

Supporting Information

RAFT/MADIX method finely regulating the copolymerization of ethylene and polar vinyl monomers under mild conditions

Qian-Bao Chen, Tian-You Zeng, Lei Xia, Ze Zhang, Chun-Yan Hong,* Gang Zou*

and Ye-Zi You*

1. Experimental Procedures

Materials. Vinyl acetate (VAc, 99%) and N,N-dimethylformamide (DMF, 99.9%) were purchased from Aladdin, N-Vinyl pyrrolidone (NVP, 99%), N-vinylcaprolactam (NVCL, 99%), methyl 2-bromopropionate (MBP, 98%), carbon disulfide (99%) and dimethyl carbonate (DMC, 99%) were purchased from Energy, 2-hydroxyethyl vinyl ether (HOVE, 98%) was purchased from Beelink, vinyl trifluoroacetate (VTFAc, 99%) was purchased from TCI, potassium hydroxide (99%), sodium sulfate anhydrous (97%), n-hexane (97%), methanol (99.7%), chloroform (99%) and diethyl ether anhydrous (99.7%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Pro. Vinyl acetate (VAc, 99%) was dried over CaH_2 and purified by distillation under vacuum. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%) was purified by recrystallization from ethanol. All other reagents were used as received.

Characterization. All NMR spectra were performed using Bruker AV400 NMR spectrometer, all samples were dissolved in chloroform-d, with tetramethylsilane (TMS) as an internal reference. M_w and PDI were determined by GPC, the system was equipped with a PL-RI differential refractive index detector (DRI), PL-BV 400RT viscometer (Visc), and a Precision Detectors PD2020 light scattering detector (LS). LiBr/DMF (0.1%, w/w) solution with a flow rate of 1.0 mL/min was used as eluent. The system was calibrated using polystyrene (PS) standards. Water contact angles on polymer films were measured with Contact Angle Meter SL200B (Solon Tech. Co., Ltd.) by the dynamic sessile drop method. Samples were prepared by the evaporation of 20 % (w/w) solutions in dry THF onto glass slides and THF was evaporated under ambient conditions. Differential scanning calorimetry (DSC) analysis was performed using a TA Q2000 differential scanning calorimeter instrument with a heating rate of 10 °C/min under a flowing nitrogen atmosphere from -50 °C to 100 °C. The glass transition temperature (T_g) was determined from the inclination point in the second heating curve.

Synthesis of O-Me xanthate. Carbon disulfide (5 mL) was added dropwise to the solution of potassium hydroxide (1.67 g) in methanol (10 mL) under stirring. After 5 h, solvents were removed under reduced pressure at room temperature. The resulting product was suspended in diethyl ether (50 mL) and a mixture of MBP (2.5 mL) and diethyl ether (5 mL) was added at 0 °C. The reaction mixture was stirred overnight, and then filtered, followed by adding hexane (20 mL) and washed with water (3 times). The organic phase was dried with magnesium sulfate and solvents were removed under reduced pressure to give transparent yellow oil. Yield: 55%. ¹H NMR (300 MHz, CDCl₃): δ = 4.35 ppm (q, 1 H, CHCH₃), 4.11 (s, 3 H, CH₃O), 3.69 (s, 3 H, COOCH₃), 1.52 (d, 3 H, CHCH₃).

