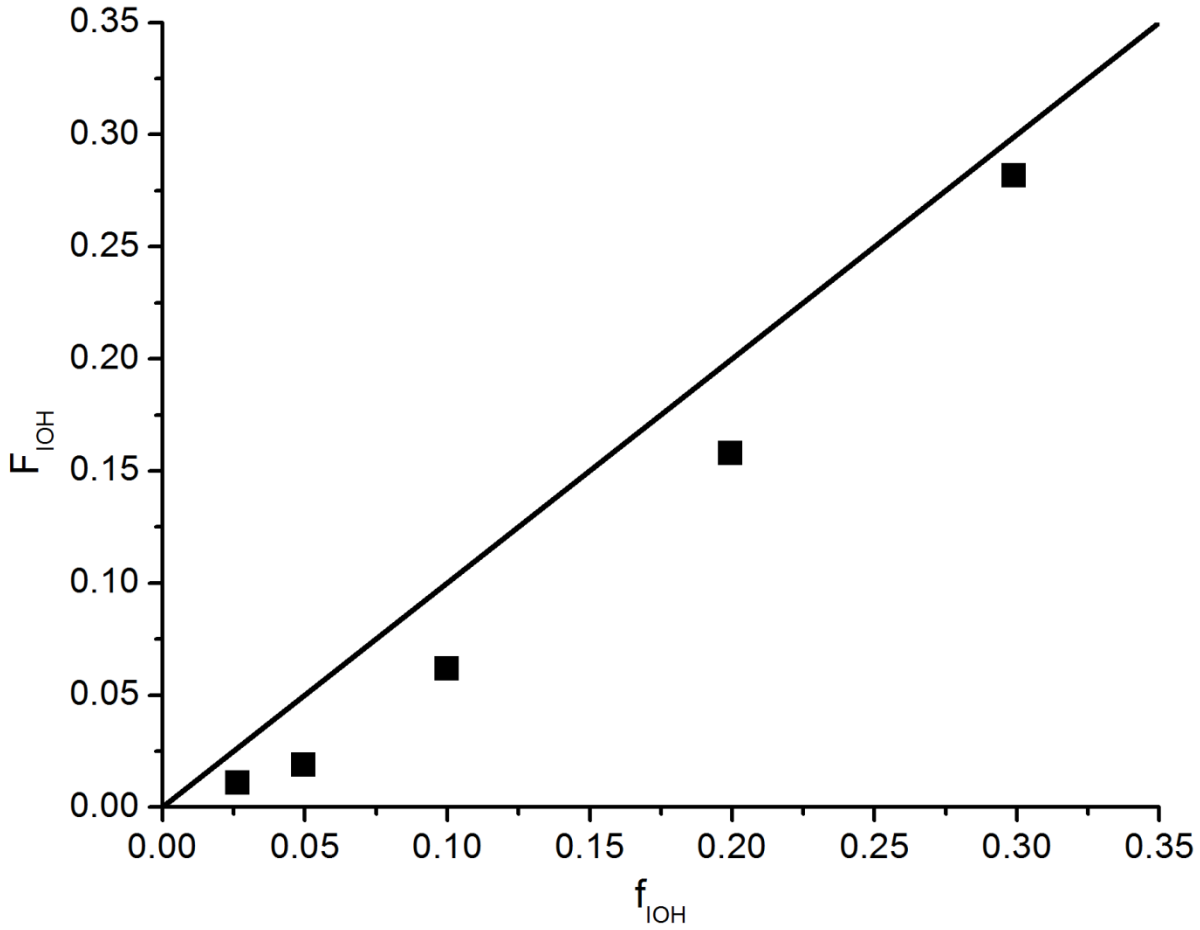

Figure S19. Copolymer IOH mole fraction for the emulsion copolymerization of IOH and isoprene (F_{IOH}) as a function of IOH mole fraction fed (f_{IOH}) at low x_M values (5–14%). The solid line represents where F_{IOH} equals f_{IOH}. F_{IOH} is less than f_{IOH} over the range of values tested. Higher f_{IOH} copolymers at similar conversions furnished products that were not soluble in a variety of solvents. Interestingly, as the f_{IOH} increases (ca. 0.3) the F_{IOH} and f_{IOH} values become more similar, suggesting that the composition curve may cross the $F_{IOH} = f_{IOH}$ line at higher f_{IOH}.

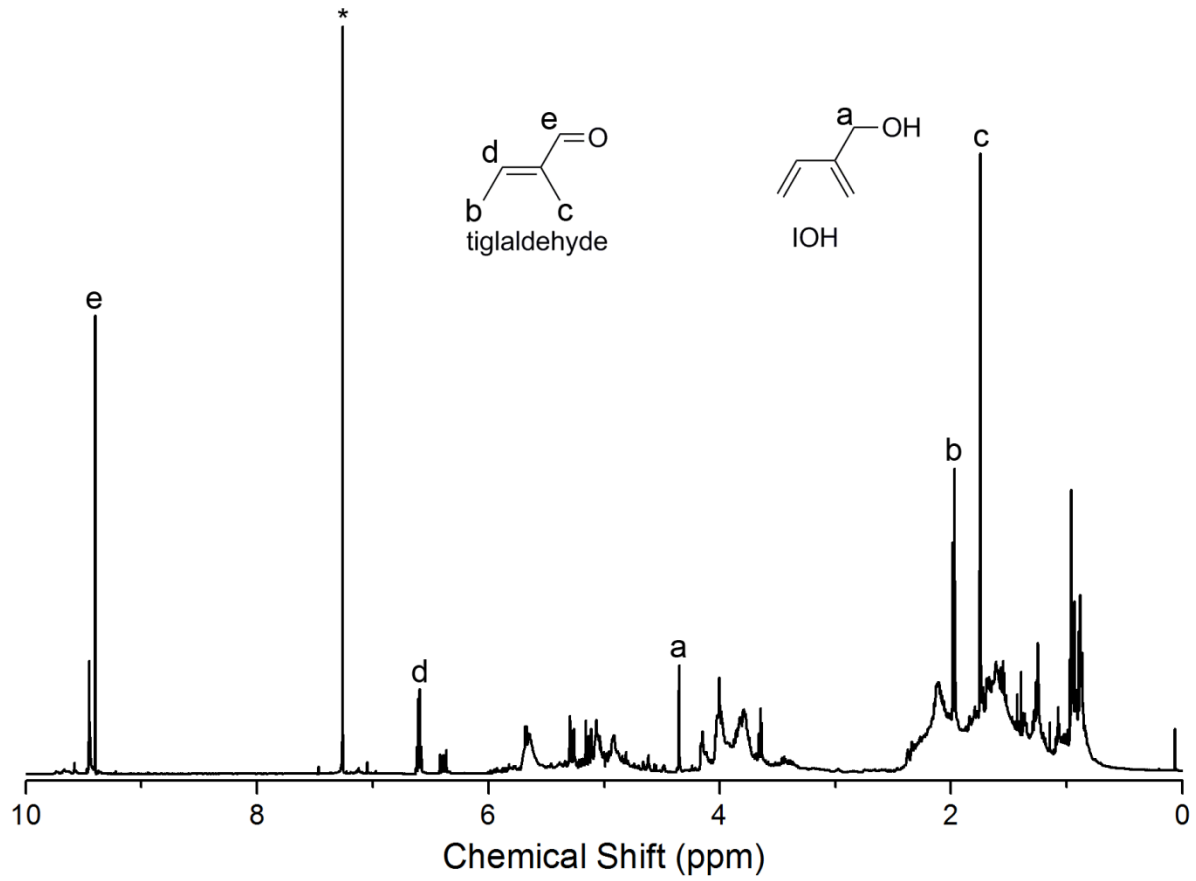

Figure S20. ^{1}H NMR spectrum of crude reaction solution of bulk RAFT controlled radical polymerization of IOH at 125 °C for 24 h. Original monomer remains as indicated by the peak labeled "a," but is a minor component of the mixture. Broad peaks at 6–3 ppm and 2.5–0.7 ppm resonances are indicative of polymer formation. New peaks that correspond to IOH isomerized to tiglaldehyde are now present in the mixture after heating (see labeled peaks on spectrum).[3] The exact mechanism for the isomerization of IOH to tiglaldehyde is unclear. Fourier transform-infrared (FT-IR) spectroscopy confirmed the presence of aldehydes as there was an absorption at 1725 cm^{-1}.

