Supporting information

Facile Synthesis of Functionalized High Vinyl Polybutadiene by Using 1,2-Dipiperidinoethane Derivatives as Polar Modifier

Qiqi Dai^{†,}^a, Yao Long^{†,}^a, Xupeng Han^{†,}^a, Yang Yang^a, Yi Yang^a, Yawen Fu^a, Wenjun Yi^b, Xiaoxing Gu^c, Kun Liu^{*,}^a, Lijun Li^{*,}^a

^a Province Key Laboratory for Fine Petrochemical Catalysis and Separation, College of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang, 414006, P. R. China.

^b College of Materials Science and Engineering, Changsha University of Science & Technology, Changsha, 410082, P. R. China. ^c Shandong Xingshun New Materials Co., Ltd, Jiangsu, 213000, P. R. China.

* Corresponding authors: <u>liukun328@126.com</u> and <u>lilijun115@163.com</u>.

[†] These authors contributed equally to this work.

Experimental section

Reagents. Butadiene (BD, 99.9%, polymerization grade) was supplied by YueYang BaLing Petrochemical Chem. *Co. Ltd.* 4-Dimethylaminomethylstyrene (VBA, 99%) was self-made according to our previous work, and then distilled from CaH₂ under vacuum and stored at 0°C under nitrogen. *n*-BuLi (2.5 mol/L in *n*-hexane) was used without further purification. Cyclohexane (CH, 99.8%, polymerization grade) came from the Rubber Division of Baling Petrochemical *Co. Ltd.*, Sinopec. Before use, CaH₂ was used for dehydration and distillation purification and then soaked in the molecular sieve for 48 h for dehydration and sealed preservation. Methanol (MeOH, 99.5%, analytical purity) was purged with nitrogen before use as a terminator to prevent the coupling of living chains with oxygen and carbon dioxide. Other reagents such as deuterium chloroform (CDCl₃) were purchased from Aladdin Reagents and used directly without any treatment.

Synthesis of NN1-10. Taking **NN-2** for example, in a three-necked flask immersed in an ice-water bath, 68.1 g (99%, 0.8 mol) of piperidine and 4.0 g (96%, 0.1 mol) of NaOH solid were added and stirred. After cooling the system to 0°C, 37.6 g (99%, 0.2 mol) of 1,2-dibromoethane was slowly added via a constant-pressure dropping funnel. The reaction released a significant amount of heat, raising the system temperature to 50°C after completion, accompanied by the formation of a large quantity of sodium bromide precipitate. The mixture was then heated to reflux temperature and maintained for 7 hours. Subsequently, excess cyclohexane was added, and the mixture was extracted three times until phase separation occurred. The upper organic phase was retained, and calcium hydride was added for dehydration via distillation under reduced pressure. Cyclohexane and excess piperidine were removed under low temperatures, while pure DPE was collected in a Schlenk tube (or flask) at elevated temperature, purged with nitrogen, and stored in a glovebox for later use. All other DPE-derived polar modifiers were synthesized using this method.

Synthesis of 4-dimethylaminomethylstyrene. In a three-necked flask immersed in an ice-water bath, 135.2 g of dimethylamine (40wt.% solution in water, 1.2 mol) was added and stirred. After cooling the

system to 0°C, 93.5 g (98%, 0.6 mol) of 4-chloromethylstyrene was slowly added via a constant-pressure dropping funnel. The reaction released a significant amount of heat, and after completion, the mixture was allowed to react for an additional 2 hours. Subsequently, the mixture was transferred to a separatory funnel and left undisturbed for phase separation. The upper organic phase was retained, and calcium hydride was added for dehydration via distillation under reduced pressure. The purified distillate was transferred to a Schlenk flask (or tube), purged with nitrogen, and stored refrigerated.

Synthesis of HVPB via LCAP. All polymerization reactions were conducted in a glove box (with water/ oxygen index lower than 1 ppm). The specific operation steps are as follows: (1) After drying the 10 mL Schlenk tube, transfer it to a small transition chamber while it is hot, continuously vacuum and replace it with argon several times to control the water oxygen index to qualified; (2) Number the reaction tubes in sequence, add a magnetic stirrer, and then start the stirrer. Use a pipette gun to remove 1 mL of cyclohexane, and then use a pipette gun to remove 0.2~0.3 g of the desired mixed monomer to the Schlenk tube. Finally, add *n*-BuLi to the solution, and rapidly transfer to a setting temperature IKA reactor to initiate a polymerization reaction; (3) After a predetermined time of reaction, take out and add a drop of degassed methanol to terminate the reaction. Transfer the reaction liquid into a centrifuge tube using a pipette, and repeatedly precipitate with methanol 5 times to remove residual monomers and solvents. After the polymer has completely settled, add trace antioxidant to the product and transfer the centrifuge tube to a 40 °C vacuum drying oven (-0.1 MPa) for drying for more than 48 h until the centrifuge tube has constant weight.