Incorporation of polar monomer into PE chain. In a typical experiment, to the mixture of 1 mL of polar monomers (NVP) and 2 mL of solvent (dichloromethane) was added AIBN (4.9 mg) and O-Me xanthate (7.5 mg). The mixture was introduced into a 100 mL stainless steel reactor, followed by freeing from oxygen with argon. Ethylene was then introduced until the desired pressure and the mixture was heated to 70 °C under stirring (450 rpm). Ethylene was continuously introduced to the reactor to maintain a constant ethylene pressure. After the polymerization finished, the reactor was cooled to room temperature and the crude polymerization mixture was precipitated into hexane followed by centrifugation, the resulting polymer was dissolved into chloroform and precipitated into excess of cold hexane, and dried under vacuum. Ethylene pressure was then changed and other procedures remain the same to obtain copolymers under different pressures. Yields for PNVP-co-PE: 1.056 g (0 bar), 1.094 g (5 bar), 1.142 g (20 bar), 1.194 g (35 bar), 1.335 g (60 bar), 1.487 g (75 bar). Yields for other copolymers: 0.987 g (VAc, 5 bar), 0.965 g (VAc, 15 bar), 1.078 g (VAc, 20 bar), 1.277 g (VAc, 30 bar), 1.309 g (VAc, 40 bar), 0.654 g (HOVE, 10 bar), 0.696 g (HOVE, 20 bar), 0.882 g (HOVE, 30 bar), 0.389 g (VTFac, 20 bar), 1.365 g (NVCL, 75 bar).

The incorporation of polar monomers was calculated based on ¹H NMR spectra. Here we take PVAc-co-PE as an example, the peak around 4.87 ppm was assigned to the CH proton and the integration was 1. The peak around 1.915 ppm to 0.845 pm was assigned

to protons of CH₂ in VAc and all ethylene protons, the total integral value was I_t . The integral value of all ethylene protons is $I_t - 1 \times 2$. For PVAc-co-PE, the incorporation of polar monomer was calculated based on the following equation:

$$\text{Polar monomer incorporation\%} = \{1 - [(I_t - 2)/4] / [1 + (I_t - 2)/4]\} \times 100\%$$

Synthesis of PNVP-*b*-PE block copolymer in one-pot. To the mixture of NVP (666 mg, 6 mmol) and dichloromethane (3 mL) was added AIBN (5 mg, 0.03 mmol) and O-Me xanthate (19.4 mg, 0.1 mmol). The mixture was introduced into a 100 mL stainless steel reactor, followed by removing oxygen with argon. The mixture was heated to 70 °C under stirring (450 rpm). After 10 h of reaction, an aliquot was taken out for analyzing the conversion of PNVP and the molecular weight of the resulting PNVP, then ethylene was introduced to 35 bar and allowed for another 24 h of polymerization until the block copolymer was formed. Yields for block copolymer: 0.646 g.

Synthesis of a copolymer with one PE-poor block (61.3 mol% NVP/38.7 mol % ethylene) and one PE-rich block (37.0 mol% NVP/63.0 mol % ethylene) in one-pot simply changing the pressure of ethylene. To the mixture of NVP (1 mL) and DMC (5 mL) was added AIBN (6 mg, 0.04 mmol) and O-Me xanthate (15 mg, 0.077 mmol). The mixture was introduced into a 100 mL stainless steel reactor, followed by freeing from oxygen with argon. Ethylene was introduced to 35 bar and the mixture was heated to 70 °C under stirring (450 rpm). After 2.5 h of reaction, an aliquot was picked out to determine the conversion of NVP and the molecular weight of the resulting copolymer, then ethylene was increased to 75 bar and allowed for another 4 h of copolymerization until the copolymer was formed. Yields for copolymer: 1.189 g.

Synthesis of a copolymer with one PE-co-PNVP block (53.7 mol% NVP/46.3 mol % ethylene) and one pure PNVP block in one-pot simply changing the pressure of ethylene. To the mixture of NVP (1 mL) and DMC (5 mL) was added AIBN (6 mg, 0.04 mmol) and O-Me xanthate (15 mg, 0.077 mmol). The mixture was introduced into a 100 mL stainless steel reactor, followed by freeing from oxygen with argon. Ethylene

was introduced to 40 bar and the mixture was heated to 70 °C under stirring (450 rpm). After 4 h of reaction, an aliquot was picked out to determine the conversion of NVP and the molecular weight of the resulting copolymer, then ethylene was decompressed and allowed for another 4 h of polymerization until the copolymer was formed. Yields for copolymer: 1.074 g.

