Efficient Terpolymerization of Ethylene/Propylene/ENB with Half-Titanocene Cayalytic System

Yi-Cong Wang,[#] Pei-Yi Cheng,[#] Zhi-Qian Zhang, Ke-Xin Fan, Rui-Qi Lu, Shu Zhang* and Yi-Xian Wu*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China.

Email: zhangshu@mail.buct.edu.cn; wuyx@mail.buct.edu.cn

Electronic Supplementary Information (ESI)

Additional data for polymerization

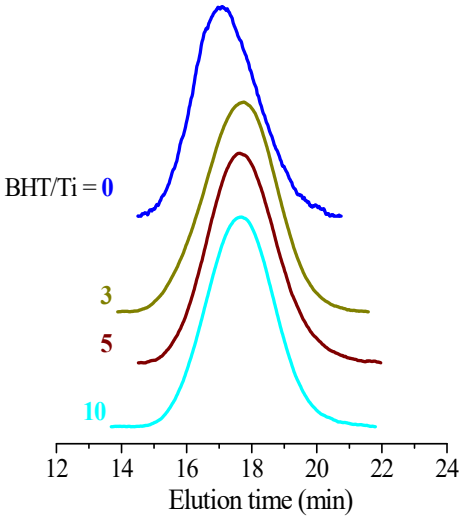

Figure S1 The GPC traces of copolymers obtained with **T5**/TIBA/BHT/MAO catalytic system at various BHT/Ti molar ratios. (Polymerization conditions are similar to that in Figure 1.)

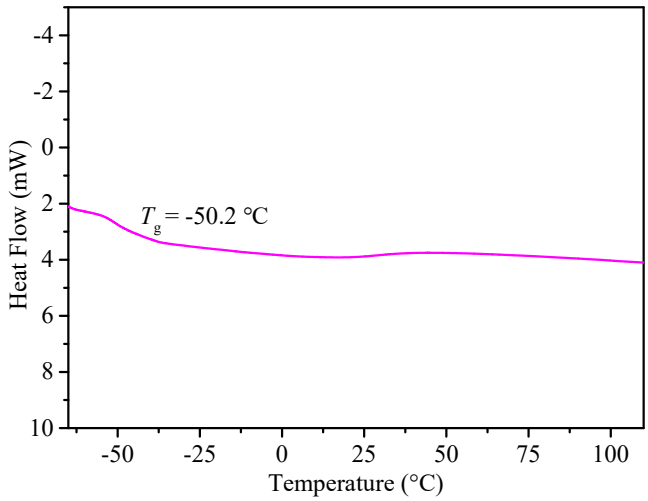

Figure S2 DSC heating curves of ethylene-propylene copolymer prepared by **T5**/BHT/TIBA/MAO catalytic system (BHT/Ti = 20)

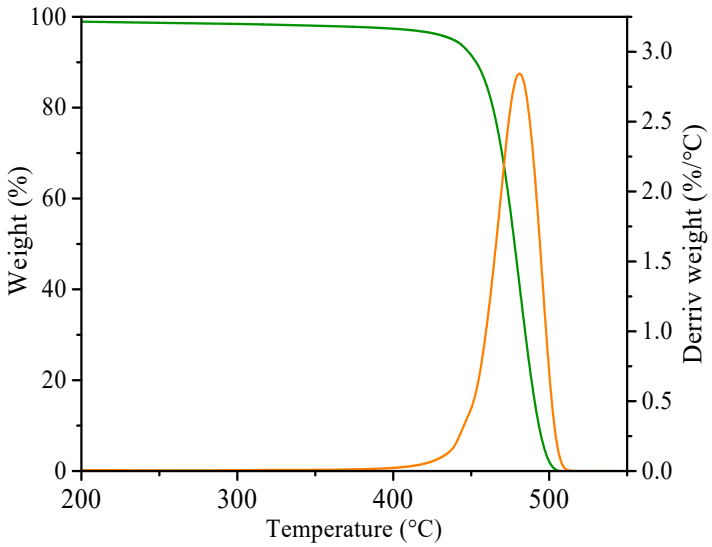

Figure S3 TGA curve (in N_2 atmosphere at 10 °C·min^{-1}) of ethylene-propylene copolymer prepared by **T5**/BHT/TIBA/MAO catalytic systems (BHT/Ti = 20)