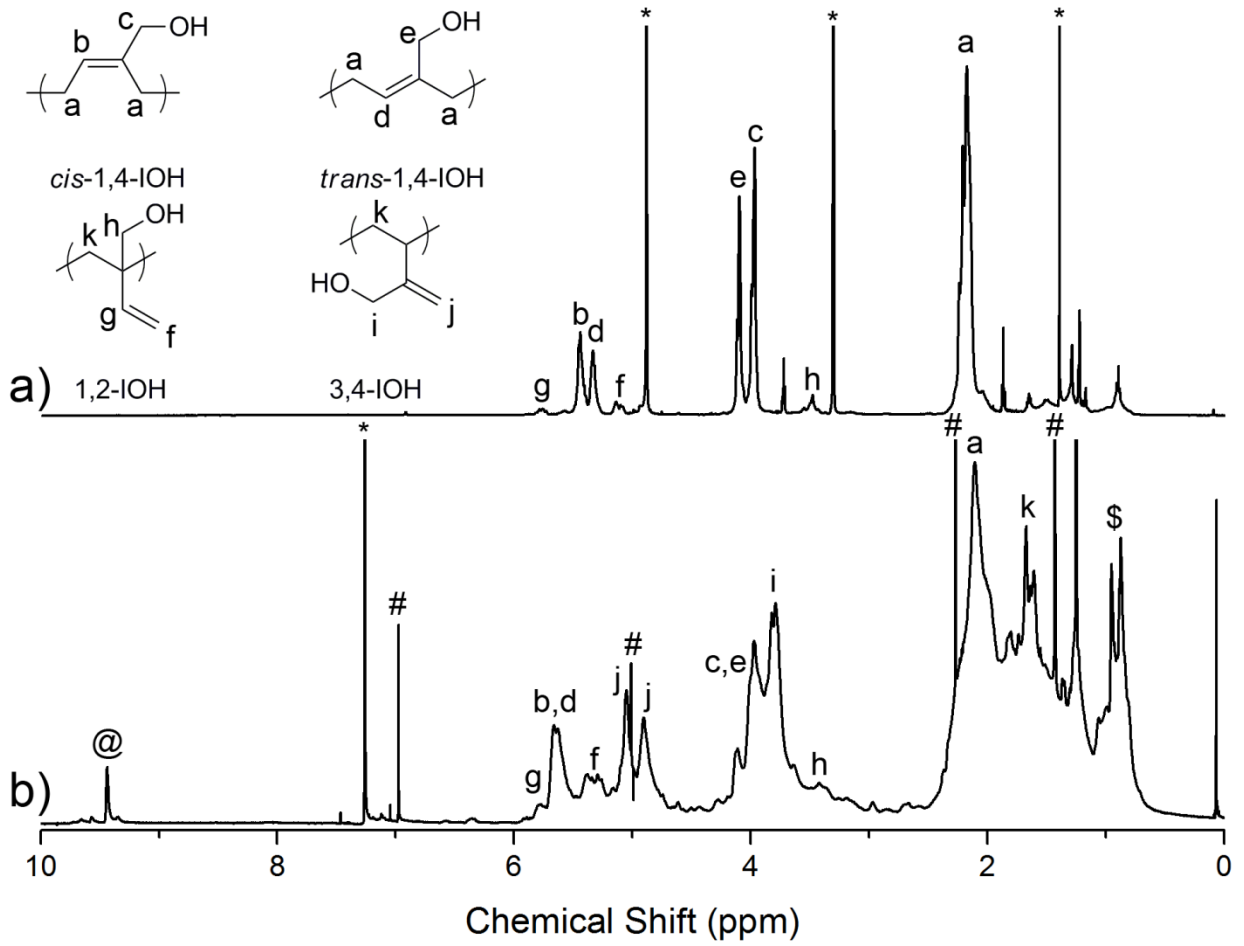

Figure S21. ^{1}H NMR spectra of (a) emulsion synthesized PIOH (500 MHz, CD_3OD) and (b) bulk RAFT control radical polymerized PIOH (500 MHz, $CDCl_3$) with tentative peak assignments. Asterisks (*) mark peaks of residual NMR solvent. The pound sign (#) denotes peaks belonging to butylated hydroxytoluene (BHT). The isomer composition of the emulsion synthesized PIOH is 5.3% 1,2-IOH, 41.8% *trans*-1,4-IOH, and 52.9% *cis*-1,4-IOH. No 3,4-addition products were observed in the emulsion polymerized PIOH. The RAFT polymerized PIOH has a significantly different molecular architecture than the emulsion PIOH with 45% 3,4-IOH, 48% 1,4-IOH, and 7% 1,2-IOH. Additionally, peaks associated with pendent methyl groups ($) and aldehydes (@) are present in the ^{1}H NMR spectrum of the RAFT synthesized PIOH, which do not correspond to any of the expected IOH repeat unit isomers. The protons that correspond to the $ and @ labeled peaks may be a result of the aldehyde side product, discussed in Figure S20, reacting with the growing polymer chain. FT-IR of the RAFT polymerized PIOH is consistent with the presence of aldehydes in the polymer sample (1727 cm^{-1}). The FT-IR of the emulsion polymerized PIOH is devoid of such absorptions. The different isomeric composition of the IOH homopolymers results in different solubilities. The RAFT polymerized PIOH is insoluble in hexanes and methanol while soluble in tetrahydrofuran, chloroform, and methylene chloride. The emulsion polymerized PIOH is insoluble in hexanes and chloroform, slightly soluble in tetrahydrofuran, and soluble in methanol and ethanol. The T_g values of the emulsion polymerized PIOH and RAFT controlled radical polymerized PIOH were 16 and 13 °C, respectively.