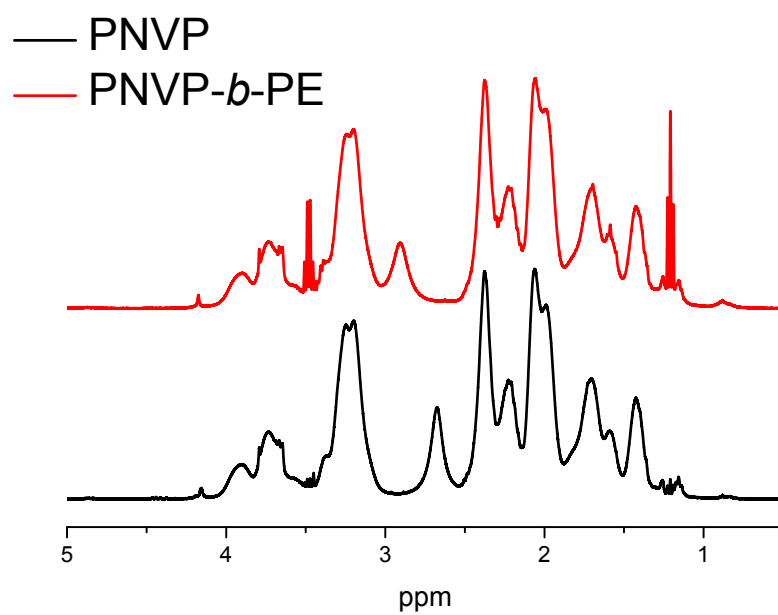
Results

Table S1. Incorporation under different NVP concentration

Entry	NVP (mL)	X ₁	X ₂
1	1.5	74.5	26.5
2	1.0	66.4	33.6
3	0.5	62.2	37.9
4	0.2	61.5	38.5
5	0.1	60.9	39.4

X₁ = NVP composition (mol %), determined by ¹H NMR spectroscopy, X₂ = ethylene composition (mol %).

a



b

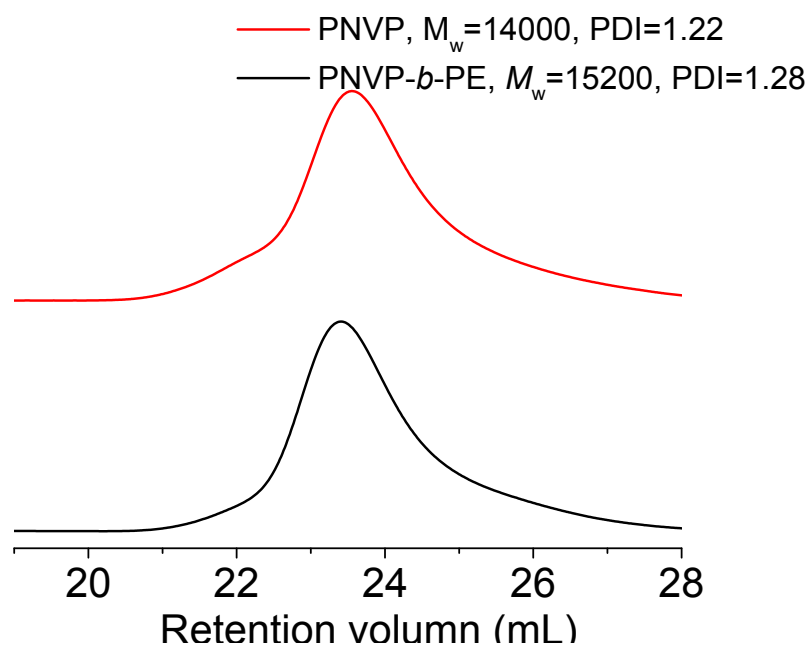
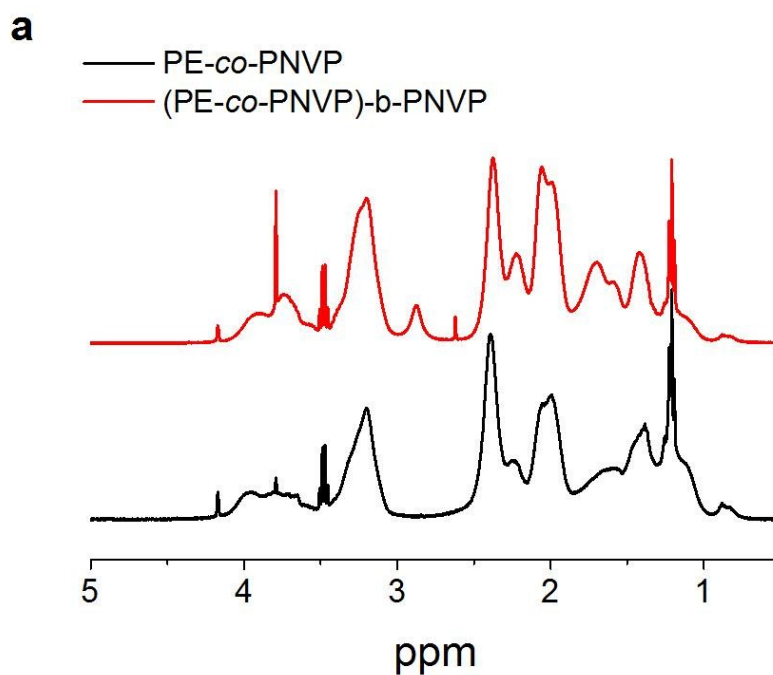


