

Supporting Information

Experimental Section

Materials. All reagents were purchased from Aldrich unless otherwise specified. DPE and PD (polymer grade) as well as polymerization solvents (including Cyclohexane, THF and Toluene) were refluxed over CaH₂ and then distilled under vacuum before use. n-BuLi (1.6 mol/L in n-hexane) and 1,2-DPE were used without further purification. Methanol (99.5%) was sparged with nitrogen for 10 mins to remove dissolved oxygen.

DPE, supplied by YueYang BaLing Petrochemical Chem. Co. Ltd., was distilled from CaH₂ under vacuum and then stored at 0 °C under nitrogen. TP (≈ 93.2%, containing 2.1% (cis)-1,3-pentadiene, 0.5% isoprene, 0.5% 1-pentene, 1.2% cyclopentadiene, 2.5% cyclopentane), CP (≈ 98.2%, 1.8% cyclopentane) are supplied as components from C5 fractions by ShangHai Petrochemical Chem. Co. Ltd.

Purification of 1,3-Pentadiene. The purification of 1,3-pentadiene is a time-consuming procedure because the purity of monomer material is low (< 95%). The main purpose of such a thorough procedure was to eliminate cyclopentadiene and C5 alkynes, which in trace amounts (> 50 ppm) could easily lead to initiator deactivation. The procedure used consisted of the following several steps: (a) the crude materials were exposed overnight under stirring in silver ammonia solution at room temperature; (b) step (a) was repeated at least three times until no visible precipitate was noticed, followed by distillation under an atmosphere of dry nitrogen; (c) the materials were left stirring overnight at room temperature in calcium hydride; (d) stirring was continued overnight at room temperature in n-BuLi (the slow propagation reaction at room temperature allows this relatively long-term exposure), if necessary, (d) was repeated; (e) the final purified monomer was collected and transferred into Schlenk tube under dry nitrogen after distillation. Step (b) was necessary for reducing the concentration of terminal alkyne and cyclopentadiene to the greatest extent. Step (d) was very crucial as it increases the monomer's purity by more than 2% (EP from 94.0% to 95.1%, 1,3-pentadiene mixture from 96.5% to 98.1%) and decreases the percent of the remaining cyclopentadiene and unreacted alkyne to as low as 10 ppm or less, as detected by gas chromatography spectroscopy (GC) on HP-1 capillary column (60 m × 0.32 mm × 0.25 μm).

Anionic Alternating Copolymerization of 1,3-Pentadiene with DPE. All operations were carried out in glove box (H₂O, O₂ < 1 ppm) at room temperature, and the typical synthesis is as follows: 3 mL anhydrous solvent was added to a 10 mL Schlenk tube equipped with a magnetic stir bar at room temperature using 5000 μL pipette. The measured amount of initiator was then supplied to this solution with 200 μL pipette. To start the polymerization, the purified [M₁]/[M₂] comonomers with varying feeding ratios (wt % = 10% ~ 15%) were introduced to this solution, and the Schlenk tube was transferred from glove box to oil bath at setting temperature. After the polymerization, the living polymerization was terminated by adding a few drops of degassed MeOH, followed by transferring the solution to a 10 mL centrifuge tube. The solution was washed several times by a large volume of MeOH to precipitate out the polymer. The separated product was dried under vacuum at 40 °C for 48 hrs. To investigate the kinetics of 1,3-pentadiene copolymerization, the polymerization mixture was needed to stand for a prescribed polymerization time and quenched with degassed MeOH. All conversions were determined by weighting capacity unless otherwise stated.

Measurements. The concentration of impurity in 1,3-pentadiene was measured in a HP gas chromatograph (GC) equipped with FID detector (180 °C) and a HP-1 column at oven temperature 18 ° C ~ 20 ° C (first step: keep the temperature of 20 ° C for 15 mins; second step: increase the temperature to 180 °C at ramp rate of 10 °C/min).

