

**Electronic Supplementary Information (ESI) for
Catalytic synthesis and post polymerization functionalization of conjugated
polyisoprene**

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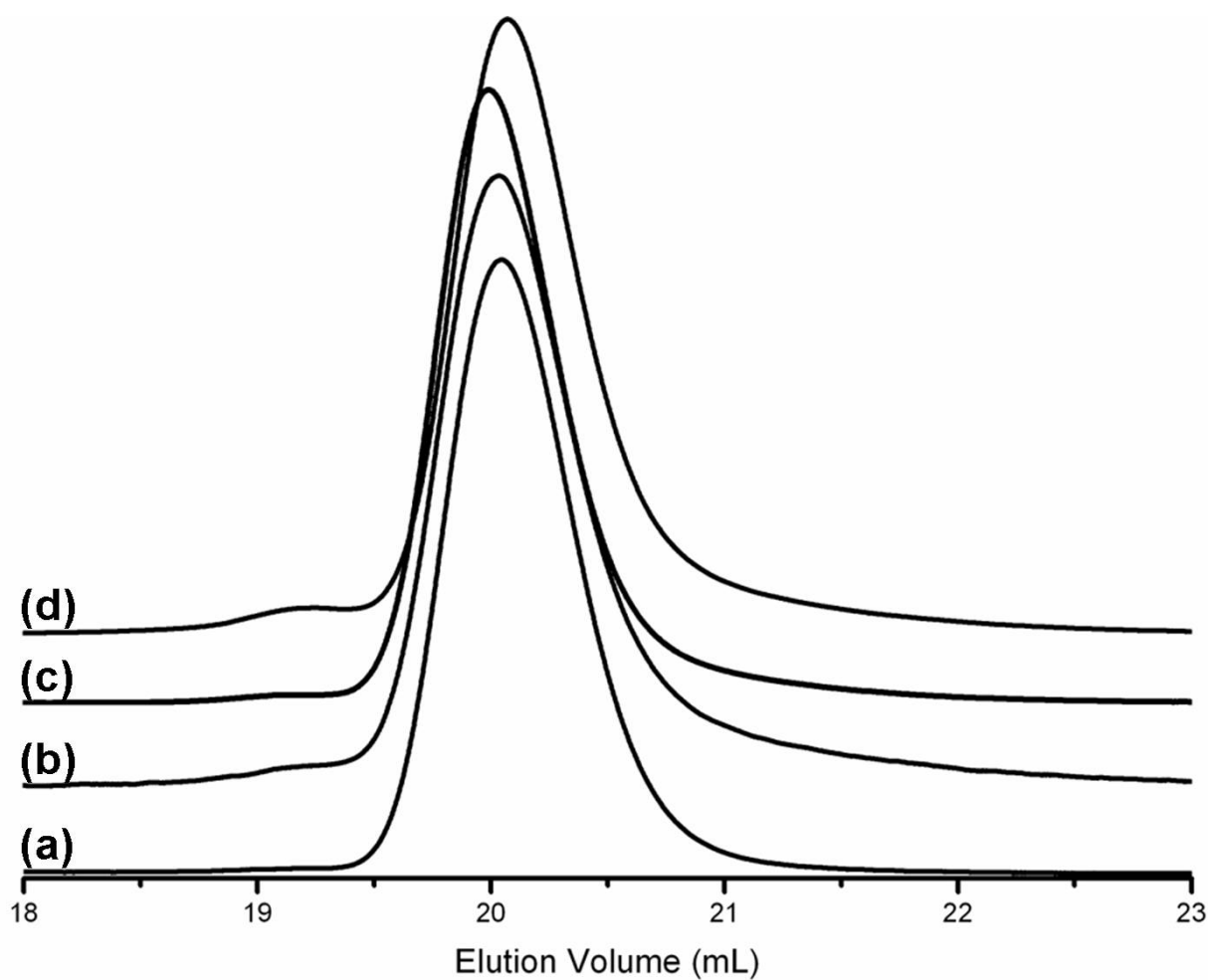


Figure S1. SEC elution curves of (a) PI, (b) CPI – 4.4, (c) CPI-17, and (d) CPI-30. All SEC traces are monomodal with the conjugated polyisoprene (CPI) products having a small high molecular weight shoulder due to coupling and a slight tail due to degradation – likely oxidative degradation.

Table S1. Reaction conditions and results for the synthesis of conjugated polycyclooctadiene (CPCOD)^a

Sample Designation ^b	Reaction Temperature (°C)	Reaction Time (h)	Percent C=C Conjugated (%) ^c	M _n (kg/mol) ^d	PDI ^d
PCOD				10	1.79
CPCOD-12	60	44	32	14	1.79
CPCOD-23	75	160	61	15	2.19

^aPolycyclooctadiene (PCOD) was synthesized by a previously discussed method¹ and was conjugated using the following procedure. Specifically, PCOD (1 g) was dissolved in benzene (5.7 mL) to which RuHCl(CO)(PPh₃)₃ (28.8 mg) was added to create a slurry. The slurry was transferred to a 10 mL side arm pressure vessel where it was degassed by three freeze-pump-thaw cycles and backfilled with 3 psig argon. The vessel was placed in a 75 °C oil bath to react for 160 h. Reaction time and temperature were varied for subsequent conjugations. After reaction, the solvent was removed by vacuum at ambient temperature. Once the raw product was dry, the catalyst was removed by bringing the evacuated vessel into a nitrogen atmosphere dry box and dissolving the product in 11 mL of dry CH₂Cl₂. To the solution P(CH₂OH)₃ (37 mg) was added and the vessel was removed from the dry box to stir for several days. The cloudy solution was then passed through a silica gel column with CH₂Cl₂ as the mobile phase to collect the product. To the solution, 7.3 mg BHT was added and the solution was concentrated by rotary evaporation and concentrated by blowing N₂ before drying under vacuum to give the final product. ^bSample designation CPCOD-#### where #### indicates the number of *E,E* conjugated dienes per polymer chain. ^cCalculated from ¹H NMR spectroscopy. ^dCalculated from size exclusion chromatography calibrated with polystyrene standards.

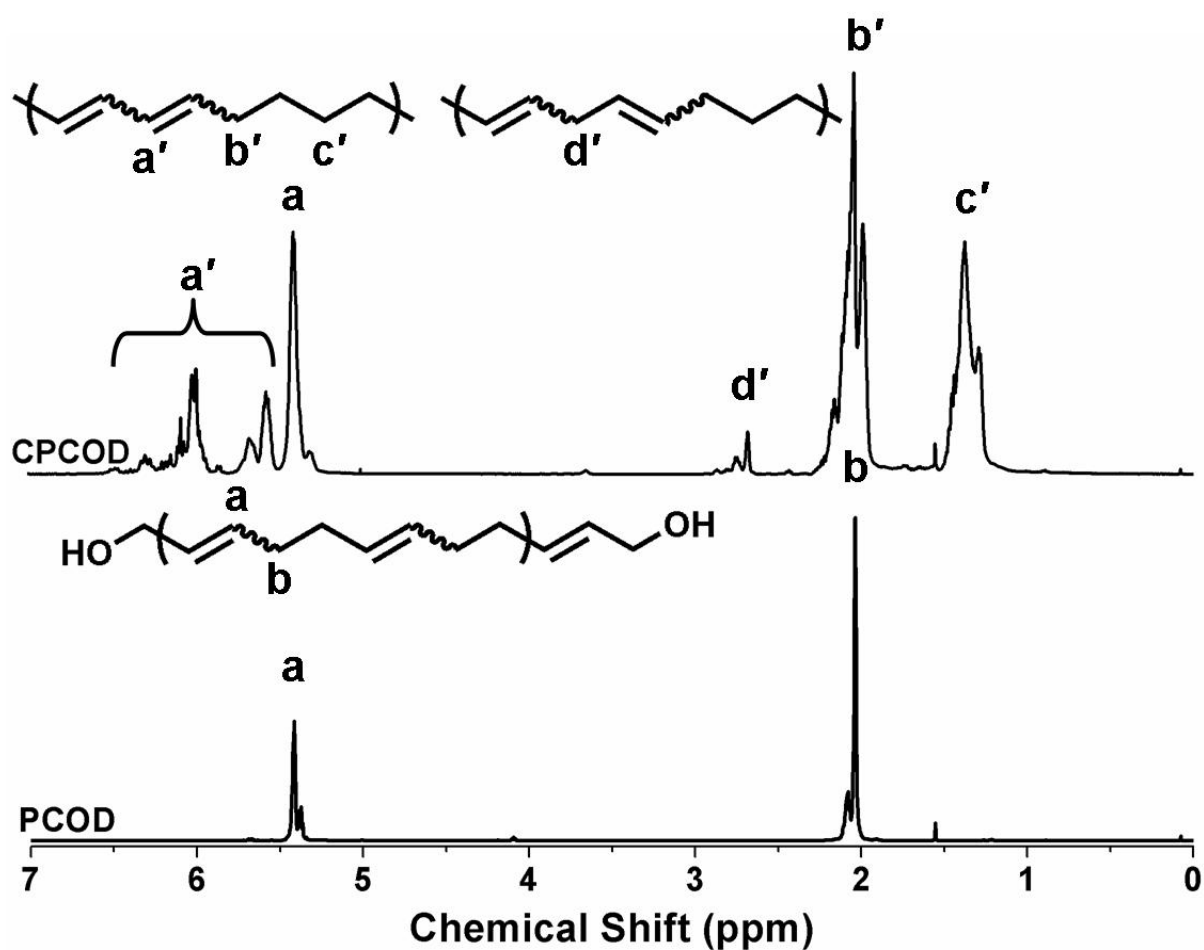


Figure S2. ¹H NMR spectra of PCOD and CPCOD-23 with peak assignments. Peak assignments labeled with a prime (') belong to protons in the isomerized double bond systems. Evidence of conjugation is evidenced as the existence of peaks in the 5.5 – 6.5 ppm range, corresponding to the olefinic protons in the conjugated systems. Evidence of the bis-allylic intermediate is also present as peaks in the 2.5 – 3.0 ppm range. The formation of small segments of polyethylene as a result of the isomerization results in the broad peaks in the 1.0 – 1.5 ppm range of the CPCOD-23 spectrum.