Figure S1. a), ¹H NMR spectroscopy of PNVP and PNVP-*b*-PE. b), GPC traces of homoPNVP and copolymer.

Table S2. Synthesis of copolymer with one PE-*co*-PNVP block and one pure PNVP block

	NVP conversion ^[a]	Composition		M _w ^[c] (10 ⁴ g/mol)	PDI
	(%)	X ₁ ^[b] (%)	X ₂ ^[b] (%)		
Block-1	35.7	46.3	53.7	1.26	1.21
Block-2	86.6	0	100	1.09 ^[d]	-
copolymer	-	20.5	79.5	2.35	1.47

Conditions: NVP (1 mL), DMC (5 ml), O-Me xanthate (15 mg), 70 °C. First block was obtained after 4 h of copolymerization under 40 bar of ethylene pressure, second block was formed after another 4 h in the absence of ethylene. [a] Determined by ¹H NMR spectroscopy. [b] X₁ = Ethylene incorporation (mol %), determined by ¹H NMR spectroscopy, X₂ = NVP incorporation (mol %), calculated from X₁. [c] Determined by GPC. [d] Calculated based on the M_w of block-1 and copolymer.



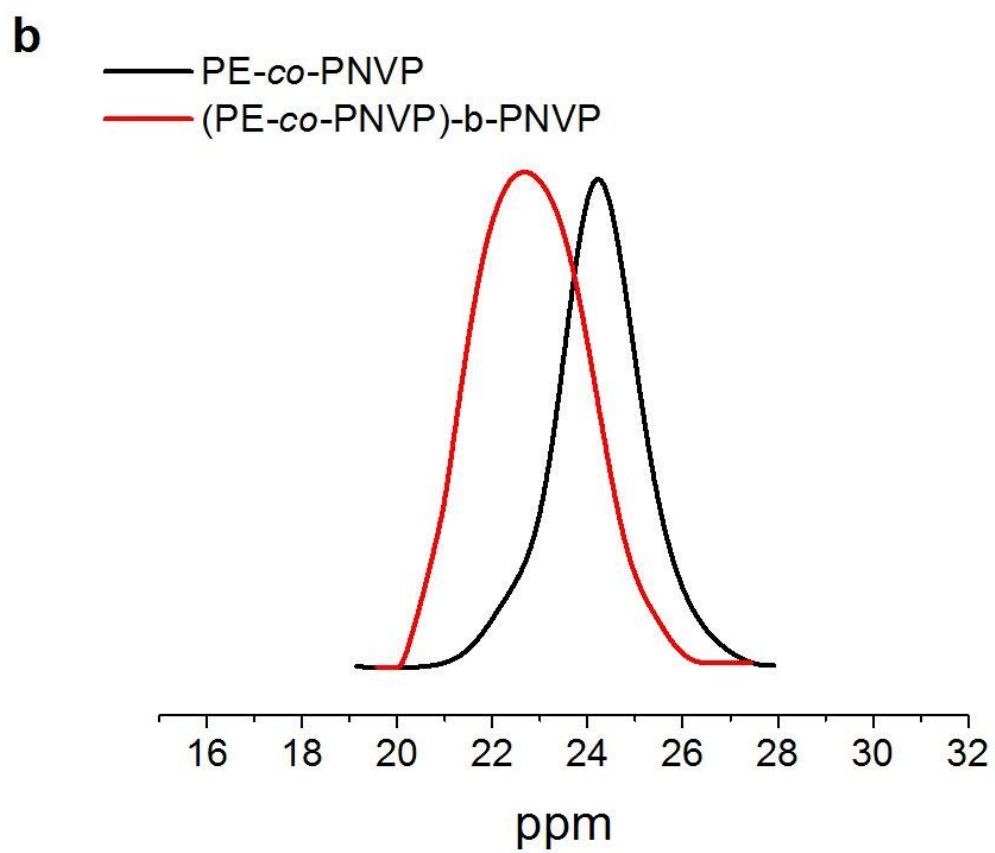
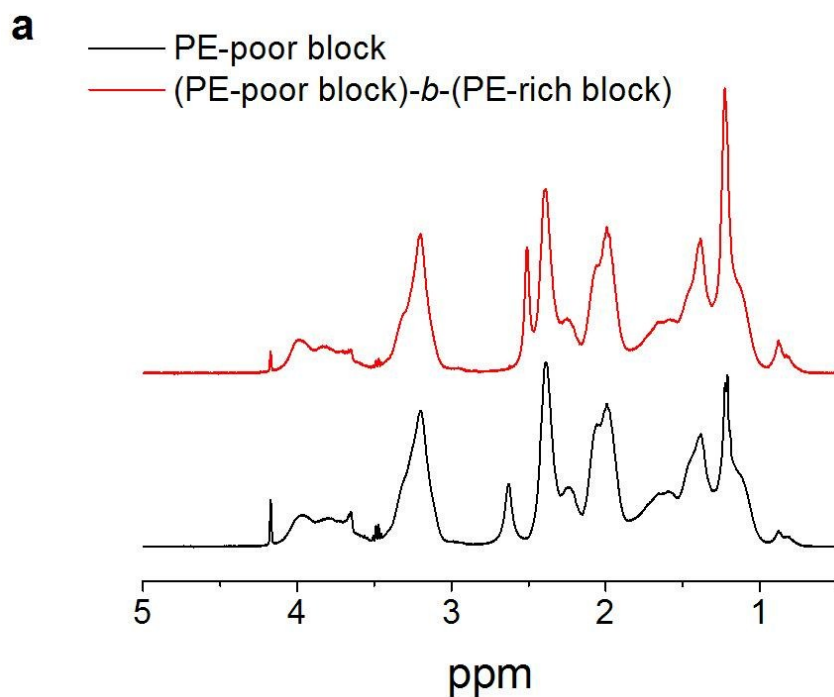


Figure S2. a), ^1H NMR spectroscopy of copolymer with one PE-co-PNVP block and one pure PNVP block. b), GPC traces of PE-co-PNVP and copolymer.