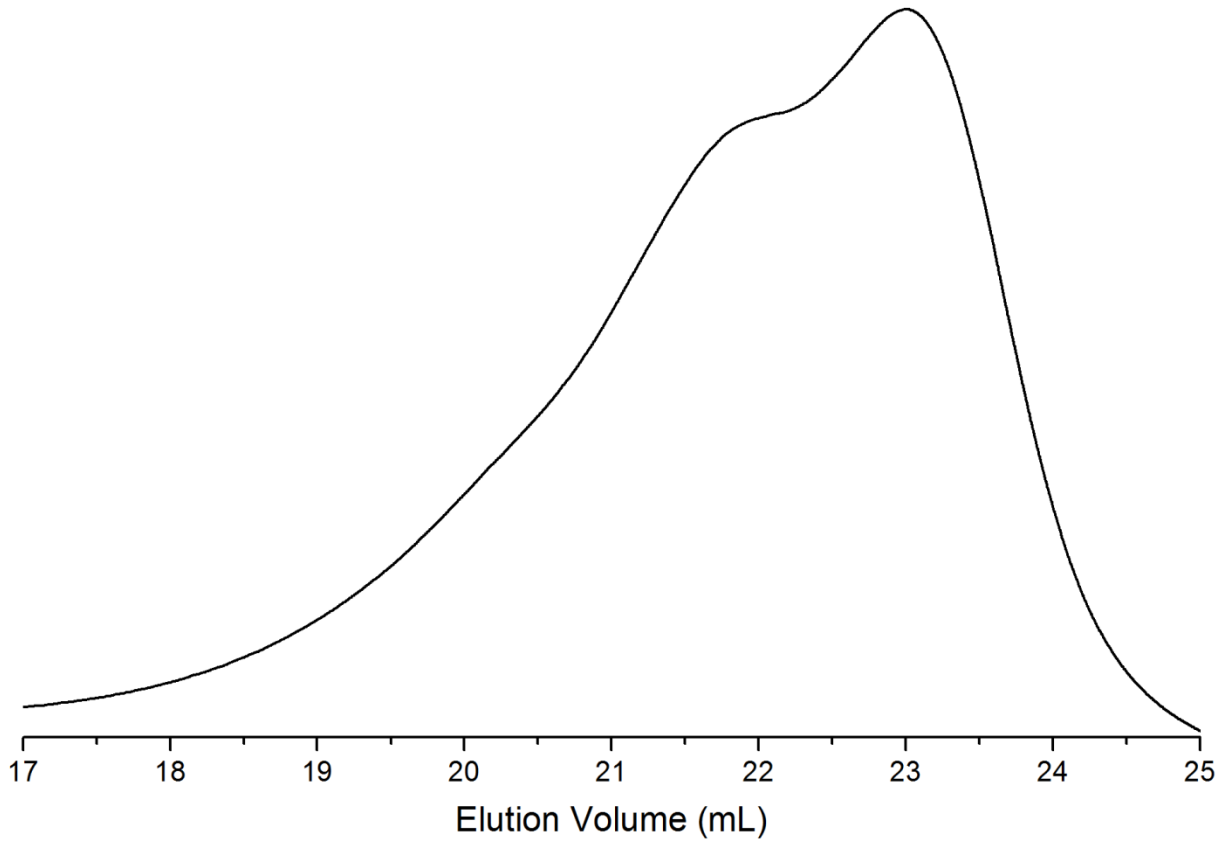

Figure S22. SEC elution curve of RAFT controlled radical polymerized PIOH. Using polystyrene standards, the M_n is 16 kg/mol and the Đ is 2.75. The bimodal nature of the peak and broad Đ indicate that the polymerization was not controlled. The high molecular weight tail suggests that the PIOH interacts with the column, perhaps explaining some of the broadness of the elution curve.

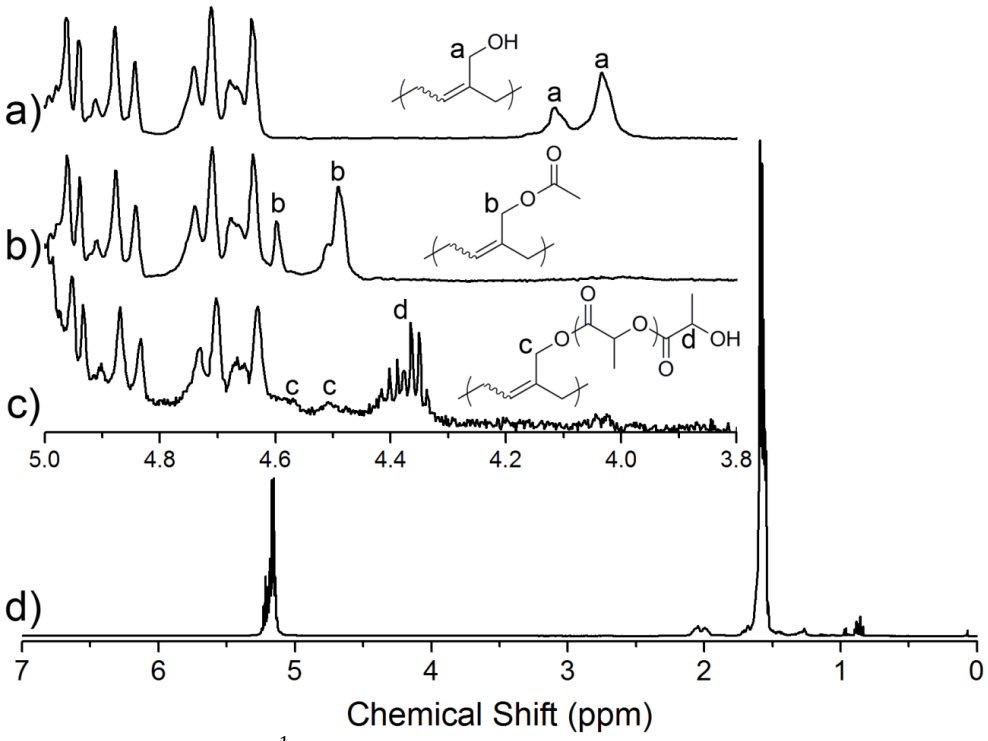

Figure S23. Magnified ^{1}H NMR spectra and chemical structure peak assignments for (a) emulsion synthesized P(I-co-IOH), (b) acetylated P(I-co-IOH), and (c) P(I-co-IOH)-g-PLA using the emulsion P(I-co-IOH) as a macroinitiator. The (d) full ^{1}H NMR spectrum for P(I-co-IOH)-g-PLA is also given. The peaks at 5.17 and 1.58 ppm belong to the PLA repeat units. The P(I-co-IOH) used as the macroinitiator had F_{IOH} = 0.025, a M_n (SEC with polystyrene standards) of 74 kg/mol, and a Đ of 6.35. The P(I-co-IOH)-g-PLA synthesized using this macroinitiator targeted 95 wt % PLA using TBD as the catalyst ([M]:[TBD] = 1000). After 35 min at room temperature, the polymerization had reached 98% conversion of D,L-lactide, giving a P(I-co-IOH)-g-PLA polymer with theoretical PLA arms with a M_n of 55 g/mol and a total theoretical M_n of 1600 kg/mol. Calculation of the actual PLA arm M_n by ^{1}H NMR spectroscopy was complicated by the overlapping of end group peaks and the polymer chain. Acetylation of the same polymer demonstrates that other types of reactions can occur with the pendent hydroxyl groups of P(I-co-IOH). Additionally, the similar chemical structure of acetylated P(I-co-IOH) to the P(I-co-IOH)-g-PLA confirms the ^{1}H NMR spectra peak assignments for the graft copolymer. The SEC elution curve of the P(I-co-IOH)-g-IOH (Figure S24) supports the formation of graft copolymer as the trace shifts to lower elution volume as compared to the starting P(I-co-IOH). The M_n of the graft copolymer calculated from the SEC trace calibrated with polystyrene standards is 330 kg/mol as compared to 77 kg/mol for the original P(I-co-IOH). The multimodal nature of the graft copolymer distribution is due to both the nature of the polymerization and limitations of the SEC instrument. Peaks and shoulders at high elution volume (19.5 and 24.5 mL) may be due to PLA homopolymer formation due to an unknown advantageous initiator present in the system. The high molecular weight peak around 15 mL is a result of the molecule size limitations of the columns used on the SEC.