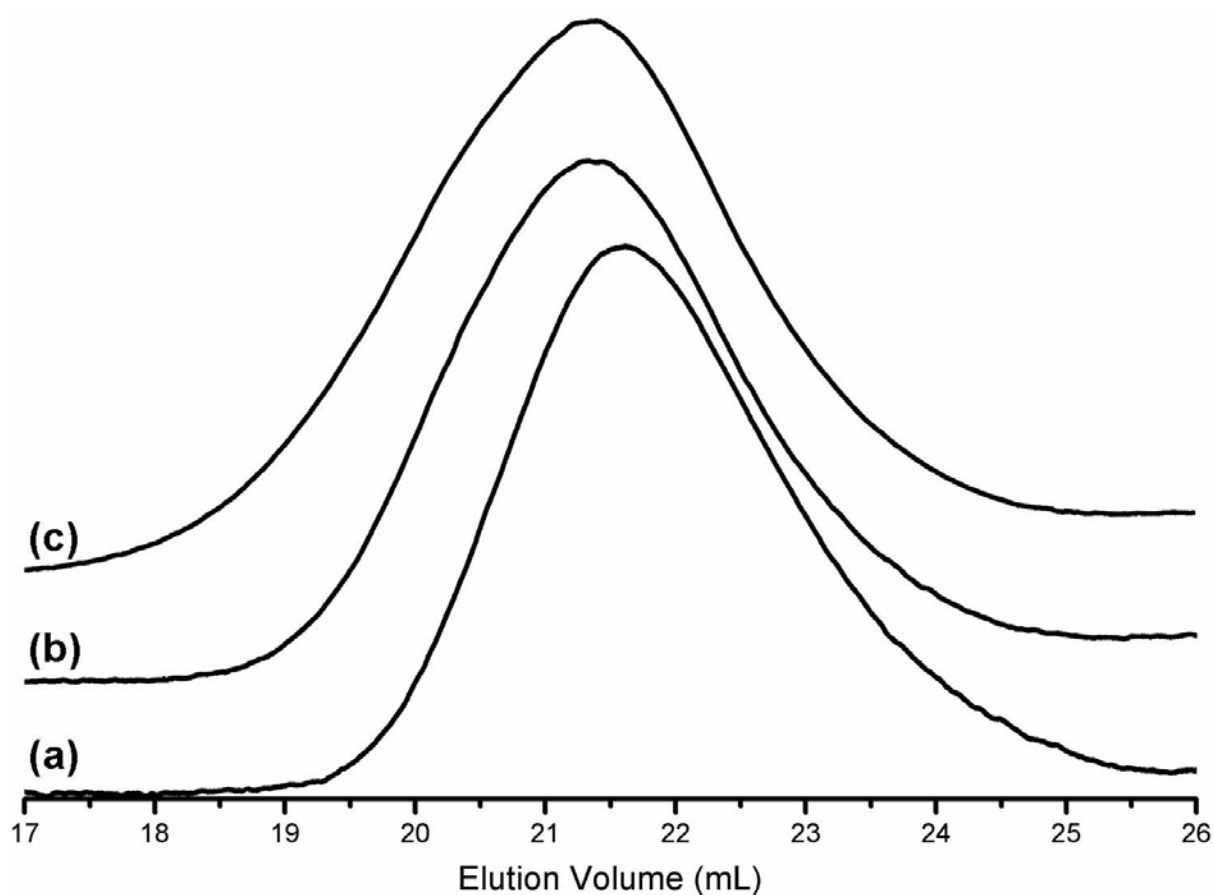


Figure S3. SEC elution curves of (a) PCOD, (b) CPCOD-12, and (c) CPCOD-23. Increasing the degree of conjugation in CPCOD shifts the elution curve to lower elution volume – possibly due to coupling of the CPCOD or a change in the hydrodynamic radius as a result of the change in chemical structure.

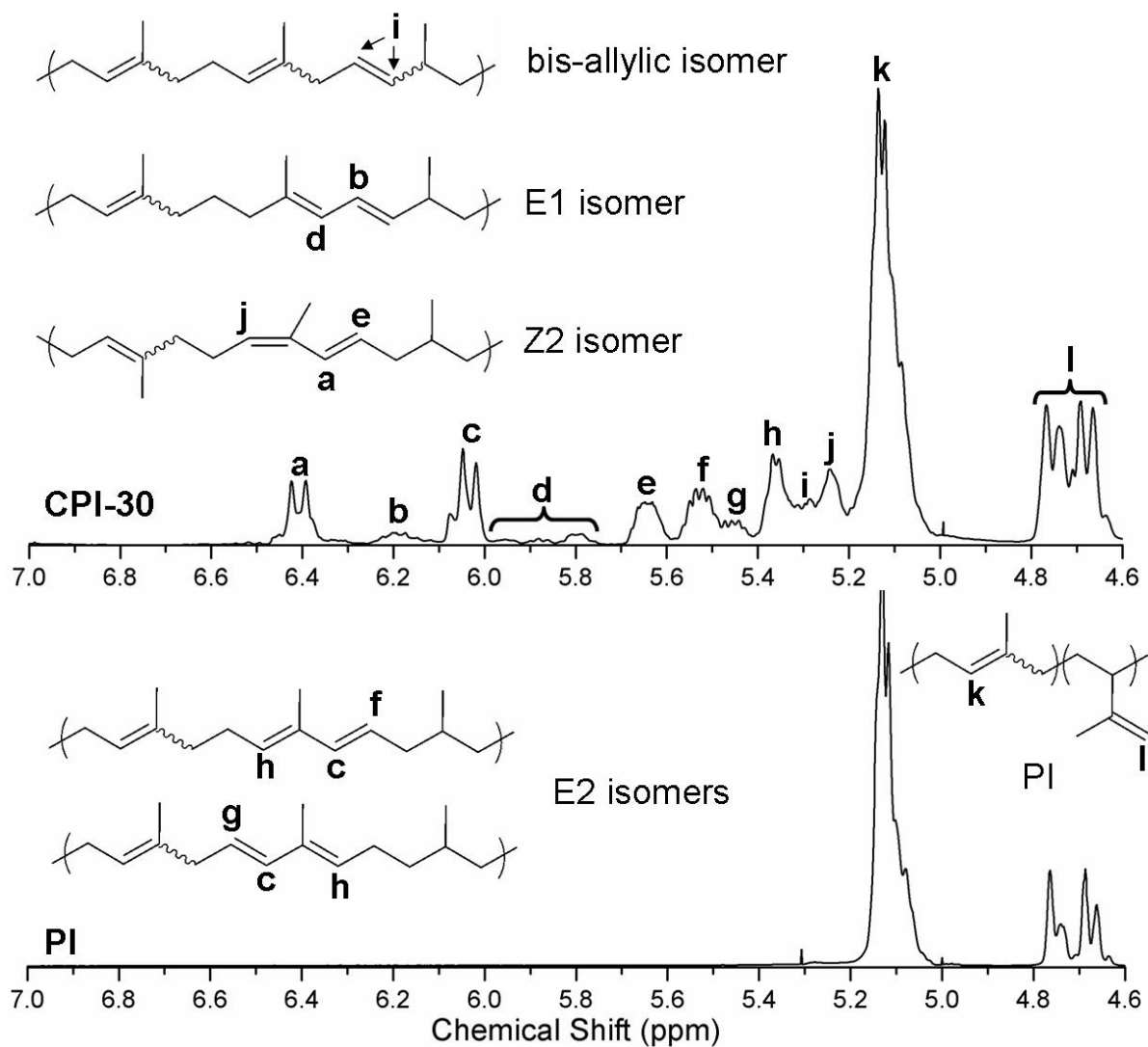


Figure S4. Detailed ^1H NMR spectra and peak assignments for CPI-30 and PI in the 7.0 – 4.6 ppm range. Peaks belonging to both the original PI polymer and CPI are present. Literature references with ^1H NMR assignments for small molecules with similar conjugated diene structures were used to determine the peak assignments and presence of CPI isomers.^{2,3,4} The chemical shifts (δ) for the given isomers: bis-allylic isomers 5.23 (m, **i**); E1 isomer 6.24 – 6.09 (br s, **b**), 5.96 – 5.72 (br m, **d**); Z2 isomer 6.41 (d, $J = 14.8$ Hz, **a**), 5.63 (br m, **e**), 5.23 (s, **j**); E2 isomers 6.05 (d, $J = 12.9$ Hz, **c**), 6.02 (d, $J = 14.7$ Hz, **c**), 5.51 (m, **f**), 5.45 (m, **g**), 5.35 (d, $J = 7.2$ Hz, **h**).