The number-average molecular weights (M_n) and molecular weight distributions (\mathcal{D}) of the polymer samples were determined using a Waters GPC liquid chromatograph (Waters, USA) equipped with gel columns (300 × 7.8 mm). THF was used as the eluent, and the flow rate was 1.0 mL/min at room temperature. A molecular weight calibration was established using polystyrene (PS) standards.

^1H NMR spectra of the polymer samples were recorded with a Varian INOVA-400 spectrometer at room temperature. ^{13}C NMR measurements were performed on a Varian INOVA-400 spectrometer using an "Inverse Gate" (delay time = 5 s) procedure, allowing a quantitative determination. Chemical shifts were recorded in ppm downfield relative to CDCl_3 ($\delta = 7.26$ ppm) and CDCl_3 ($\delta = 77.2$ ppm) for ^1H NMR and ^{13}C NMR as standard, respectively.

T_g and T_m values of polymer samples were measured by DSC using a NETZSCH instrument DSC200F3 apparatus under nitrogen. The polymer samples were first heated to 300 °C, cooled to 25 °C, and then scanned at a rate of 10 °C /min.

Figure caption

Figure S1. Possible substructure generated in the alternating copolymerization of DPE and 1,3-pentadiene.

Figure S2. The FTIR spectrum of the P(DPE-alt-PD) (CS_2 as solvent).

Figure S3. Typical DSC of the P(DPE-alt-TP) at 50 °C.

Figure S4. Typical DSC of the P(DPE-alt-CP) at 50 °C.

Figure S5. Typical DSC of the P(DPE-alt-PD) at 50 °C.

Figure S6. Typical XRD of the P(DPE-alt-CP) at 50 °C.

Figure S7. Typical ^1H NMR spectra of the P(1,2-DPE-co-CP) at 70 °C (1,2-DPE/CP=4/6).

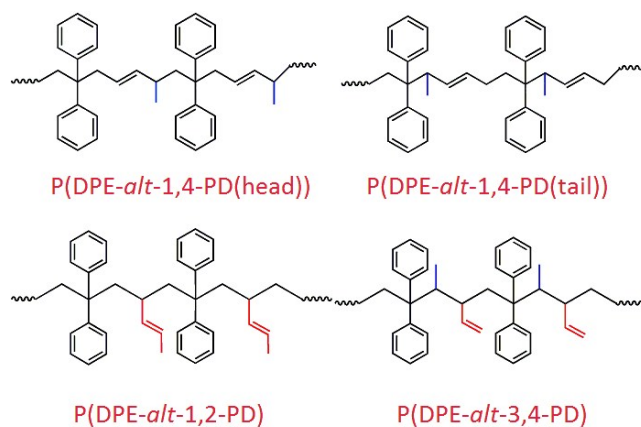


Figure S1. Possible substructure generated in the alternating copolymerization of DPE and 1,3-pentadiene.

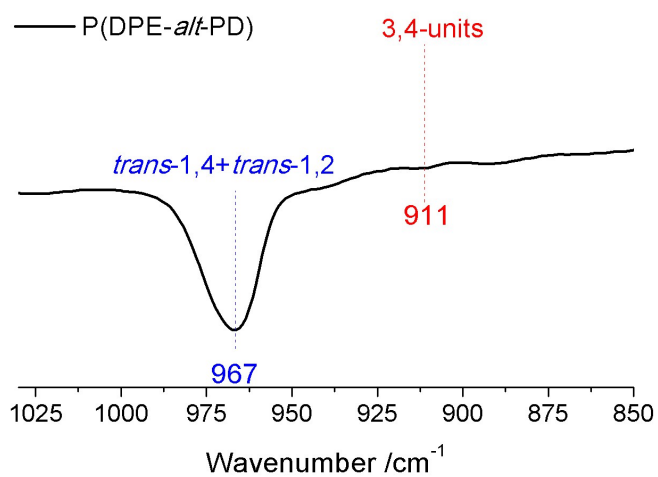


Figure S2. The FTIR spectrum of the P(DPE-*alt*-PD) (CS_2 as solvent).