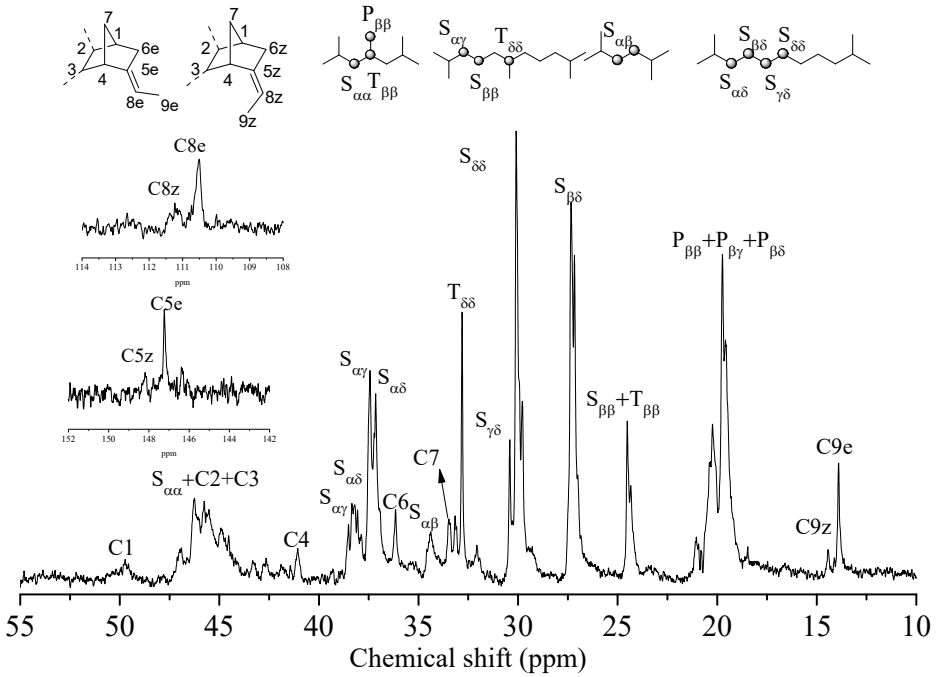

Figure S4 ^{13}C NMR spectrum of EPDM-ENB6.8 ($CDCl_3$, 25 °C)

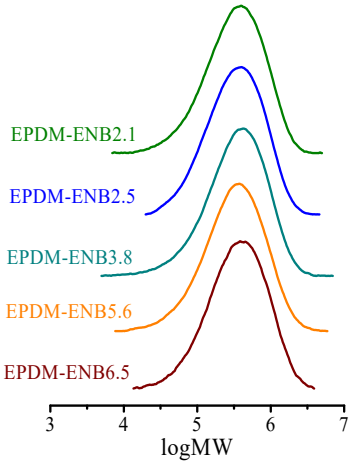

Figure S5 The GPC traces of resulting EPDMs with various contents of ENB unit

(Polymerization conditions are similar to that in Table 1.)