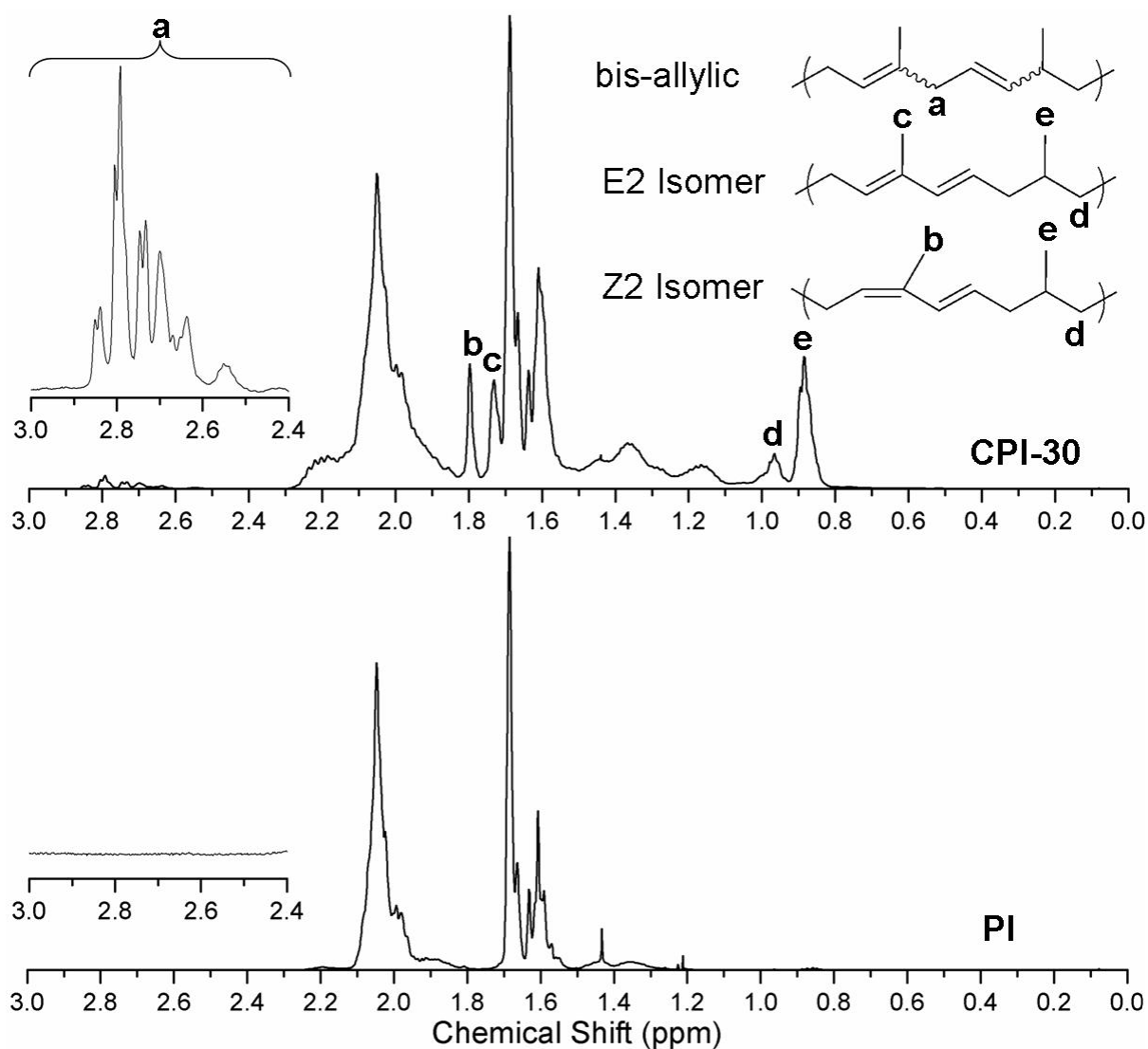


Figure S5. Detailed ¹H NMR spectra and peak assignments for CPI-30 and PI in the 3.0 – 0.0 ppm range. Peaks belonging to both the original PI polymer and CPI are present. Literature references with ¹H NMR assignments for small molecules with similar conjugated diene structures were used to determine the peak assignments and presence of CPI isomers.^{2,3,4} The chemical shifts (δ) for the given isomers: bis-allylic isomers 2.86 – 2.48 (m, **a**), peak at 2.79 (d, $J = 6.9$ Hz) appears to belong to bis-allylic protons adjacent to E2 isomers as the peak disappears during Diels-Alder reactions; Z2 isomer 1.79 (s, **b**); E2 isomers 1.72 (s, **c**); 0.96 (br m, **d**); 0.87 (br m, **e**).

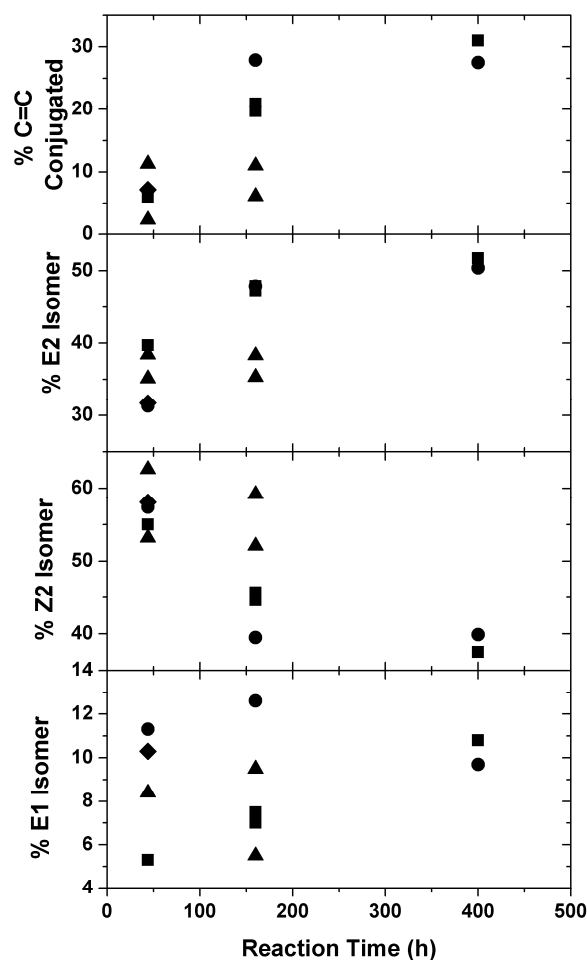


Figure S6. Mole % of total carbon-carbon double bonds conjugated and % of conjugated dienes adopting the three major isomers at various reaction temperatures and times. Temperatures investigated were 60 °C (square), 75 °C (circle), 90 °C (triangle), and 120 °C (diamond). For the 90 °C reaction, multiple runs were conducted at 44 and 160 h to investigate the reproducibility and these runs are indicated by multiple data points. Mole percents were calculated using ^1H NMR spectroscopic analysis on the final products. Generally as reaction time increased the number carbon-carbon double bonds that isomerized to give conjugated dienes increased. At temperatures above 60 °C and 44 h reaction gave high degrees of conjugation, but as the reaction times were increased the attainable degree of conjugation remained the same as that at shorter

reaction times. Examples of this effect can be seen at 90 °C increasing the reaction time from 44 h to 160 h and at 75 °C increasing the reaction time from 160 h to 400 h. Such results suggest that the catalyst become deactivated over the course of the reaction.

The exact cause for deactivation of the catalyst is unclear. The $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ catalyst is stable up to 210 °C in inert atmosphere for several hours as evidenced by its ability to conjugate vegetable oils under these conditions – so thermal degradation is unlikely at the temperatures investigated.^{5,6} For the reactions performed at 90 and 120 °C, the color of the reaction mixture changed from yellow/orange to green over the course of the reaction. Also, small dark insoluble particles were also observed in these solutions. The change in color and formation of solid precipitate corresponded with the decreased activity of the catalyst (i.e. lower conversion to conjugated double bonds). Such a color change is consistent with the catalyst becoming inactivated by reaction with oxygen;^{7,8} although the reaction mixture was degassed, the degassing procedure may not have removed all the oxygen from the system. Another possible cause of the observed color change is that the Ru-H species could have been converted to ruthenium alkyl, alkyl-alkene, or allylic complexes that may be insoluble in the solvent, explaining the observation of solid particles.^{9,10} Such ruthenium species would be inactive at the temperatures investigated.^{8,10} Thus, both explanations of the color change would be consistent with the deactivated catalyst behavior that was observed. Possibly increasing the reaction temperature further may result in the ruthenium complexes becoming activated once again, yielding an increased rate of conjugation.

The isomer composition of the conjugated dienes changed with both reaction time and temperature. CPI synthesized at reaction temperatures above 75 °C have a higher fraction of E1 isomers compared to those synthesized at 60 °C, presumably due to the increased available

energy to conjugate across the pendent methyl group along the backbone. As the reaction time is increased, the fraction of conjugated dienes as E2 isomers increases as the fraction of conjugated dienes as the Z2 isomer decreases, suggesting that Z2 isomers are being isomerized over time to E2 isomers – the major isomer at short reaction times is Z2 and at longer times it is E2. Previous studies¹¹ have indicated that the RuHCl(CO)(PPh₃)₃ catalyst prefers to isomerize double bonds to the *E* configuration. Initially, the majority of carbon-carbon double bonds in PI are the *Z* isomer, allowing for the initial conjugated dienes to be the Z2 isomer with just one double bond migrating. Over time, the carbon-carbon double bonds will be isomerized to the *E* configuration prior conjugation, resulting in a higher concentration of E2 isomer in the final product at longer reaction times.

Increasing Concentration of Catalyst

Catalyst loading was increased from 1.6×10^{-3} [Ru]/[C=C] to 4.9×10^{-3} [Ru]/[C=C] while keeping all other reaction conditions the same (PI in benzene 0.18 w/v, 60 °C, 44 h). At 60 °C with the increased catalyst concentration not all the catalyst went into solution as evidenced by the solution being cloudy and brown as opposed to the yellow color observed for fully solubilized catalyst. Analysis of the product indicated that the conversion of carbon-carbon double bonds to conjugated dienes was 4 %. The lower catalyst loading product synthesized at the same temperature and over the same reaction time had 6 % conversion of the carbon-carbon double bonds into conjugated dienes. Presumably, the limited solubility of the catalyst in benzene leads to the similar conversions in both systems. The result also suggests that the benzene solution at 60 °C is saturated in catalyst around 1.6×10^{-3} [Ru]/[C=C] (4.0 mg catalyst/mL benzene).

