## **Supporting Information**

## **Experimental Section**

**Materials**. All reagents were purchased from Aldrich unless otherwise specified. PD isomers (polymer grade) as well as polymerization solvents (including Cyclohexane, THF, Toluene and so on) were refluxed over CaH<sub>2</sub> and then distilled under vacuum before use. Methanol (99.5%) was sparged with nitrogen for 10 mins to remove dissolved oxygen. AIBN or BPO were recrystallized in Methanol or CHCl<sub>3</sub> solvent for two times respectively before use. MAH and NPMI monomer were used without further purification. TP ( $\approx$  95.3%, containing 0.5% isoprene, 0.5% 1-pentine, 1.2% cyclopentadiene, 2.5% cyclopentane), CP ( $\approx$  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 (< 96%). 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).

Radical Alternating Copolymerization of 1,3-Pentadiene with MAH. All polymerizations were performed in a 10 mL schlenk tube equipped with a magnetic Teflon stir bar in glovebox ( $H_2O$ ,  $O_2$ ) < 1 ppm). A specific formulation for an initial feed composition of PD ( $f_{PD,0}$ , including trans, cis and mixed isomers) equal to 0.50 is given as an example. MAH(0.1962 g, 2 mmol), PD(0.2 mL, 2 mmol), AIBN (0.002 g, 0.012 mmol) or BPO (0.003g, 0.012mmol), and THF (1.00 mL) were added to the tube reactor, and mixing commenced with the stir bar. The IKA reactor was then heated to the appropriate temperature (from 60 to 100°C) at a rate of about 5 °C/min while maintaining for 10 min. The initial polymerization time was taken when the schlenk tube was inserted to the reactor. Samples were taken out and quenched with a drop of anhydrous MeOH periodically. Polymers from the samples taken were precipitated with large amount of CH/THF mixture solvent (8/2 v/v) for 5 times. For the specific example cited, the polymerization was stopped after 4 h. After precipitation, the crude polymer was redissolved in THF and precipitated once more into CH/THF (8/2) to remove the unreacted MAH more effectively. And finally, the samples were dried for 72 h in a vacuum oven at 40 °C to remove any additional solvent. The final yield was determined by weighting method and the molar composition of the final copolymer sample with respect to PD was 50% as determined by NMR.

**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 (Mn) and molecular weight distributions ( $\oplus$ ) 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.

<sup>1</sup>H NMR spectra of the polymer samples were recorded with a Varian INOVA-400 spectrometer at room temperature. <sup>13</sup>C NMR measurements were performed on a Varian INOVA-400 spectrometer. Chemical shifts were recorded in ppm downfield relative to CDCl<sub>3</sub> ( $\delta$  = 7.26 ppm) and DMSO ( $\delta$  = 39.6 ppm) for <sup>1</sup>H NMR and <sup>13</sup>C NMR as standard, respectively.

Tg 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. UV spectrum of MAH(black) and MAH/CP(red) in THF (MAH:CP=1:1).

Figure S2. The 1:1 scaled conversion vs time and the relationship of -lnkp" with temperature.

([M<sub>total</sub>]=2 M; [AIBN]=[BPO]=12 mM; A&D:MAH/St=1:1; B&E:MAH/PD=1:1 and

I&F:MAH/CP=1:1).

**Figure S3.** The <sup>1</sup>H NMR spectrum of poly(CP-alt-NPMI) in DMSO.

Figure S4. Real-time <sup>1</sup>H NMR analysis of poly(NPMI-alt-CP) (NPMI:CP=1:1).

Figure S5. Real-time <sup>1</sup>H NMR analysis of poly(MAH-alt-CP)(MAH:CP=1:1).

Figure S6. FTIR spectrum of the poly(MAH-alt-CP) (MAH:CP=1:1;CS<sub>2</sub> as solvent).

**Figure S7.** Typical TGA and DSC of the poly(MAH-alt-PD) (MAH:PD=1:1).

Figure S8. Real-time <sup>1</sup>H NMR analysis of poly(MAH-alt-St)( MAH:St=1:1).

Figure S9. <sup>13</sup>C NMR analysis of poly(MAH-alt-CP) derived from different feeding ratios.