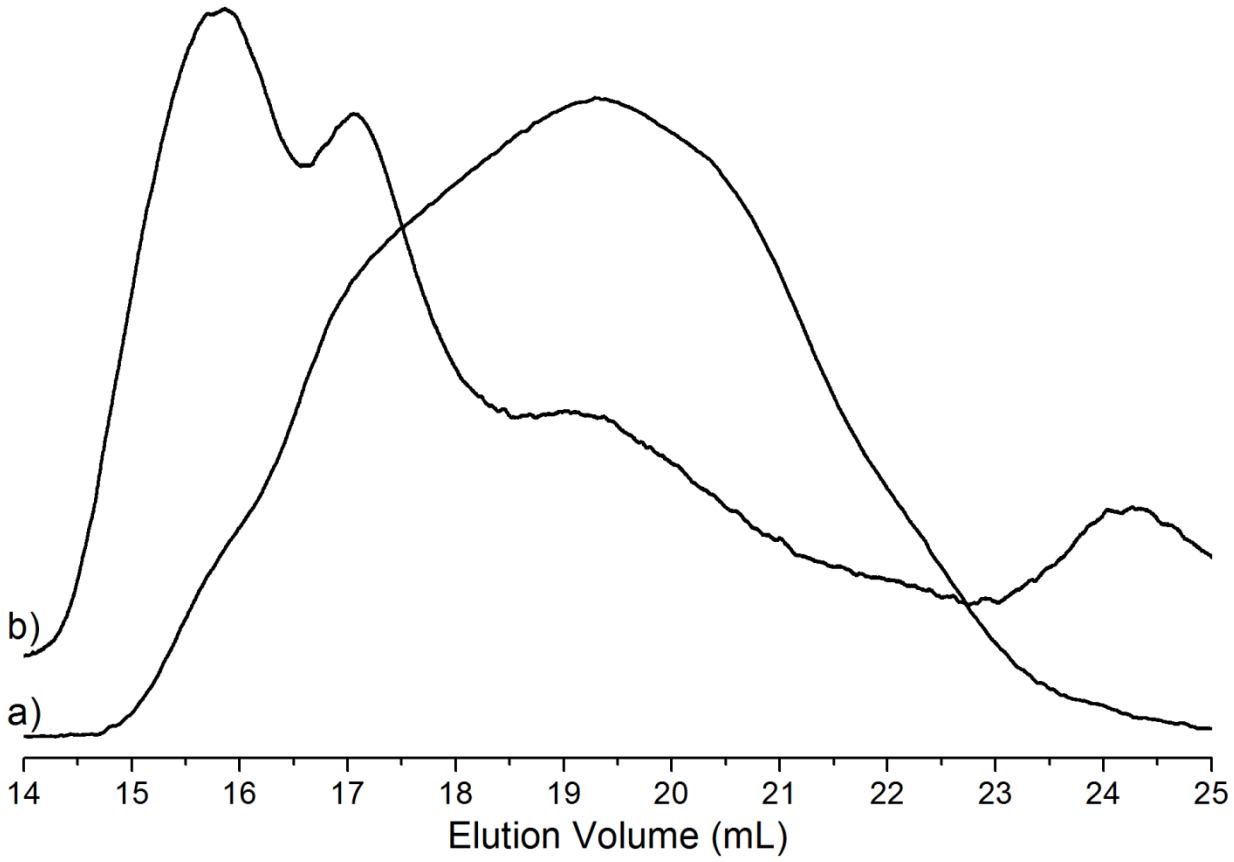

Figure S24. SEC elution curves for (a) emulsion synthesized P(I-co-IOH) macroinitiator (M_n = 77 kg/mol, Đ = 6.35, F_{IOH} = 0.025) and (b) 95 wt % PLA P(I-co-IOH)-g-PLA graft copolymer (M_n = 330 kg/mol, Đ = 5.93) polymerized off the P(I-co-IOH).

Experimental Details

General methods and materials

All chemicals were purchased from Sigma-Aldrich and used without further purification unless otherwise noted. HPLC grade CH_2Cl_2 was dried on an MBraun solvent purification system. Isoprene was purified by passing it through neutral alumina prior to use unless otherwise noted. D,L-lactide (Purac) was recrystallized from ethyl acetate, dried under reduced pressure and stored under dry nitrogen prior to use. HEA and HEMA were passed through basic alumina prior to use. The RAFT CTA (2-(((dodecylthio)carbonothioyl)thio)-2-methylpropanoic acid) was synthesized following a previously reported procedure.[4]

^{1}H NMR spectroscopy was performed on a Varian Inova 500 MHz spectrometer in $CDCl_3$ (Cambridge) using the residual $CHCl_3$ peak as reference. Size exclusion chromatography was performed on an Agilent 1100 high-pressure liquid chromatograph at 35 °C equipped with a PLgel (Varian) 5 μm guard column followed by three PLgel columns with varying pore sizes with HPLC grade chloroform as the mobile phase. Molecular weights and dispersity (Đ) were measured by a Hewlett-Packard P1047A refractometer calibrated with either polystyrene (Polymer Laboratories) or polyisoprene (Scientific Polymer Products Inc.) standards. Differential scanning calorimetry (DSC) was performed on a TA Instruments Discovery Series instrument with the P(I-co-IOH) samples cycled between -85 and 200 °C at 10 °C/min with two heating and one cooling cycle. Glass transition temperatures were measured from the second heating ramp. Infrared spectroscopy was performed on a Nicolet Magna-IR 550 (Thermo Scientific) spectrometer on NaCl salt plates at ambient temperature.

Synthesis of IOH

Using either 2-methyl-2-vinyloxirane (MVO) synthesized in house (see Figure S25 and Figure S26 below) or MVO purchased from Alfa-Aesar, the MVO was degassed by three freeze-pump-thaw cycles prior to synthesizing IOH. Using a modified literature procedure,[5] to a degassed 3-neck flask, nBuLi (2.5 M, 62 mL) in hexanes was cannula transferred and the hexanes were removed by evacuating the system. The nBuLi was cooled in ice and anhydrous Et_2O (240 mL) was cannula transferred to the flask. The nBuLi/Et_2O solution was cooled in dry ice/acetone and degassed diisopropylamine/Et_2O (20.2 mL/40 mL) was cannula transferred to the 3-neck reactor. The solution was stirred for 30 min prior to addition of MVO (10 g) by syringe to the cold mixture. The dry ice/acetone bath was removed and the system warmed up slowly to room temperature. Once the solution had become orange (20 min), it was poured into ice cold 2 M HCl (250 mL per 10 g MVO) to quench the reaction. The organic fraction was separated from the aqueous and the aqueous fraction was washed 3 times with Et_2O. The organic fractions were combined and washed with sodium bicarbonate solution, brine, and dried over $MgSO_4$. The dry fractions were concentrated by rotary evaporation at room temperature and 250 torr. The remaining solvents were distilled off at atmospheric pressure. IOH was distilled from the crude product (45 °C, 14 torr) to give 98% pure IOH (18.4% overall yield, 54% purification yield). By massing a known volume of the purified IOH, the density of IOH was estimated to be 0.9 g/mL at 25 °C. Solubility of IOH in water was estimated by adding IOH to D_2O (99.9 % purity) until two phases were realized. The D_2O phase was collected, analyzed by ^{1}H NMR spectroscopy, and the integrations of representative IOH resonances were compared to the integration of the residual solvent H_2O peak to give an approximate solubility (8 g/L). ^{1}H NMR spectroscopy (500 MHz, $CDCl_3$) **δ** 6.39 (dd, J = 18.0 Hz J = 11.4 Hz, -CH=C$H_a$$H_b$), 5.29 (s, -C=C$H_a$$H_b$), 5.27 (d, J = 18.3 Hz, -CH=C$H_a$$H_b$), 5.15 (s, -C=C$H_a$$H_b$), 5.12 (d, J = 11.4 Hz, -CH=C$H_a$$H_b$), 4.35 (s, -C$H_3$),

and 1.58 (br s, -O*H*). ^{13}C NMR (125 MHz, $CDCl_3$) **δ** 145.2, 136.3, 115.7, 114.1, and 62.6. FT-IR (cm^{-1}) 3337 (-OH stretch), 3090, 3008 (H-C= stretch), 2981, 2927, 2871 (-CH- stretch), 1597 (-C=C- stretch), 1083 (C-O stretch), 1023, and 903 (C=C-H, vibrations).