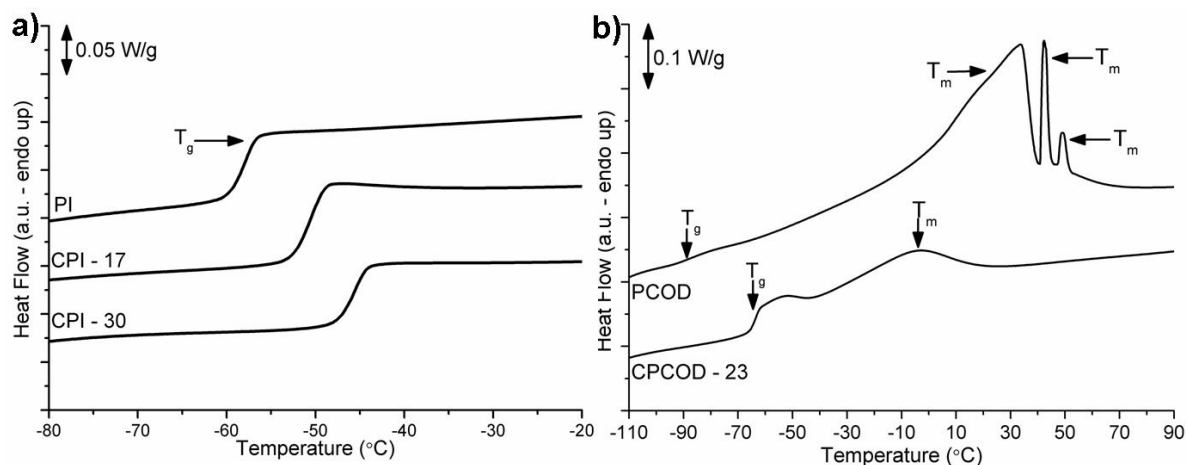


Figure S7. Differential scanning calorimetry (DSC) thermal traces for (a) select CPI/PIs and (b) select PCOD/CPCODs. DSC analysis was performed on a Texas Instruments TA Q1000 calorimeter at a 10 °C/min temperature ramp rate. PI/CPI samples were cycled between -90 and 30 °C with two heating and one cooling cycle. PCOD/CPCOD samples were cycled between -120 and 100 °C with two heating and cooling cycle. The DSC traces given for all samples are of the second heating ramp. The glass transition temperature (T_g) of the CPIs increases with increasing degrees of conjugation, indicating a stiffening of the polymer chain due to the introduction of the more rigid conjugated diene systems. Similarly, the T_g of CPCOD was higher than that of the original PCOD. The PCOD is semicrystalline as indicated by the multiple melting transition temperatures (T_m). In the CPCOD, the relative intensity of the melting transition decreased as well as the T_m . The decrease suggests that the conjugated dienes impede the ability of CPCOD chains to crystallize and shorten the segments of the polymer chain that are able to crystallize. The decreased crystallinity of the CPCOD was further evidenced by the observed properties of the polymer – the original PCOD was a waxy solid at room temperature while the CPCOD was a viscous liquid.

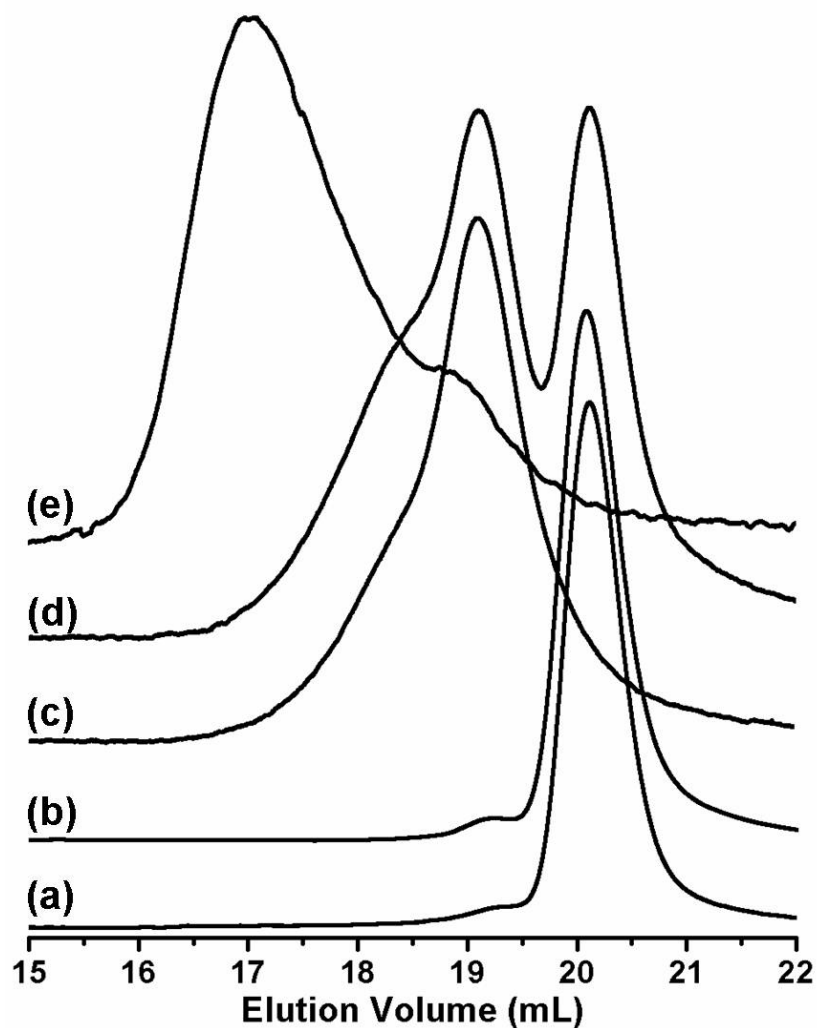


Figure S8. SEC elution curves of (a) PI, (b) CPI-17, (c) HEMI-PLLA, (d) control blend of HEMI-PLLA and PI, and (e) reactive blend of HEMI-PLLA and CPI-17. In the reactive blend (e) the HEMI end group reacted with the conjugated double bonds of CPI-17 to produce a graft copolymer as evidenced by the shift to lower elution volume while the HEMI-PLLA and PI blend (d) did not. There is a small shoulder in the reactive blend (e) in the region where the HEMI-PLLA was initially, suggesting that some of the HEMI-PLLA did not react with the CPI. ^1H NMR spectroscopic analysis suggests that all the HEMI end groups and CPI reacted, though

some unreacted HEMI-PLLA could be present and not visible in spectroscopy due to its low concentration.

Experimental Details for HEMI-PLLA coupling reactions to CPI and PI.

HEMI-PLLA was synthesized following a previously reported procedure (67 kg/mol).¹¹ CPI-17 and PI are the same polymers mentioned in the body of the paper. The coupling reaction was performed as follows. BHT (2.2 mg, 1 wt % to CPI-17/PI) and either CPI-17 or PI (22.5 mg) were dissolved in 6 mL of HPLC grade toluene in a 25 mL round bottom flask. Solid HEMI-PLLA (200 mg) was added to the flask which was then fitted with a condenser and placed into a 110 °C oil bath at which time the HEMI-PLLA went into solution. After 139 h the flasks were removed from heat and allowed to cool to ambient temperature. The solutions were diluted with CH₂Cl₂ and were subsequently precipitated in 10X excess methanol.