Figure S10. Real-time <sup>13</sup>C NMR analysis of poly(MAH-alt-CP) with 1:1 feeding ratio.

Figure S11. Radical alternating copolymerization of NPMI and CP.

Figure S12. Typical GPC of the poly(MAH-alt-PD) (MAH:PD=1:1;Mn=34.5kg/mol;PDI=1.48).



**Figure S2.** The 1:1 scaled conversion vs time and the relationship of -lnkp" with temperature. ([M<sub>total</sub>]=2 M; [AIBN]=[BPO]=12 mM; A&D:MAH/St=1:1; B&E:MAH/PD=1:1 and I&F:MAH/CP=1:1).



Figure S3. The <sup>1</sup>H NMR spectrum of poly(CP-alt-NPMI) in DMSO.



Figure S4. Real-time <sup>1</sup>H NMR analysis of poly(NPMI-alt-CP) (NPMI:CP=1:1).



Figure S5. Real-time <sup>1</sup>H NMR analysis of poly(MAH-alt-CP) (MAH:CP=1:1).



Figure S6. FTIR spectrum of the poly(MAH-alt-CP) (MAH:CP=1:1;CS<sub>2</sub> as solvent).



Figure S7. Typical TGA and DSC spectra of poly(MAH-alt-PD) (MAH:PD=1:1); .



Figure S8. Real-time <sup>1</sup>H NMR analysis of poly(MAH-alt-St) (MAH:St=1:1).



Figure S9. <sup>13</sup>C NMR analysis of poly(MAH-alt-CP) derived from different feeding ratios.



Figure S10. Real-time <sup>13</sup>C NMR analysis of poly(MAH-alt-CP) with 1:1 feeding ratio.



Figure S11. Radical alternating copolymerization of NPMI and CP.



Figure S12. Typical GPC of the poly(MAH-alt-PD) (Mn=34.5kg/mol;PDI=1.48).

## Table caption

Table S1. The radical coplymerization of pentadiene isomers with MAH/NPMI.

Mı	M2	M1:M2	Yield /%	<i>M</i> <sub>n</sub> <sup>b</sup> /10 <sup>4</sup>	$D^b$	F <sub>M1</sub> <sup>c</sup>	1,4-unit <sup>d</sup>	$T_{\rm g}(T_{\rm d})^e$ /°C
СР	MAH	0.25/1	9%	-	-	0.34	0.85	-
СР	MAH	0.33/1	10%	-	-	0.32	0.86	-
СР	MAH	0.5/1	9%	-	-	0.32	0.84	-
СР	MAH	1/1	12%	-	-	0.51	0.87	-
СР	MAH	1.5/1	11%	-	-	0.50	0.82	-
СР	MAH	2/1	7%	-	-	0.50	0.85	-
СР	MAH	4/1	8%	-	-	0.51	0.83	-
СР	MAH	1/1	99%	9.8	1.39	0.50	0.83	97(343)
PD	MAH	1/1	60%	3.5	1.48	0.50	0.85	96(330)
TP	MAH	1/1	20%	-	-	0.51	0.86	90(335)
IP	MAH	1/1	35%	3.6	1.71	0.48	-	-
СР	NPMI	1/1	99%	7.5	1.59	0.50	0.99	97(340)
PD	NPMI	1/1	55%	5.0	1.65	0.50	0.98	96(338)
TP	NPMI	1/1	25%	3.4	1.87	0.51	0.99	-
IP	NPMI	1/1	30%	-	-	0.49	-	-

Table S1. The radical coplymerization of pentadiene isomers with MAH/NPMI.<sup>a</sup>

<sup>*a*</sup> All polymerization reactions were performed in THF with AIBN as initiator: Monomer/solvent = 0.3 g/1.0 mL, [AIBN] =  $2.0 \sim 3.0$  mg/mL. <sup>*b*</sup> Determined by GPC. <sup>*c*</sup> Determined by <sup>1</sup>H NMR and <sup>13</sup>C NMR, <sup>*d*</sup> Determined by IR and NMR. DSC. <sup>*e*</sup> Determined by DSC and TGA.