General controlled radical RAFT copolymer synthesis procedure

Comonomer, TBP, and RAFT CTA were dissolved in isoprene at the desired ratios (0.06 mol of total monomer). The solution was transferred to a 10 mL side arm pressure vessel, degassed by 3 freeze-pump-thaw cycles, and backfilled with 3 psig argon. The vessel was then placed in a 125 °C oil bath to heat. To take aliquots for the kinetics study, the procedure from Germack and Wooley was followed.[6] The flask was removed from the oil bath and placed in liquid nitrogen to freeze the reaction mixture and quench the reaction. The mixture was thawed in an ice bath and an aliquot (ca. 500 µL) was taken under flowing argon. The flask was resealed, evacuated by 3 freeze-pump-thaw cycles, backfilled with argon, and placed back in the oil bath to continue reacting. A portion of the aliquot was placed directly into $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy to give a crude solution spectrum which was used to calculate isoprene conversion to limonene and total conversion of hydroxyl comonomers. The remainder of the aliquot was diluted with tetrahydrofuran (THF) inhibited with BHT and dried under reduced pressure at 50 °C to remove all the volatile monomers and byproducts. The dried aliquots were analyzed by SEC and ^{1}H NMR spectroscopy to determine the conversion of monomers to polymer. After 24 h of total heating time and the final aliquot was taken, the remaining viscous yellow liquid was diluted in THF and precipitated in 10 volume excess methanol, twice. The product was dissolved in THF, concentrated by N_2, and dried under reduced pressure at 50 °C for 48 h. The product was characterized by ^{1}H NMR spectroscopy and SEC. ^{1}H NMR spectroscopy for polymer repeat units (500 MHz, $CDCl_3$) **δ** for PI isomers 5.76 (m, 1,2 isomer -C*H*=CH_2), 5.13 (br, *cis* and *trans* 1,4 –C*H*=C-), 5.0–4.8 (m, 1,2 isomer -CH=CH_2), 4.75–4.60 (m, 3,4 isomer -C=CH_2), 2.2-1.9 (br m, allylic), 1.68 (s, *cis* –CH_3), 1.60 (s, *trans* –CH_3), and 0.94 (s, 1,2 -CH_3); for IOH repeat units 5.41 (br, *cis* 1,4 -C*H*=C-), 5.31 (br, *trans* 1,4 -C*H*=C-), 4.11 (s, *trans* 1,4 =C-CH_2-OH), and 4.02 (s, *cis* 1,4 =C-CH_2-OH); for HEA repeat units 4.20 (br, OC-CH_2-CH_2-OH) and 3.81 (br, OC-CH_2-CH_2-OH); and for HEMA repeat units 4.20 (br, OC-CH_2-CH_2-OH) and 3.83 (br, OC-CH_2-CH_2-OH).

Calculation of monomer conversions in RAFT controlled radical polymerizations

Using the ^{1}H NMR spectrum of the aliquot from the crude reaction solution, the conversion of isoprene to limonene ($x_{I\rightarrow L}$) and overall conversion of the hydroxyl monomer (x_{OH}) were calculated with the following procedures. Sample calculations are given for the HEMA/isoprene copolymerization at 12 h unless otherwise noted. For $x_{I\rightarrow L}$, the integration of the limonene peak at 4.72 ppm (878.7) was subtracted by the integration of the isoprene 3,4-addition product peak at 4.65 ppm (99.5) to correct for the concurrent peaks at 4.72 ppm. This value was divided by the integration of the RAFT CTA peak at 3.36 ppm, corrected to give a molar equivalent (50.4/2). The value was then divided by the known ratio of isoprene to RAFT CTA added to the reactor (184.3). Sample calculation for $x_{I\rightarrow L}$ is below.

$$x_{I\rightarrow L} = \frac{\frac{(878.7 - 99.5)}{(50.4/2)}}{184.3} = 0.17$$

To calculate x_{OH} of hydroxyl monomer (HEMA), the integration value of the peak at 4.2 ppm (282.0), corresponding to reacted monomer, was divided by the sum of the integration

values of the 4.2 ppm peak and the unreacted monomer peak at 4.31 ppm (10.0). For HEA, the monomer and reacted monomer peaks were 4.32 and 4.24 ppm, respectively. Sample calculation for hydroxyl monomer conversion is below.

$$x_{OH} = \frac{282.0}{282.0 + 10.0} = 0.96$$

For the x_{OH} of IOH (12 h), the procedure above had to be modified to correct for protons with concurrent resonances. The integration of the reacted monomer region at 4.20–3.96 ppm (47.5) had the integration of the RAFT CTA peak at 3.36 ppm (10.0) subtracted from it to account for the peak overlap from protons of the terminal end of the polymer chain. The integration of the unreacted monomer peak at 4.36 ppm (8.3) was summed with the corrected reacted IOH integration value and divided the corrected value. See below for sample calculation.

$$\text{IOH } x_{OH} = \frac{47.5 - 10.0}{47.5 - 10.0 + 8.3} = 0.79$$

All conversions to polymer were calculated from the dried crude aliquots. Conversion of isoprene to polymer ($x_{I \rightarrow P}$) was calculated by summing the normalized integrations of the various addition isomers: 1,2-addition (5.76 ppm, 13.6); 3,4-addition (4.8–4.6 ppm, 36.6/2); and 1,4-addition (5.13, 472.7) products; dividing by the normalized integration of the RAFT CTA end group (3.34 ppm, 10.7); and dividing that value by the ratio of isoprene to RAFT CTA fed to the reactor (184.3). Sample calculation is below.

$$x_{I \rightarrow P} = \frac{\frac{13.6 + 36.6/2 + 474.7}{10.7/2}}{184.3} = 0.31$$

Conversion of hydroxyl monomer to polymer ($x_{OH \rightarrow P}$) was calculated by dividing the normalized integration of the polymer peak (4.2 ppm, 12.6/2) by the normalized integration of the RAFT CTA peak (3.34 ppm, 10.7/2) and dividing that value by the known ratio of hydroxyl monomer to RAFT CTA fed to the reactor (5.7). The sample calculation is below.

$$x_{OH \rightarrow P} = \frac{\frac{12.6/2}{10.7/2}}{5.7} = 0.21$$

To calculate the x_{OHP} of IOH (12 h), the integration of the polymerized IOH peak (26.8) was corrected by subtracting the integration of the RAFT CTA resonance (10.0), divided by the integration of the RAFT CTA resonance, and then divided by the know ratio of IOH to RAFT CTA fed to the reactor (5.7). Sample calculation is below.

$$\text{IOH } x_{OH \rightarrow P} = \frac{\frac{26.8 - 10.0}{10.0}}{5.7} = 0.30$$

The validity of calculating the $x_{I\rightarrow P}$ using the CTA as an internal standard was confirmed gravimetrically. For the isoprene homopolymerization and HEMA copolymerization, aliquots of the final crude solutions (24 h) were taken and quickly massed. The aliquots were dried under reduced pressure at 50 °C to remove all volatiles and the samples were massed again, calculating the $x_{I\rightarrow P}$ by dividing the initial sample mass by the dry sample mass. The gravimetrically determined $x_{I\rightarrow P}$ of the isoprene homopolymerization and HEMA/isoprene copolymerization were 47% and 50%, respectively. These conversions compare favorably with those calculated by ^{1}H NMR spectroscopic end group analysis of the isoprene and HEMA polymerizations, which were 46% and 50%, respectively. The close agreement of the gravimetric and spectroscopic methods to calculate monomer conversion to polymer confirms the validity of the spectroscopic method.

Emulsion copolymer synthesis procedure

Following a modified literature procedure for isoprene homopolymerization,[2] sodium dodecyl sulfate (SDS) was massed into a 10 mL side arm vessel sealed with a PTFE stopcock and degassed with three evacuate/backfilled with 3 psig argon cycles. Under flowing argon, degassed deionized (DI) water was added to the flask to dissolve the SDS (69.4 mM solution). Comonomer and isoprene were mixed before adding to the reactor under flowing argon to give a 1.47 mM monomer in water emulsion. The mixture was allowed to stir for 1 h. The tBHP and TDM were added under flowing argon at the desired ratio and allowed to stir for 30 min. Under flowing argon, a 1.5 M solution of tetraethylenepentamine (TEPA) in DI water was added to start the reaction. TEPA and tBHP were always added at 1:1 ratio as the two chemicals made up the redox pair. TEPA, tBHP, and TDM were added at a 1:1:0.5 ratio, respectively. The reaction vessel was then placed in a 25 °C oil bath to keep a constant reaction temperature. After the desired polymerization time, the reaction was quenched by adding a 200 ppm hydroquinone solution in methanol at a 0.2:1 ratio to the reaction emulsion. To determine conversion by mass, a known volume of the emulsion was taken, concentrated under blowing N_2, and dried under reduced pressure over night. The bulk of the emulsion was coagulated by pouring it into excess acetone. The coagulated material was then dissolved in THF and precipitated in 10 volume excess methanol. The sample was collected by dissolving in THF, concentrating with nitrogen, and drying under reduced pressure. Polymers were a yellow to orange color due to the oxidized TEPA. The materials were characterized by ^{1}H NMR spectroscopy and SEC. ^{1}H NMR spectroscopy for the isoprene/IOH copolymer repeat units (500 MHz, $CDCl_3$) **δ** 5.76 (m, -C*H*=CH_2), 5.41 (br, IOH *cis* -C*H*=C-), 5.31 (br, IOH *trans* -C*H*=C-), 5.13 (br, isoprene *cis* and *tran* –C*H*=C-), 5.0–4.8 (m, -CH=CH_2), 4.75–4.60 (m, -C=CH_2), 4.11 (s, *trans* =C-CH_2-OH), 4.02 (s, *cis* =C-CH_2-OH), 2.2–1.9 (br m, allylic), 1.68 (s, *cis* –CH_3), 1.60 (s, *trans* –CH_3), and 0.94 (s, 1,2 -CH_3).