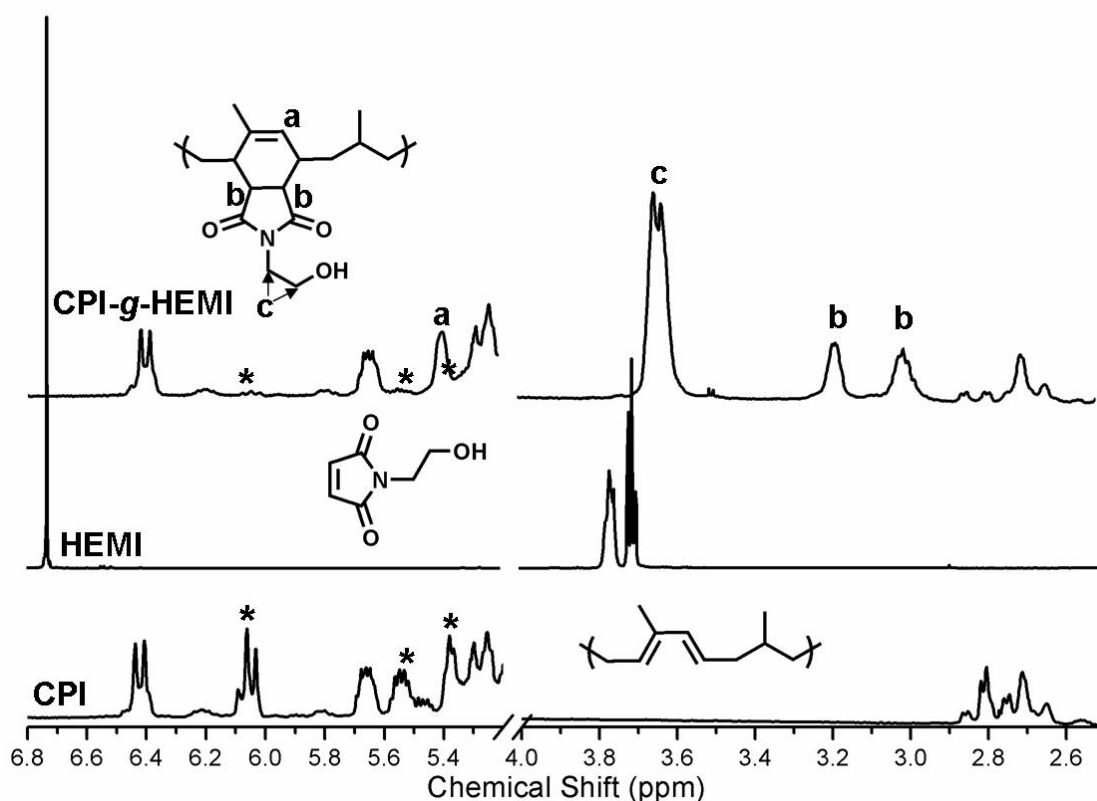


Figure S9. ¹H NMR spectra of the original CPI-17, N-2-hydroxyethyl maleimide (HEMI), and the product of HEMI grafting to CPI (CPI-g-HEMI). The peak corresponding to the vinyl protons of HEMI is no longer present and the peaks belonging to the methylene protons of HEMI have shifted up field, indicating that HEMI reacted. Peaks at chemical shifts corresponding to the E2 isomer of CPI-17 are marked with asterisks. The intensities of the E2 peaks reduce upon reaction with HEMI while the peaks associated with the Z2 and E1 isomers remain at relatively constant intensities. Conversions of each isomer were calculated to be 92.7 % for the E2 isomer, 9.6 % for the E1 isomer, and -3.8 % for the Z2 isomer, using the peak integrations in ¹H NMR spectroscopy for each isomer, which confirms that the E2 isomer is the most reactive. The peak belonging to bis-allylic protons at 2.8 ppm reduced in intensity during the reaction, suggesting that conjugated dienes adjacent to a bis-allylic proton reacted. Presumably, these bis-allylic protons are adjacent to the E2 isomer system.

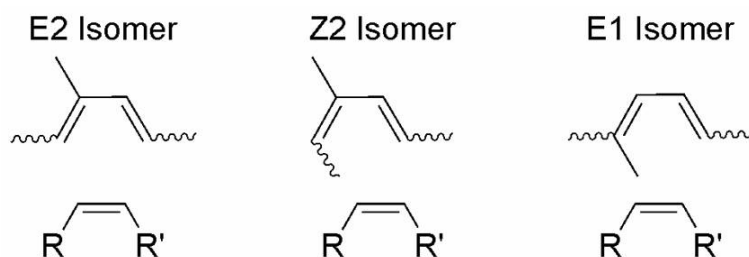


Figure S10. Conformations of CPI isomers required for Diels-Alder addition. The conjugated dienes must adopt the *s-cis* conformation for the Diels-Alder reaction to proceed.¹² When the E2 isomer adopts the required conformation the reaction site is open and unhindered, therefore; the Diels-Alder reaction proceeds as observed experimentally (Figure S9). Conversely, when the Z2 isomer adopts the conformation, the polymer backbone extends into the reaction site hindering the addition. Similarly, when the E1 isomer adopts the conformation, the methyl group extends in the reaction site. The methyl group in the E1 case should provide less hindrance than the polymer chain in the Z2 case and consequently a Diels-Alder reaction would be more apt to occur to the E1 isomer. The less hindrance of the E1 isomer may explain why small molecules react with it to some extent (Figure S9).

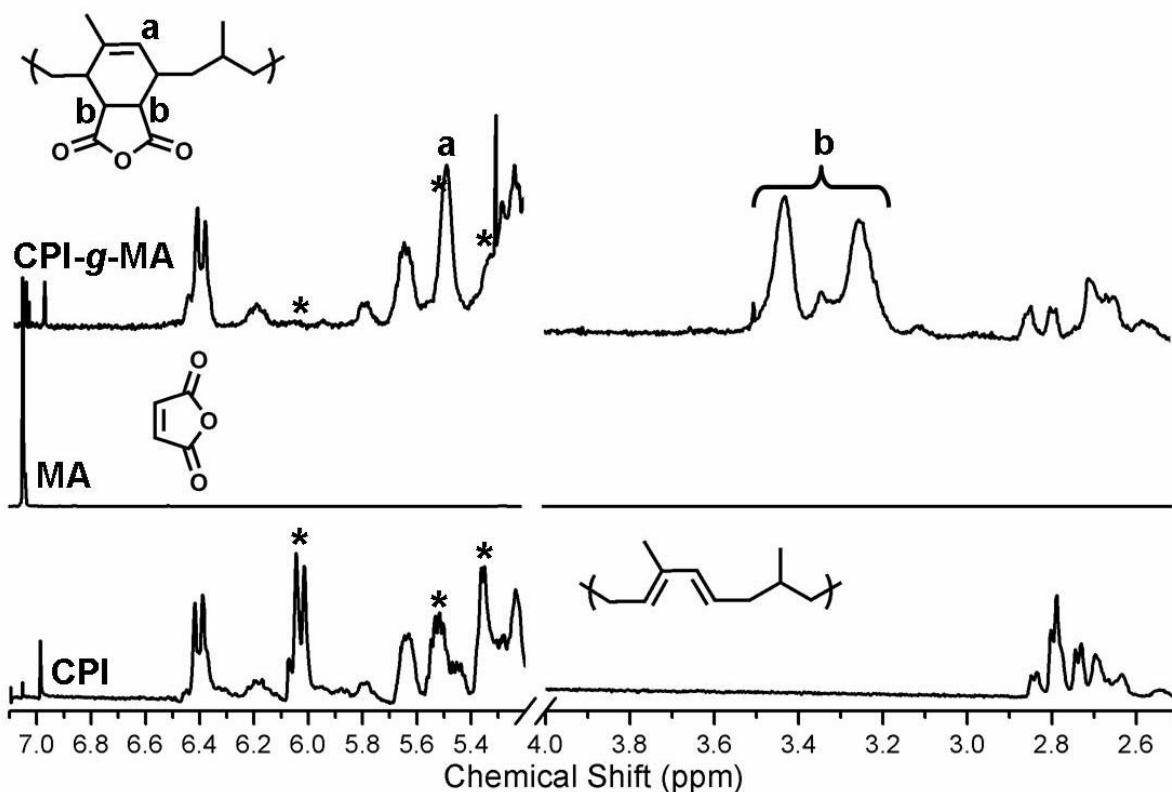


Figure S11. ¹H NMR spectra of CPI-30, maleic anhydride (MA), and the product of MA grafting to CPI-30 (CPI-g-MA). Asterisks mark the peaks associated with the E2 isomer in the original CPI spectrum and the where the peaks should be in the CPI-g-MA product spectrum. As with the HEMI/CPI reaction, MA predominately reacts with the E2 isomer of CPI-30 with complete conversion of the E2 isomer, 34.1 % conversion of the E1 isomer, and 5.7 % conversion of the Z2 isomer. Peaks labeled **a** and **b** on the product ¹H NMR spectrum indicate that MA did react to produce a bicyclic compound as shown. The fact that more than two peaks in the 3.0 – 3.5 ppm region are present may indicate that different isomers of the product may exist.

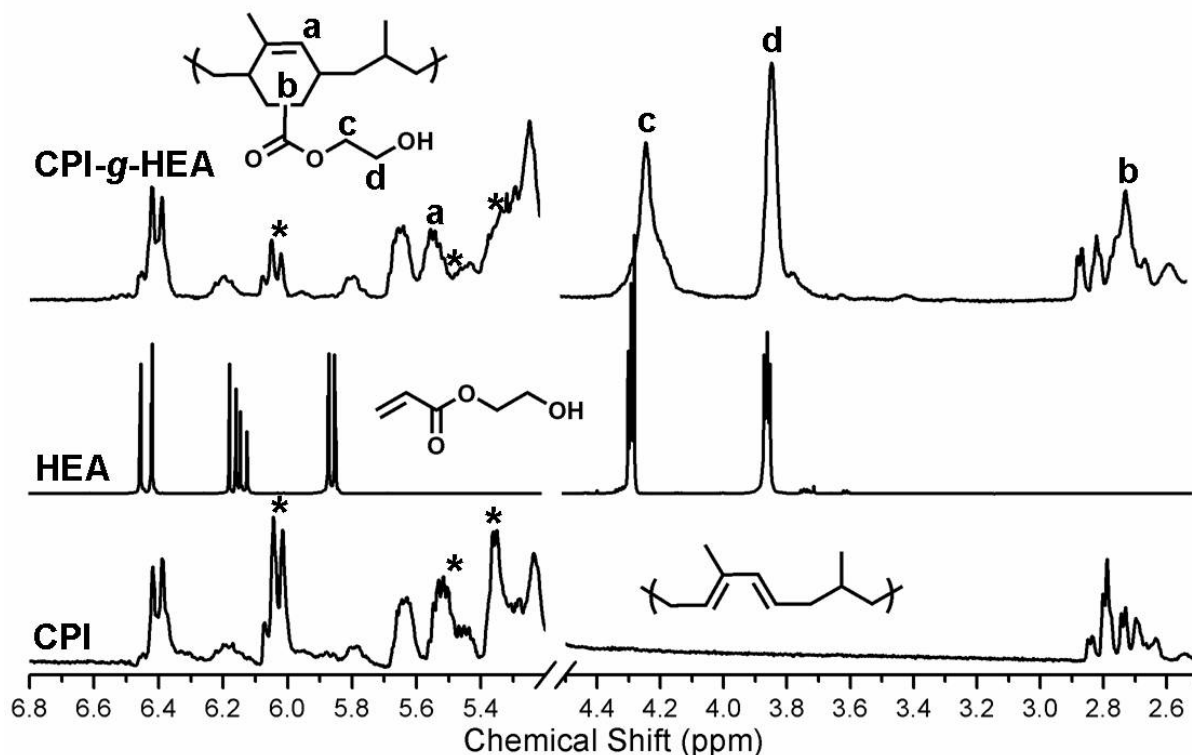


Figure S12. ¹H NMR spectra of CPI-30, 2-hydroxyethyl acrylate (HEA), and the reaction product of HEA and CPI-30 (CPI-g-HEA) after precipitation in MeOH. Asterisks mark the peaks associated with the E2 isomer in the original CPI spectrum and where these peaks should be in the CPI-g-HEA product spectrum. The peaks labeled **c** and **d** in the spectrum of the product belong to the methylene protons of HEA grafted to CPI. Since these peaks have shifted slightly from pure HEA and remain after precipitation in MeOH (HEA is soluble in MeOH), the peaks likely belong to HEA grafted to CPI. The formation of the peaks labeled **a** and **b** also corroborate the formation of CPI-g-HEA, corresponding to protons in the product. The HEA predominately reacted with the E2 isomer of CPI. CPI conversions were 82.5 % for the E2 isomer, 19.0 % for the E1 isomer, and 7.2 % for the Z2 isomer. Conversion of the HEA was estimated to be 86.7 %.