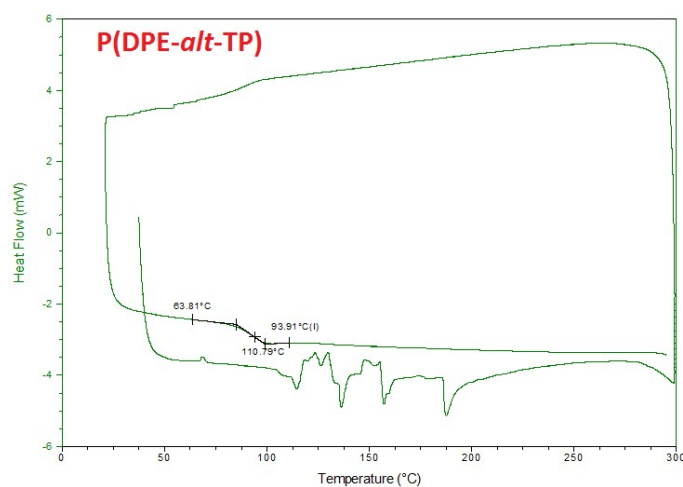


Figure S3. Typical DSC of the P(DPE-*alt*-TP) at 50 °C.

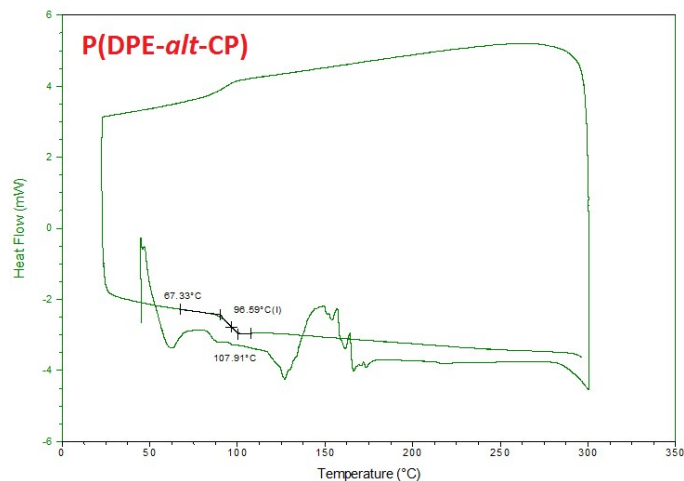


Figure S4. Typical DSC of the P(DPE-alt-CP) at 50 °C.

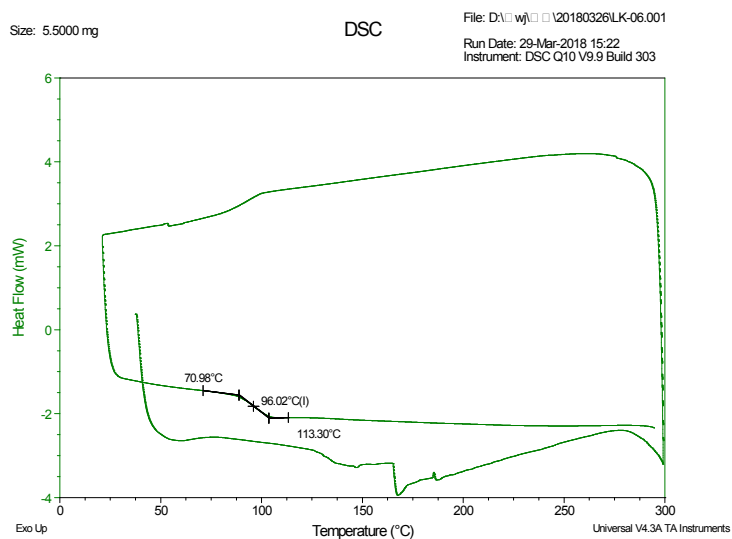


Figure S5. Typical DSC of the P(DPE-alt-PD) at 50 °C.