Analytical methods. Nuclear magnetic resonance instrument (NMR), INOVA400, 400 MHz, Varian Company, USA, equipped with an automatic sampler. The microstructure of polyolefin compounds is analyzed using CDCl₃ as a deuterium reagent and TMS as a marker. ¹H NMR and ¹³C NMR spectra are mainly used to analyze the chemical structure of DPE derivative modifiers and the structures of 1,4-/1,2 units and to analyze and calculate the composition of the resultant copolymer. FT-IR spectrum was recorded with Vector-22 FT-IR spectrometer (Bruker Company, Germany) by KBr technique. The molecular weight and molecular weight distribution analysis of the copolymer were determined by Gel permeation chromatography (GPC), performed in THF (Waters series). The calibration was performed by using different PS standards with narrow molecular weight distributions and molar masses ranging from 1000 to 1000000 g/mol. Differential scanning calorimeter (DSC), American TA differential scanning calorimeter, model DSC-25, test method: Use an electronic scale to weigh about 10 mg of sample, evenly spread it on the bottom of the crucible (to reduce thermal resistance), cover the crucible cap to press the finished product, place it in the corresponding sample tank for testing, start the instrument, under nitrogen atmosphere, raise the temperature from 20°C ~120°C at a rate of 20°C /min, and then lower the temperature to 120°C ~ -80°C at the same rate, Finally, raise the temperature to 50°C twice at 10°C/min. It is mainly used to analyze the glass transition temperature of the polymer.

Figures capture

Figure S1. The ¹H NMR and ¹³C NMR spectra of NN-1 polar modifier Figure S2. The ¹H NMR and ¹³C NMR spectra of NN-2 polar modifier Figure S3. The ¹H NMR and ¹³C NMR spectra of NN-3 polar modifier Figure S4. The ¹H NMR and ¹³C NMR spectra of NN-4 polar modifier Figure S5. The ¹H NMR and ¹³C NMR spectra of NN-5 polar modifier Figure S6. The ¹H NMR and ¹³C NMR spectra of NN-6 polar modifier Figure S7. The ¹H NMR and ¹³C NMR spectra of NN-7 polar modifier Figure S8. The ¹H NMR and ¹³C NMR spectra of NN-8 polar modifier Figure S9. The ¹H NMR and ¹³C NMR spectra of NN-8 polar modifier Figure S9. The ¹H NMR and ¹³C NMR spectra of NN-9 polar modifier Figure S10. The ¹H NMR and ¹³C NMR spectra of NN-10 polar modifier Figure S11. The ¹H NMR and ¹³C NMR spectra of NN-10 polar modifier Figure S11. The ¹H NMR spectrum of HVPB and determination of microstructure by equations (1)-(2) Figure S12. The relationship of 1,2-units of HVPB with the ratio of PA/Li in an ice bath

Figure S13. The ¹H NMR spectrum of functionalized HVPB and determination of composition and microstructure by equations (3)-(6)



Figure S1. The ¹H NMR and ¹³C NMR spectra of NN-1 polar modifier (CDCl₃ solvent)



Figure S2. The ¹H NMR and ¹³C NMR spectra of NN-2 polar modifier (CDCl₃ solvent)



Figure S3. The ^1H NMR and ^{13}C NMR spectra of NN-3 polar modifier (CDCl_3 solvent)



Figure S4. The ^1H NMR and ^{13}C NMR spectra of NN-4 polar modifier (CDCl_3 solvent)











Figure S8. The ¹H NMR and ¹³C NMR spectra of NN-8 polar modifier (CDCl₃ solvent)



Figure S9. The ¹H NMR and ¹³C NMR spectra of NN-9 polar modifier (CDCl₃ solvent)





Figure S11. The ¹H NMR spectrum of HVPB and determination of microstructure by equations (1) and (2)







Figure S12. The relationship of 1,2-units of HVPB with the ratio of PA/Li in an ice bath



$$BD-1,2-mol\% = \left[\frac{2 \times I_c}{2 \times I_b + I_c}\right] \times 100\%$$
(5)

$$BD-1,4-mol\% = \left[1 - \frac{2 \times I_c}{2 \times I_b + I_c}\right]_{\times 100\%}$$
(6)

Figure S13. The ¹H NMR spectrum of functionalized HVPB and determination of the composition and microstructure by

equations (3)-(6)