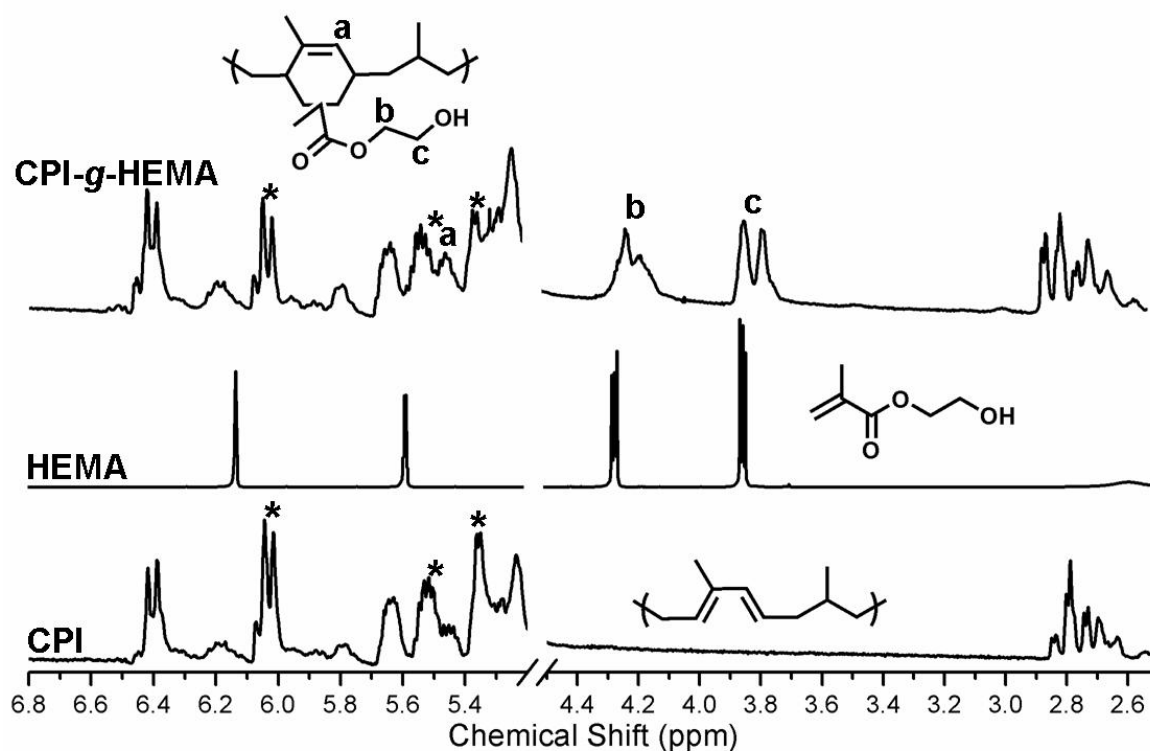


Figure S13. ^1H NMR spectra of CPI-30, 2-hydroxyethyl methacrylate (HEMA), and the reaction product of HEMA and CPI-30 (CPI-g-HEMA) after precipitation in MeOH. Asterisks mark the peaks associated with the E2 isomer in the original CPI spectrum and the where the peaks should be in the CPI-g-HEMA product spectrum. Subjectively, the peaks corresponding to the E2 isomer decrease in intensity. The apparent conversion of conjugated dienes were 51.6 % for E2, 0 % for E1, and 11.7 % for the Z2 isomers as calculated from ^1H NMR spectroscopy integration values. The methylene peaks belonging to the product (labeled **b** and **c**) shifted from the original monomer and remained after precipitation in MeOH, suggesting that they reacted with CPI. The two sets of peaks for each set of methylene protons may be due to both of the possible isomers forming during the reaction. The peak labeled **a**, though in the same region as a peak belonging to CPI, is slightly shifted and higher intensity than the peak present in the original CPI, indicating that it probably belongs to the product as assigned.

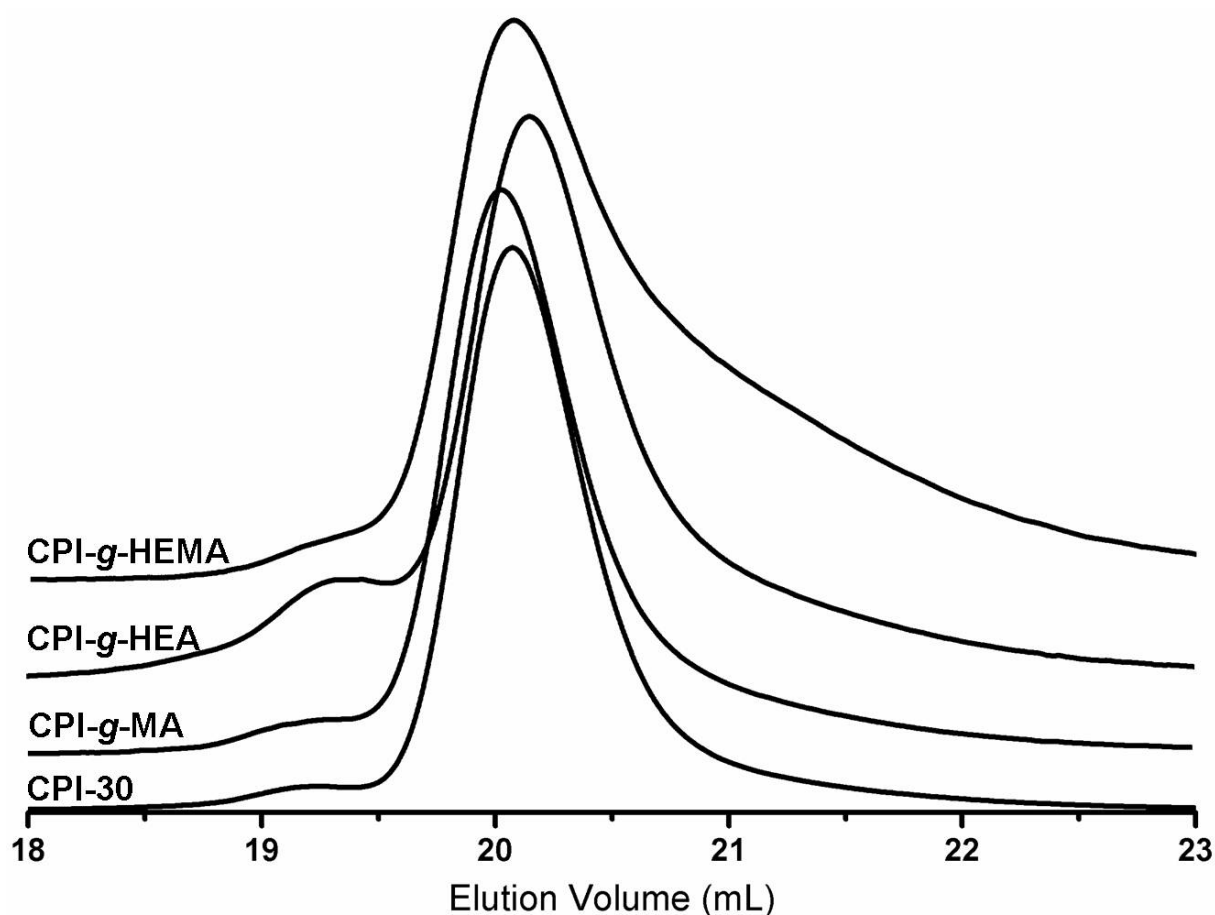


Figure S14. SEC elution curves of the resulting polymer after small molecule coupling reactions to CPI-30. Grafting MA to CPI-30 gave a polymer (CPI-g-MA) with a similar SEC trace as the original polymer. Grafting either HEA or HEMA to CPI-30 (CPI-g-HEA and CPI-g-HEMA respectively) resulted in broadened SEC traces as compared to the original polymer. The broadened distributions are likely due to both oxidative coupling (lower elution volume shoulder) and degradation (higher elution volume tail). CPI-g-HEA and CPI-g-HEMA were synthesized at higher temperatures than CPI-g-MA, presumably the higher temperature and longer couplings reactions would allow for more oxidative reactions and degradation to occur than at the lower temperatures, accounting for the difference between the systems.