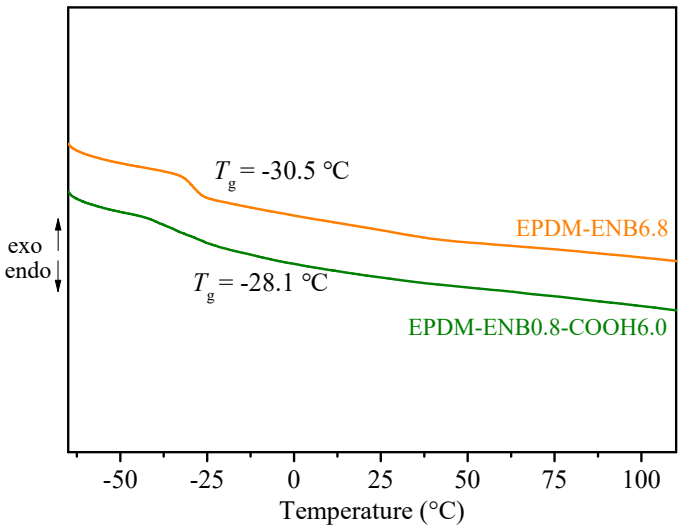

Figure S6 DSC heating curves of representative EPDM and functionalized EPDM

Effect of Al/Ti molar ratio. The copolymerizations of ethylene and propylene by **T5**/TIBA/BHT/MAO catalytic system were carried out at various amounts of MAO (described as Al/Ti molar ratio). The catalytic activity, monomer conversion and propylene incorporation ratio of resulting copolymers are displayed in Figure S7 and Figure S8, respectively. As shown in Figure S7, the catalytic activity of **T5**/TIBA/BHT/MAO catalytic system increased with an increase in the Al/Ti molar ratio from 1000 to 2000 and reached a maximum value of 2.40×10^7 g polymer·mol^{-1} of Ti·h^{-1} at Al/Ti molar ratio of 2000. The catalytic activity almost kept constant with a further increase in Al/Ti molar ratio from 2000 to 3000. It can be seen from Figure S8 that the ethylene conversion increased from 0 to 79.5% and the propylene conversion increased from 0 to 28.7% with an increase in Al/Ti molar ratio from 1000 to 2000. As shown in Figure S7, the propylene incorporation ratio of the ethylene-propylene copolymers obtained at the Al/Ti molar ratio of 1200 was relatively low (32.8 mol%). While the ethylene-propylene copolymers with propylene incorporation ratio of ~41 mol% were obtained at Al/Ti molar ratio between 1500 and 3000. The M_η decreased from 3.42×10^5 g·mol^{-1} to 2.21×10^5 g·mol^{-1} with an increase in Al/Ti molar ratio from 1200 to 3000, due to the chain transfer reaction to MAO at high Al/Ti molar ratio during the copolymerization.

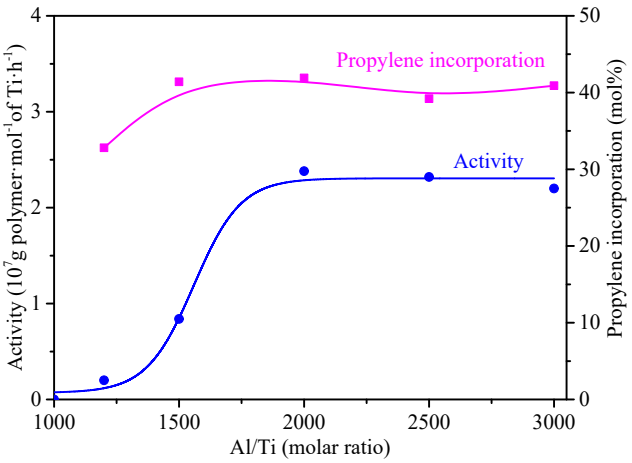

Figure S7 The catalytic activity and propylene incorporation ratio of the ethylene-propylene copolymers obtained with **T5**/TIBA/BHT/MAO catalytic system at various Al/Ti molar ratios**.** ([M] = 140 g/L, P/E = 2 (molar ratio), Ti/M = 1.3 × 10^{-6}, TIBA:BHT:Ti = 20:20:1 (molar ratio), T = 60 °C, t_p = 30 min.)

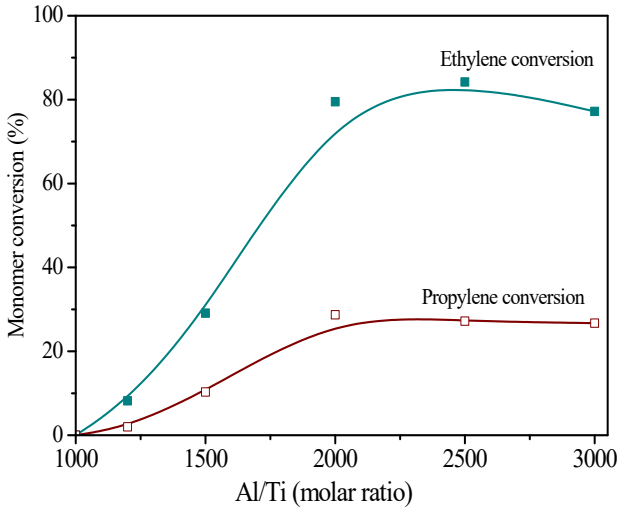

Figure S8 The monomer conversion in the copolymerization of ethylene and propylene with **T5**/TIBA/BHT/MAO catalytic system at various Al/Ti molar ratios. (Polymerization conditions are shown as in Figure S7.)