Table S3. Synthesis of copolymer with one PE-poor block and one PE-rich block

	NVP conversion ^[a]	Composition		M _w ^[c] (10 ⁴ g/mol)	PDI
	(%)	X ₁ ^[b] (%)	X ₂ ^[b] (%)		
Block-1	37.5	38.7	61.3	1.17	1.23
Block-2	67.8	63.0 ^[d]	37.0 ^[d]	0.70 ^[e]	-
copolymer	-	52.6	47.4	1.87	1.38

Conditions: NVP (1 mL), DMC (5 ml), O-Me xanthate (15 mg), 70 °C. First block was obtained after 2.5 h of copolymerization under 35 bar of ethylene pressure, second block was formed after another 4 h under 75 bar of ethylene pressure. [a] Determined by ¹H NMR spectroscopy. [b] X₁ = Ethylene incorporation (mol %), determined by ¹H NMR spectroscopy, X₂ = NVP incorporation (mol %), calculated from X₁. [c] Determined by GPC. [d] Calculated based on the incorporation in block-1 and copolymer. [e] Calculated based on the M_w of block-1 and copolymer.



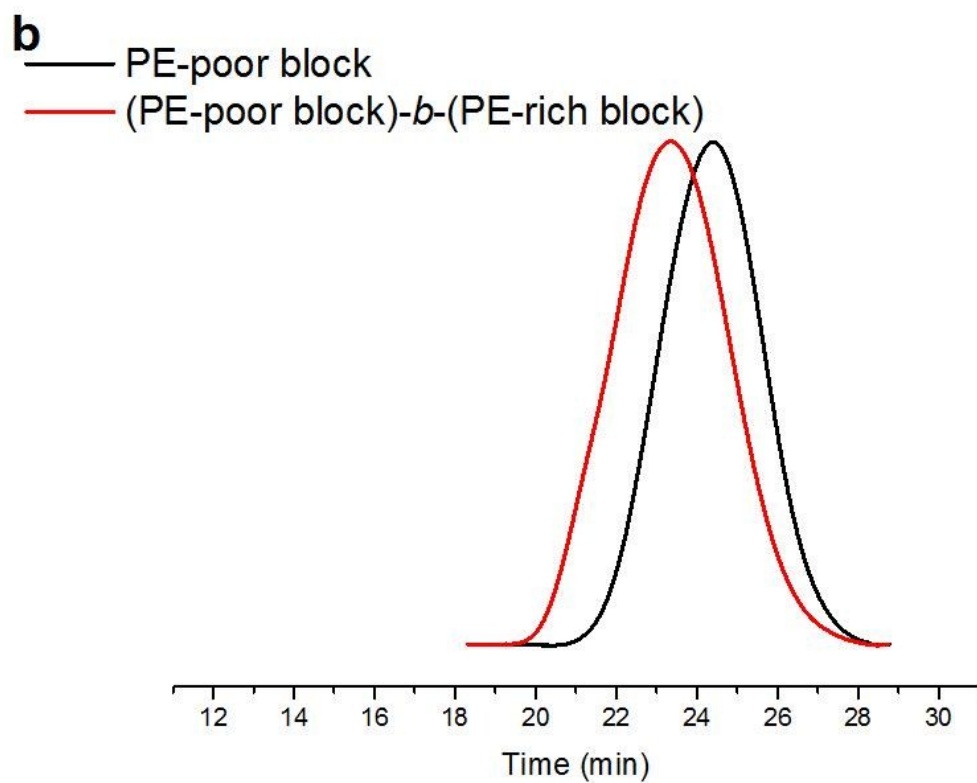


Figure S3. a), ^1H NMR spectroscopy of copolymer with one PE-poor block and one PE-rich block. b), GPC traces of PE-poor block and (PE-poor block)-*b*-(PE-rich block) copolymer.