Control Coupling Reactions

Control coupling reactions between the small molecules and polyisoprene (PI) were conducted to ensure that small molecules were coupling to CPI through a Diels-Alder mechanism and not some other process. If coupling did proceed through a Diels-Alder mechanism, less or no coupling should be observed with PI compared to CPI. Reactions were performed using the same conditions and set up as the reactions with CPI discussed in the main body of the paper. HEMI and MA were heated with PI in toluene at 110 °C for 21 h, afterwards the ^1H NMR spectra were taken of the raw solutions and we observed no peaks corresponding to the reaction products seen in spectra Figure S9 and Figure S11.

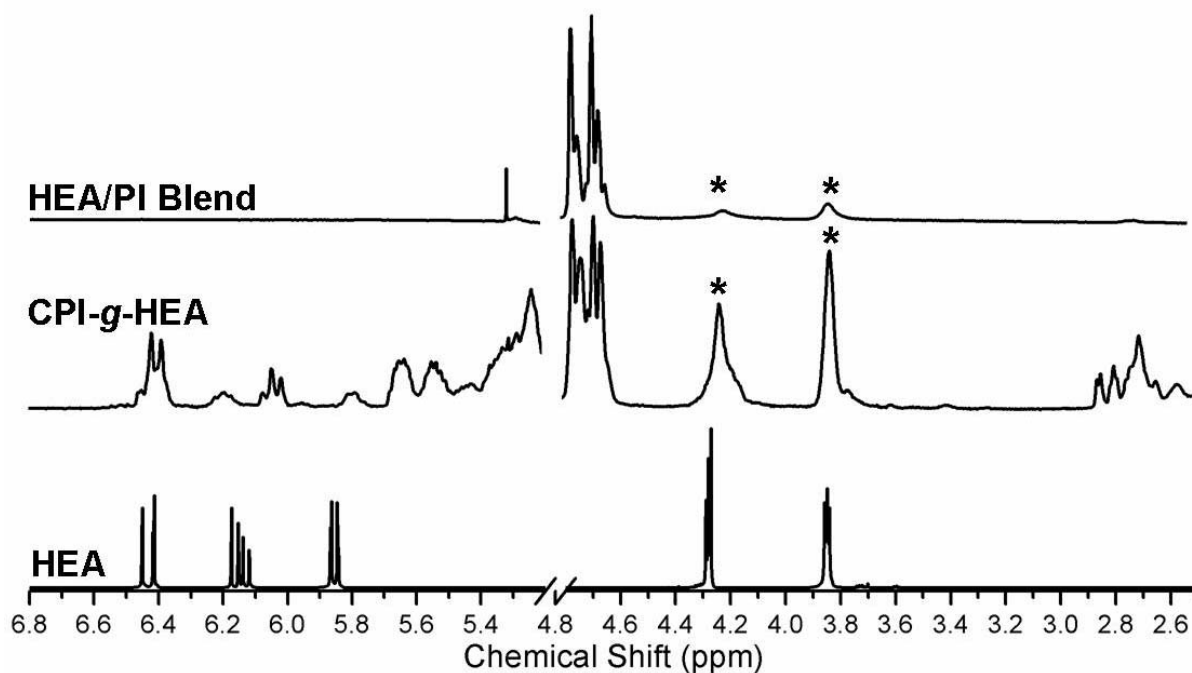


Figure S15. ^1H NMR spectra of product from solution blend of HEA and PI compared to that of CPI-g-HEA. The HEA/PI blend was prepared as follows. PI was dissolved in toluene at 3.3% (w/v) concentration with 30:1 mole ratio of HEA to PI. BHT was added at 5 wt % to the solution. The solution was sealed in a side arm pressure vessel and degassed with three freeze-

pump-thaw cycles. After the third cycle, the vessel was backfilled with 3 psig argon, sealed, and placed in a 160 °C oil bath. After 112 hrs, the vessel was removed, allowed to cool, and precipitated from CH₂Cl₂ 3 times into 10x excess MeOH. The collected product was dried under vacuum at room temperature before analysis. Peaks marked with asterisks indicate HEA that has reacted with PI, making it insoluble in MeOH. The intensity of these peaks is less than the same peaks for the CPI backbone, indicating that some HEA can graft to PI – presumably through a radical mechanism – but not to the same extent as in the CPI/HEA blend which has the potential for a Diels-Alder grafting mechanism. The HEA/PI blend has approximately 5 HEA grafts per PI backbone, while the CPI-g-HEA blend has approximately 26 grafts.

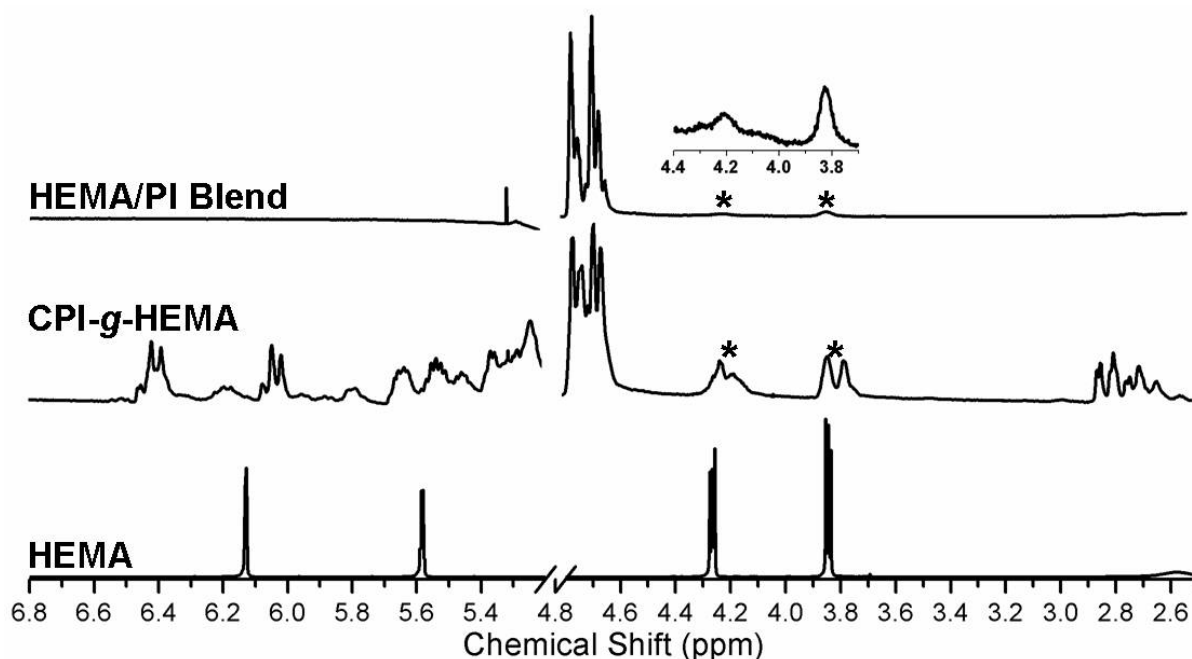


Figure S16. ¹H NMR spectra of product from solution blend of HEMA and PI compared to that of CPI-g-HEMA. The HEMA/PI blend was prepared as follows. PI was dissolved in toluene at 3.3% (w/v) concentration with 30:1 mole ratio of HEMA to PI. BHT was added at 10 wt % to the solution. The solution was sealed in a side arm pressure vessel and degassed with three

freeze-pump-thaw cycles. After the third cycle, the vessel was backfilled with 3 psig argon, sealed, and placed in a 160 °C oil bath. After 168 hrs, the vessel was removed, allowed to cool, and precipitated from CH₂Cl₂ 3 times into 10x excess MeOH. The collected product was dried under vacuum at room temperature before analysis. Peaks marked with asterisks indicate HEMA that has reacted with PI, making it insoluble in MeOH. The intensity of these peaks is less than the same peaks for the CPI backbone, indicating that some HEMA can graft to PI – presumably through a radical mechanism – but not to the same extent as in the CPI/HEMA blend which has the potential for a Diels-Alder grafting mechanism. The HEMA/PI blend has approximately 1 HEMA graft per PI backbone, while the CPI-g-HEMA blend has approximately 8 grafts.

Table S2. Reactions of small molecules with CPCOD-23^a

R ^b	[R]/[E] ^c	Grafts per Polymer ^d	M _n ^e (kg/mol)	PDI ^e
HEMI	0.8	16	19	2.23
MA	0.7	12	17	2.28

^aCoupling reactions were performed at 110 °C over 15 hrs in dry toluene. The solution was degassed by two freeze-pump-thaw cycles and backfilled with 3 psig argon prior to heating. Complete reaction of the small molecules was observed in both reactions. ^bSmall molecule coupled to CPCOD: HEMI = N-2-hydroxyethyl maleimide, MA = maleic anhydride. ^cRatio of moles of small molecule (R) per moles of *E,E* isomer in CPCOD. ^dNumber of grafts of small molecule per polymer chain, found by ¹HNMR spectroscopy. ^eFound from SEC elution curves calibrated with polystyrene standards. Original CPCOD had M_n = 15 kg/mol and PDI = 2.19. Increase in M_n and PDI may be due to polymer-polymer coupling reactions or grafted products having slightly different hydrodynamic radii.