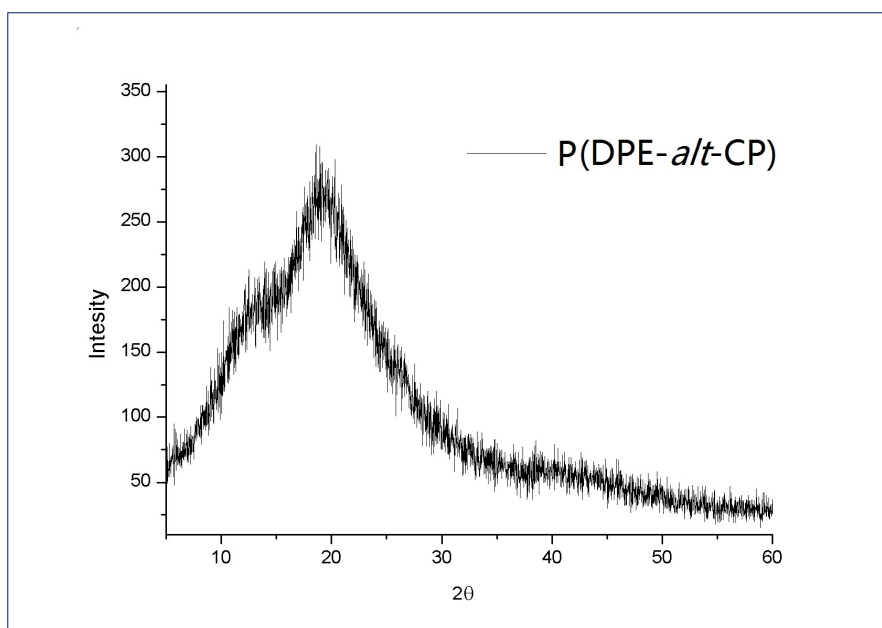


Figure S6. Typical XRD of the P(DPE-alt-CP) at 50 °C.

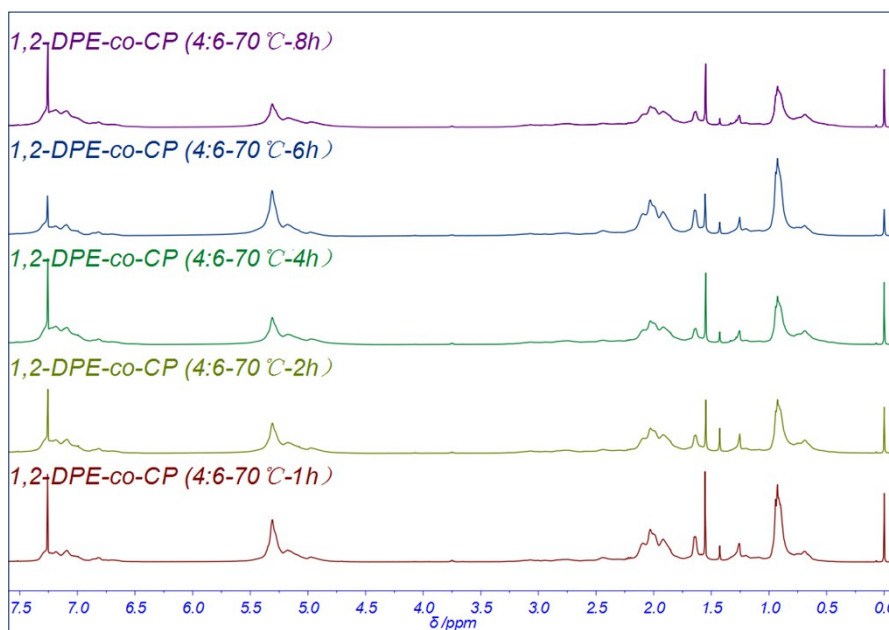


Figure S7. Typical ¹H NMR spectra of the P(1,2-DPE-co-CP) at 70 °C (1,2-DPE/CP=4/6).