Homopolymerization of IOH

IOH was homopolymerized following both the RAFT controlled radical and the emulsion procedures given above for copolymerizations. Under the RAFT conditions, IOH was homopolymerized at a [M]:[CTA] = 190 for 24 h at 125 °C in the bulk. The crude product was sampled for ^{1}H NMR spectroscopy, dissolved in CH_2Cl_2, and precipitated in 10 times volume excess methanol. The product was collected and dried under reduced pressure overnight at 50 °C, yielding a brown rubbery material. Under the emulsion conditions, IOH was homopolymerized at [M]:[I] = 50 for 17 h at 25 °C. The reaction was quenched by adding a 200 ppm

hydroquinone/methanol solution to the emulsion and the water was evaporated off. The product was dissolved in methanol and precipitated in 10 times volume excess hexanes. The product was collected and dried under reduced pressure overnight at 50 °C, yielding a yellow rubbery material. The materials were analyzed by ^{1}H NMR spectroscopy and FT-IR spectroscopy. ^{1}H NMR spectroscopy of RAFT synthesized PIOH (500 MHz, $CDCl_3$) **δ** 9.45 (s, O=C*H*), 5.98–5.76 (br, 1,2-addition isomer, -C*H*=CH_2), 5.65 (br, 1,4-addition isomer, -C*H*=C-), 5.40–5.20 (br, 1,2-addition isomer, -CH=C*H*$_2$), 5.07 and 4.92 (br, 3,4-addition isomer, -C=C*H*$_2$), 4.20–3.96 (br, 1,4-addition isomer, -C*H*$_2$OH), 4.04–3.68 (br, 3,4-addition isomer, -C*H*$_2$OH), 3.65 (br, 1,2-addition isomer, , -C*H*$_2$OH), 2.4–1.9 (br, -C*H*$_2$-C=), 1.9–1.2 (br, -C*H*$_2$-), and 1.0–0.7 (br, -C*H*$_3$). ^{1}H NMR spectroscopy of emulsion synthesized PIOH (500 MHz, $CDCl_3$) **δ** 5.77 (br, 1,2-addition isomer, -C*H*=CH_2), 5.45 (br, *cis*-1,4-addition isomer, -C*H*=C-), 5.34 (br, *trans*-1,4-addition isomer, -C*H*=C-), 4.11 (br, *trans*-1,4-addition isomer, -C*H*$_2$OH), 3.98 (br, *cis*-1,4-addition isomer, -C*H*$_2$OH), 3.49 (br, 1,2-addition isomer, , -C*H*$_2$OH), and 2.2 (br, -C*H*$_2$-C=). FT-IR of crude RAFT controlled radical polymerization solution, NaCl plate (cm^{-1}): 3434.3, 3080.1, 2924.1, 2871.5, 2703.6, 1724.7, 1684.8, 1644.9, 1081.2, 903.4, and 803.7. FT-IR of purified RAFT controlled radical PIOH, NaCl plate (cm^{-1}): 3448, 2924, 2955, 2871, 1727, 1647, 1457, 1083, 904, 807, and 733. FT-IR of emulsion synthesized PIOH, NaCl plate (cm^{-1}): 3306, 2919, 2853, 1665, 1577, 1541, 1454, 1233, 1005, 909, and 860.

PLA graft copolymer synthesis procedure at 50 wt % lactide

In a N_2 atmosphere glove box, the following components were combined in 20 mL scintillation vials. Hydroxyl copolymer macroinitiator (250 mg) and *d,l*-lactide (250 mg) were dissolved in dried CH_2Cl_2 (4.2 mL). To the solution, TBD (32.2 mg) was added as a stock solution in minimal CH_2Cl_2 to start the polymerization. After 5 min, a solution of benzoic acid (283 mg) in minimal CH_2Cl_2 was added to quench the polymerization. The quenched reaction solutions were removed from the glove box and precipitated twice into 10 volume excess methanol from CH_2Cl_2. The collected products were dried under reduced pressure at 50 °C for two days. The products were analyzed by SEC and ^{1}H NMR spectroscopy. ^{1}H NMR spectroscopy (500 MHz, $CDCl_3$) **δ** PLA repeat units 5.17 (m, -C*H*-) and 1.58 (m, -C*H*$_3$); PLA end-group protons 4.36 (m, -C*H*-); P(I-co-IOH) end-group protons 4.56 (br, =C-C*H*$_2$-O-CO) and 4.50 (br, =C-C*H*$_2$-O-CO); and P(I-co-HEMA) end-group protons 4.42–4.18 (br, O-C*H*$_2$-C*H*$_2$-O).

P(I-co-IOH)-g-PLA synthesis at 95 wt % lactide

In a N_2 dry box, P(I-co-IOH) (0.5 g) was massed into a 150 mL pressure vessel and dissolved in dry CH_2Cl_2 (88 mL). D,L-lactide (9.5 g) was dissolved and followed by 920 µL of a 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) stock solution in dry CH_2Cl_2 (20 mg/2 mL) to start the polymerization. The flask was sealed, removed from the dry box, and allowed to stir for 35 min at room temperature (ca. 22 °C). A solution of benzoic acid (81 mg) in minimal CH_2Cl_2 was added to the viscous solution to quench the polymerization. The solution was diluted with CH_2Cl_2 and precipitated in 10 volume excess methanol. The product was collected, dissolved in CH_2Cl_2, and precipitated in 10 volume excess hexanes. The collected white polymer was set to dry under reduced pressure overnight. From an aliquot of the crude solution D,L-lactide conversion was calculated to be 98% (85% yield). Product was characterized by ^{1}H NMR spectroscopy and SEC. ^{1}H NMR spectroscopy (500 MHz, $CDCl_3$) **δ** PLA repeat units 5.17 (m, -C*H*-) and 1.58 (m, -C*H*$_3$); end-group protons 4.56 (br, =C-C*H*$_2$-O-CO), 4.50 (br, =C-C*H*$_2$-O-CO), and 4.36 (m, -C*H*- and =C-C*H*$_2$-O-CO).

SAXS and TEM analysis of P(I-co-IOH)-g-PLA

Transmission electron microscopy (TEM) was performed on a FEI Tecnai Spirit BioTWIN at an operating voltage of 80 keV. Samples for TEM were microtomed at 25 °C on a Leica EM UC6 Ultramicrotome to a thickness of approximately 70 nm, placed on a copper grid, and then stained with OsO_4 vapor (4 wt % aqueous solution) for 20-30 minutes prior to imaging. Room temperature synchrotron small-angle X-ray scattering (SAXS) was carried out at the Advanced Photon Source (APS) at Argonne National Laboratories at the Sector 5-ID-D beamline maintained by the Dow-Northwestern-Dupont Collaborative Access Team (DND-CAT) with a source that produces x-rays with a wavelength of 0.728 Å. Scattering intensity was monitored by a Mar 165 mm diameter CCD detector with a resolution of 2048 × 2048. The two-dimensional scattering patterns were integrated azimuthally, giving one-dimensional scattering profiles. In each scattering profile, the lowest spatial frequency (q) peak was designated as q* – the principle scattering peak. From the q* value, the domain spacing (d) of each sample was calculated using $d = 2\pi/q^*$.