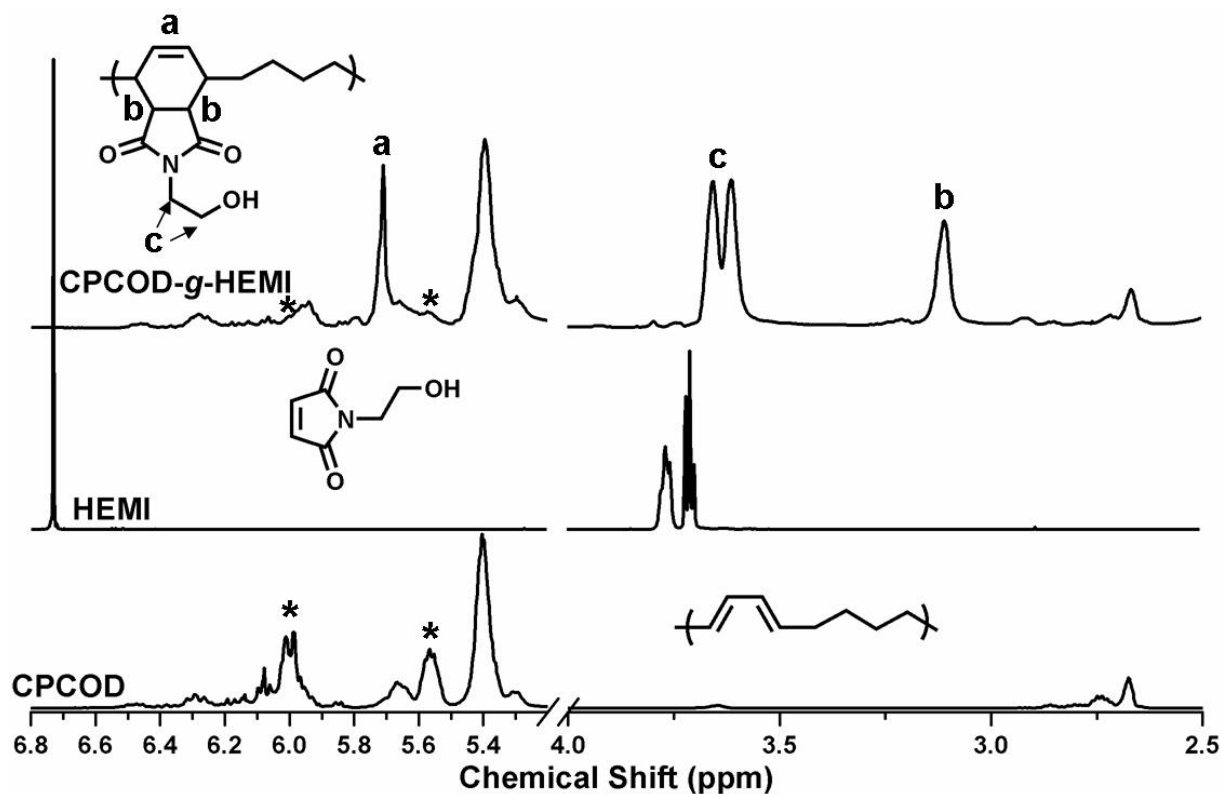


Figure S17. ¹H NMR spectra of CPCOD, HEMI, and the coupling reaction product of CPCOD and HEMI (CPCOD-g-HEMI). Asterisks mark the peaks associated with the *E,E* conjugated isomer of CPCOD in the starting material and final product. Primarily the *E,E* isomer of CPCOD reacts with HEMI. Conversion of the *E,E* isomer was 75 % while the conversion of the *E,Z* isomer was 5 % as determined by ¹H NMR spectroscopy. The peak assignments given further indicate the reaction of HEMI with CPCOD with the methylene peaks of HEMI shifting up field after grafting and the generation of peaks **a** and **b**.

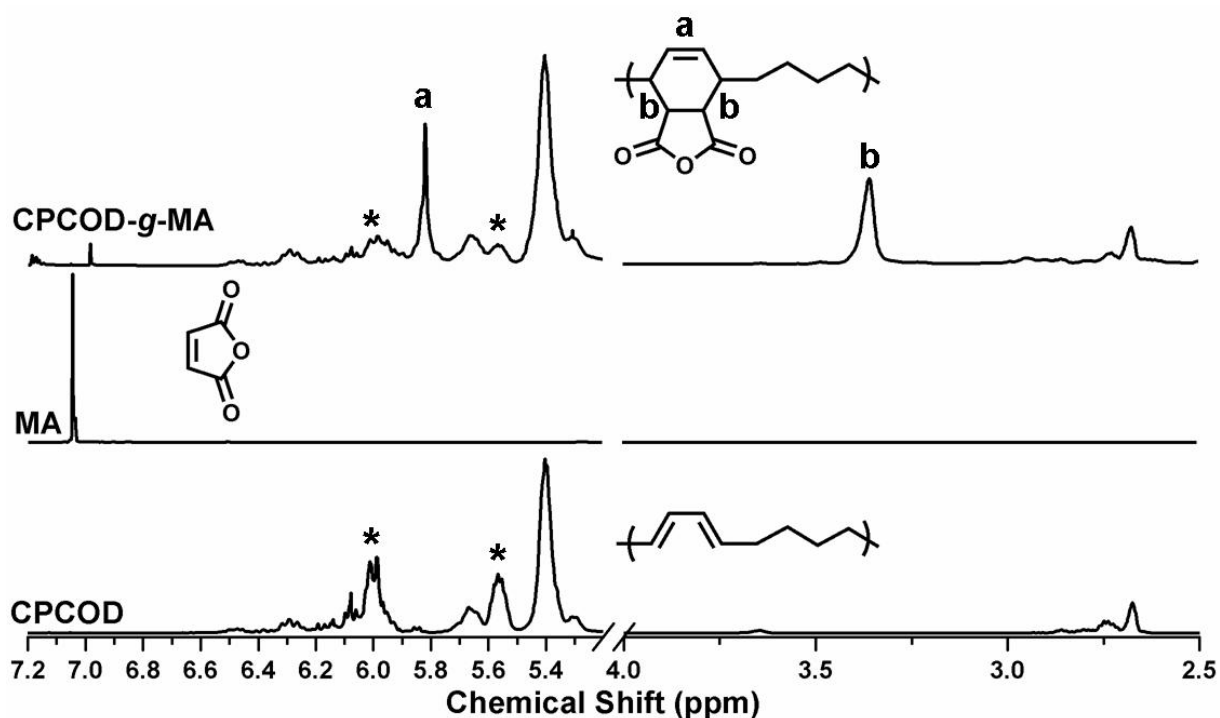


Figure S18. ¹H NMR spectra of CPCOD, MA, and the coupling reaction product of CPCOD and MA (CPCOD-*g*-MA). Asterisks mark the peaks associated with the *E,E* conjugated isomer of CPCOD in the starting material and final product. Primarily the *E,E* isomer of CPCOD reacts with HEMI. Conversion of the *E,E* isomer was 71 % while the conversion of the *E,Z* isomer was 6 % as determined by ¹H NMR spectroscopy. The peak assignments given further indicate the reaction of HEMI with CPCOD with the generation of peaks **a** and **b**.

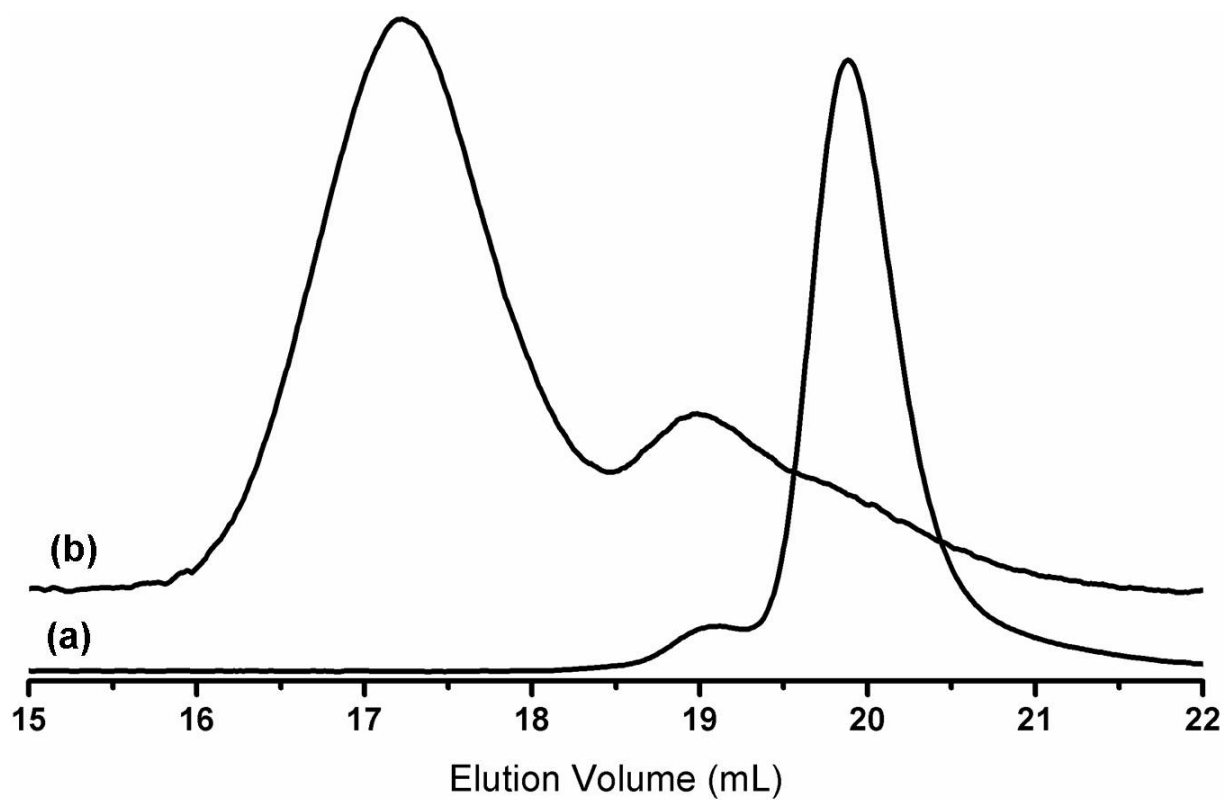


Figure S19. SEC elution curves of (a) CPI-g-HEMI and (b) CPI-g-PLLA synthesized with AlEt₃ catalyst.

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