Acetylation of emulsion synthesized P(I-co-IOH)

P(I-co-IOH) (50 mg) was dissolved in 3 mL of THF to which acetic anhydride (0.5 mL) and pyridine (0.5 mL) were added. The solution was allowed to stir for 20 h at which time the volatiles were blown off with N_2 and the resulting polymer was set to dry under reduced pressure. Complete acetylation of the hydroxyl groups was realized as the peaks associated with the pendent hydroxyl groups are no longer present. ^{1}H NMR spectroscopy of new peaks (500 MHz, $CDCl_3$) **δ** 4.59, 4.50, and 4.48 (s, =C-CH_2-O-CO).

Synthesis of 1-bromo-2-methylbut-3-en-2-ol (IBrOH)

De-ionized water (2 L) was cooled to less than 5 °C in a round-bottom-flask followed by isoprene (192 mL) and stirred to create a suspension. *N*-bromosuccinimide (310.6 g) was added portion wise such that the reactor temperature remained below 5 °C. The solution was stirred at 5 °C for 3 h and sat overnight at room temperature. The aqueous phase was extracted twice with diethyl ether and the organic fractions were combined, washed with brine, dried with $MgSO_4$, and concentrated with rotary evaporation. Concentrated product was purified by reduced pressure distillation (38–42 °C, 5 torr) to give a clear product, 47% yield. ^{1}H NMR spectroscopy (300 MHz, $CDCl_3$) **δ** 5.90 (dd, *J* = 17.6 Hz *J* = 10.9 Hz, -C*H*=CH_aH_b), 5.37 (d, *J* = 18.3 Hz, -CH=C$H_a$$H_b$), 5.19 (d, *J* = 9.5 Hz, -CH=CH_aH_b), 3.48 (s, -CH_2-Br), 2.19 (s, -O*H*), and 1.43 (s, -CH_3).

Synthesis of 2-methyl-2-vinyloxirane (MVO)

IBrOH (100 mL) was cooled to 0 °C in a round-bottom-flask and a 30% aqueous NaOH solution (120 mL) was added drop wise over 1 h, keeping the reactor temperature below 5 °C. Upon complete addition of NaOH solution, two phase mixture was stirred for 1.5 h at 0 °C. The organic fraction was separated from the aqueous fraction and used without further purification (97% pure, 98% yield). ^{1}H NMR spectroscopy (300 MHz, $CDCl_3$) **δ** 5.63 (dd, *J* = 17.1 Hz *J* = 10.8 Hz, -C*H*=CH_aH_b), 5.35 (d, *J* = 17.6 Hz, -CH=C$H_a$$H_b$), 5.23 (d, *J* = 11.7 Hz, -CH=CH_aH_b), 2.82 (d, *J* = 5.2 Hz, OC$H_a$$H_b$), 2.73 (d, *J* = 5.1 Hz, OCH_aH_b), and 1.45 (s, -CH_3).

Alternative Synthesis of 2-methylenebut-3-en-1-ol (IOH) with bis(trimethylsilyl)amide (LiHMDS)

Using either MVO synthesized by the above procedure or MVO purchased from Alfa-Aesar, the MVO was degassed by three freeze-pump-thaw cycles. In a N_2 dry box, LiHMDS (37 g) was added to a 500 mL side arm round-bottom-flask sealed with a septum. The flask was removed from the glove box, dry THF (150 mL) was cannula transferred to the LiHMDS flask. Anhydrous Et_2O (150 mL) was cannula transferred to a degassed 3-neck flask fitted with a condenser and septum. The THF/LiHMDS solution was subsequently cannula transferred to the 3-neck flask. Flask was backfilled with 3 psig argon, MVO (14.3 g) was added drop wise by syringe, and the mixture was heated to 60 °C for 20 h. Reaction was quenched by pouring the solution into ice cold 2 M HCl (250 mL per 10 g MVO). The organic fraction was separated from the aqueous fraction, which was washed 3 times with anhydrous Et_2O. The combined organic fractions were washed with sodium bicarbonate solution, brine, and dried over $MgSO_4$. The organic fractions were concentrated by rotary evaporation at room temperature and 250 torr. IOH was purified by column chromatography. The sample was loaded onto silica gel column with pentanes as the mobile phase. The column was washed with pentanes to remove impurities. The solvent was switched to a 5:1 pentanes:Et_2O mobile phase and fractions were collected. IOH had a R_f = 0.27 in 5:1 pentanes:Et_2O. The pentanes and Et_2O were distilled off at 45 °C and atmospheric pressure. To collect IOH, the solution was vacuum distilled (800 mtorr, 33 °C), giving IOH product with 89% purity and 30% yield on purification. ^{1}H NMR spectroscopy (500 MHz, $CDCl_3$) **δ** 6.39 (dd, *J* = 18.0 Hz *J* = 11.4 Hz, -C*H*=CH_aH_b), 5.29 (s, -C=C$H_a$$H_b$), 5.27 (d, *J* = 18.3 Hz, -CH=C$H_a$$H_b$), 5.15 (s, -C=$CH_a$$H_b$), 5.12 (d, *J* = 11.4 Hz, -CH=$CH_a$$H_b$), 4.35 (s, -C$H_3$), and 1.58 (br s, -O*H*). ^{13}C NMR (125 MHz, $CDCl_3$) **δ** 145.2, 136.3, 115.7, 114.1, and 62.6. FT-IR (cm^{-1}) 3337 (-OH stretch), 3090, 3008 (H-C= stretch), 2981, 2927, 2871 (-CH- stretch), 1597 (-C=C- stretch), 1083 (C-O stretch), 1023, and 903 (C=C-H, vibrations).

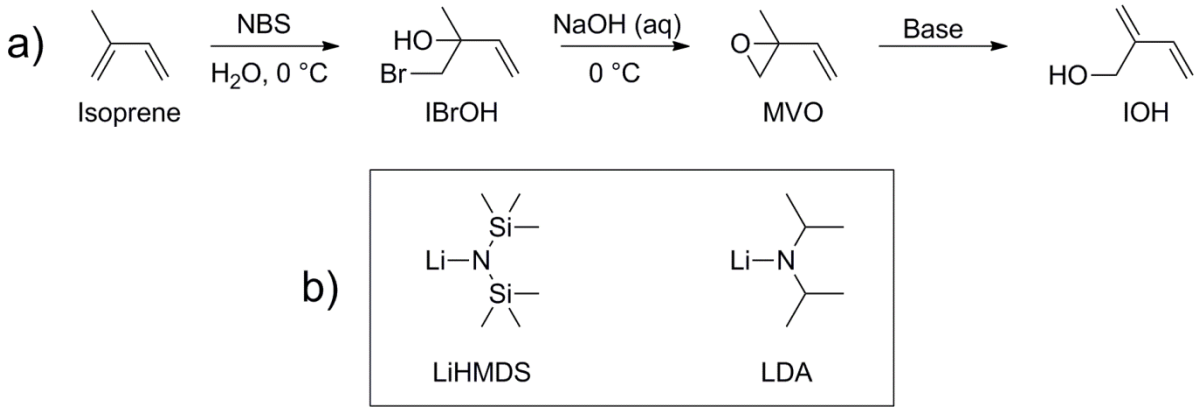

Figure S25. Synthesis of IOH (a) from isoprene and (b) the non-nucleophilic bases used to isomerize 2-methyl-2-vinyloxirane (MVO) to IOH. Two intermediate molecules are synthesized to give IOH. First a bromohydrin is formed to give 1-bromo-2-methylbut-3-en-2-ol (IBrOH) and second the intramolecular base catalyzed ring closure of IBrOH to give MVO. Several methods are reported in literature to synthesize IOH.[7,8,9,10,11] Of the schemes available, the general reaction pathway in Figure S25 is the most frequently used in literature,[7,8] utilizing the fewest steps and common reagents.

Using either the in house synthesized or purchased MVO, the oxirane isomerization was performed to give IOH. The isomerization of MVO to IOH is accomplished by the addition of a strong, non-nucleophilic base that eliminates the β-hydrogen to the oxirane, allowing for the subsequent ring opening.[12] The resulting alkoxide is then quenched by transferring the basic solution to an aqueous acid (HCl) with the desired IOH as the product. Two bases from literature were investigated: lithium bis(trimethylsilyl)amide (LiHMDS)[8] and lithium diisopropylamide (LDA).[7] In both systems MVO was completely converted, but the LiHMDS base system had higher conversion to IOH (approx. 100%) than the LDA system (65%). Purification of the IOH from the crude reaction solutions proved difficult when either base was used. The crude solution of the LiHMDS promoted reaction has significant hexamethyldisilazane (HMDS) byproduct present. HMDS has a similar boiling point (126 °C)[13] to IOH (126 °C),[14] resulting in HMDS coming over with the IOH during distillation. Furthermore, IOH and HMDS appear to react during the distillation as evidenced by an observed chemical shift in the ^{1}H NMR spectrum as compared to that of in the expected product. A majority of the HMDS can be separated by column chromatography, but a significant amount of HMDS still remains in the IOH (Figure S26d). Pure IOH can be obtained from the distillation of IOH from the LDA promoted reaction solution as the diisopropylamine byproduct has a significantly different boiling point (84 °C)[13] from the IOH product (Figure S26e). The yield in the distillation process is low (ca. 20%) as the IOH reacts while heated to form side products such as oligomers and Diels–Alder dimers.

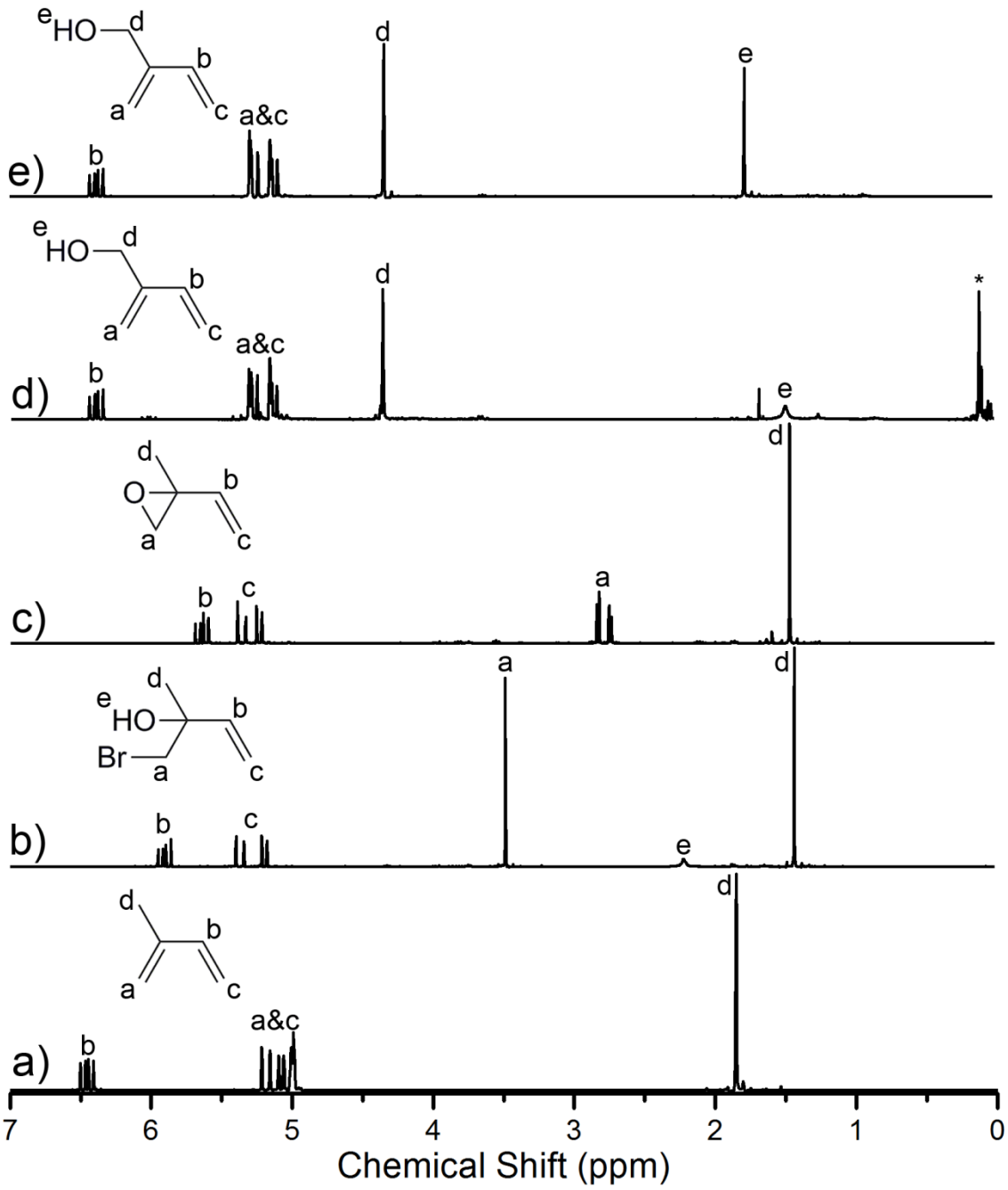

Figure S26. ^{1}H NMR spectra ($CDCl_3$) and peak assignments of (a) isoprene, (b) IBrOH, (c) MVO, (d) IOH synthesized using LiHMDS (asterisk marks residual HMDS), and (e) IOH synthesized using LDA. Synthesis of IOH from MVO using LDA with subsequent distillation leads to a product with minimal impurities.

References

[1] M. Nomura, H. Tobita, K. Suzuki, *Adv. Polym. Sci.* 2005, **175**, 1–128.

[2] I. W. Cheong, C. M. Fellows, R. G. Gilbert, *Polymer* 2004, **45**, 769–781.

[3] A. D. Fotiadou, A. L. Zografos, *Org. Lett.* 2011, **13**, 4592–4595.

[4] J. T. Lai, D. Filla, R. Shea, *Macromolecules* 2002, **35**, 6754–6756.

[5] R. G. Riley, R. M. Silverstein, J. A. Katzenellenbogen, R. S. Lenox, *J. Org. Chem.* 1974, **39**, 1957–1958.

[6] D. S. Germack, K. L. Wooley, *J. Polym. Sci. Part A* 2007, **45**, 4100–4108.

[7] R. G. Riley, R. M. Silverstein, J. A. Katzenellenbogen, R. S. Lenox, *J. Org. Chem.* 1974, **39**, 1957–1958.

[8] Y. Satake, T. Nishikawa, T. Hiramatsu, H. Araki, M. Isobe, *Synthesis* 2010, **12**, 1992–1998.

[9] T. Mandai, H. Yokoyama, T. Miki, H. Fukuda, H. Kobata, M. Kawada, J. Otera, *Chem. Lett.* 1980, 1057–1060.

[10] W. J. Bailey, G. Carpenter, M. E. Hermes, *J. Org. Chem.* 1962, **27**, 1975–1978.

[11] L. Alcaraz, J. J. Harnett, C. Mioskowski, J. P. Martel, T. Le Gall, D.-S. Shin, J. R. Falck, *Tetrahedron Lett.* 1994, **35**, 5449–5452.

[12] J. K. Crandall, M. Apparu, Base-Promoted Isomerizations of Epoxides. In *Organic Reactions*, Vol 29; Dauben, W. G., Ed.; John Wiley & Sons Inc., 1983; pp 345–443.

[13] *CRC Handbook of Chemistry and Physics* [Online]; http://www.hbcpnetbase.com/ (accessed October 21, 2011).

[14] Estimated using *ChemBioDraw Ultra*, Version 12.0.2.1076, CambridgeSoft, 2010.