

Supporting Information

Direct Amination of Polyethylene by Metal-Free Reaction

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Materials

Bis(2,2,2-trichloroethyl) azodicarboxylate (BTCEAD) was prepared according to a reported procedure.¹ Polyethylene (PE, $M_n = 7.9$ kg/mol, PDI = 1.83) was kindly supplied by the Institute of Chemistry, The Chinese Academy of Sciences. PE membranes were purchased from MingKe Plastic Company, China. Polymethyl methacrylate (PMMA, $M_n = 25.4$ kg/mol, PDI = 1.15) was prepared *via* atom transfer radical polymerization of MMA.² Di-*tert*-butyl azodicarboxylate (DBAD, 98%, Adamas), *N*-hydroxyphthalimide (NHPI, 99%, TCI), trifluoroacetic acid (TFA, 99%, Acros), dichloroethane (99%, Aladdin) and 1,1,2,2-tetrachloroethane (99%, Energy Chemical) were used as received. Methanol and toluene were analytical grade from Guangzhou Chemical Reagent Factory and were used directly.

Characterization

Nuclear Magnetic Resonance (NMR) Spectroscopy. ¹H and ¹³C NMR spectra were recorded on Bruker AVANCE III 400 MHz and DMX 300 MHz instruments, respectively. NMR tests of polymers were carried out at 110 °C with *o*-C₆D₄Cl₂ as the solvent for ¹H NMR and a mixed solvent, *o*-C₆D₄Cl₂/*o*-C₆H₄Cl₂ (v/v = 1/2), for ¹³C

NMR, respectively.

Fourier Transform Infrared Spectroscopy (FT-IR). FT-IR spectra were obtained using a Thermo Nicolet Nexus 6700 FT-IR spectrometer. The spectra were collected at 32 scans in a transmission mode with background deduction.

Size Exclusion Chromatography (SEC). Molecular weights and molecular weight distributions of polymers were performed on a Polymer Laboratories GPC-220 liquid chromatograph equipped with three Polymer Laboratories gel 10 μm Mixed-B columns, a refractive index detector, a Viscotek 220R viscosity detector and a binary angles (15° , 90°) ($\lambda = 658\text{ nm}$) light scattering detector. Analysis was carried out at 150°C in 1,2,4-trichlorobenzene with a flow rate of 1.0 mL/min . Polystyrene standards were used for calibration.

Elemental analysis (EA). The EA data of polymers were obtained on an Elementar Vario EL analyzer in C, H and N test mode.

Water Contact Angle. Water contact angle of PE membranes was performed using a Krüss DSA 100 contact angle analyzer. A rectangular PE membrane pasted to a glass slide was measured at six different positions to calculate the average data and standard errors.

Scanning Electron Microscopy (SEM). The compatibility of PE/PMMA and modified PE/PMMA blends were performed on a Hitachi S-4800 scanning electron microscope with an accelerating voltage of 10 kV . The blending samples were prepared by firstly dissolving PE (or modified PE) and PMMA together in toluene at 110°C at a certain ratio, and then pumping off the solvent. The fractured surfaces of the blends were etched with acetone. SEM images were obtained on platinum-coated fractured surfaces of the blends.

Thermogravimetric Analysis (TGA). The thermal decomposition behaviors of polymers were recorded by using a PerkinElmer Pyris TG 2000 equipment from 40 to 600°C with a heating rate of 10°C/min under a nitrogen atmosphere (20 mL/min).

Differential Scanning Calorimetry (DSC). The melting and crystallization behaviors of polymers were measured using a PerkinElmer DSC 4000 instrument

from 35 to 170 °C at 10 °C/min under a nitrogen atmosphere (20 mL/min). The melting temperature (T_m) was based on the second heating scan. The crystallinity degree (X_c) was calculated according to the following equation 1.

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100\% \quad (1)$$

where ΔH_f is the melting enthalpy of our PE sample while ΔH_f^0 is the standard melting enthalpy of PE (293 J/g).

Grafting Content Calculation. The grafting content (g , wt%) of BTCEAD and DBAD in the modified PE were calculated through the following equations 2, 3 and 4, 5, respectively. They were based on their corresponding EA results.

$$\text{C/N ratio} = \frac{24n+72m}{28m} \quad (2)$$

$$g = \frac{381m}{381m+28n} \times 100\% \quad (3)$$

where the C/N ratio of PE-*g*-BTCEAD was obtained from its EA data, and n and m represent the number of modified PE repeat units ($-\text{CH}_2\text{CH}_2-$) and the number of grafted BTCEAD units, respectively.

$$\text{C/N ratio} = \frac{24n+120m}{28m} \quad (4)$$

$$g = \frac{231m}{231m+28n} \times 100\% \quad (5)$$

where the C/N ratio of PE-*g*-DBAD was obtained from its EA data, and m represents the number of grafted DBAD units.

Experimental Procedures

Synthesis of PE-*g*-BTCEAD.³ To a 20 mL sample bottle, PE powder (150 mg, 5.36 mmol repeat units), BTCEAD (339 mg, 0.893 mmol) and NHPI (30 mg, 0.185 mmol) were added to 1,1,2,2-tetrachloroethane (9 mL). The reaction mixture was stirred for 1 h at 110 °C and then precipitated in 200 mL of methanol. The precipitated solid was redissolved in toluene at 110 °C and precipitated two more times in methanol. The

product was dried for 24 h under vacuum to obtain PE-g-BTCEAD (136 mg). ^1H NMR ($o\text{-C}_6\text{D}_4\text{Cl}_2$, 400 MHz, 110 °C): δ 0.81-1.49 (br, CH_3 and CH_2), 1.62 (br, CH_2CHNCOO), 4.17 (br, CH_2CHNCOO), 4.68 (s, OCH_2CCl_3), 6.41 (br, NHCOO); ^{13}C NMR ($o\text{-C}_6\text{D}_4\text{Cl}_2/o\text{-C}_6\text{H}_4\text{Cl}_2$, 300 MHz, 110 °C): δ 13.5-29.5 (CH_3 and CH_2), 32.4 (CH_2CHNCOO), 60.0 (CH_2CHNCOO), 75.2 (COOCH_2), 95.1 (CCl_3CH_2), 154.1, 154.4 (COOCH_2).

Synthesis of PE-g-DBAD.³ Similar to the procedure described above, to a 25 mL round bottom flask was added PE powder (300 mg, 10.71 mmol repeat units), DBAD (2.05 g, 8.91 mmol), NHPI (61 mg, 0.375 mmol) and 1,1,2,2-tetrachloroethane (9 mL). The mixture was refluxed at 110 °C for 1 h and then precipitated in 200 mL of methanol. Precipitation was repeated another two times with toluene as the dissolving solvent. The product PE-g-DBAD was obtained after drying under vacuum for 24 h (264 mg). ^1H NMR ($o\text{-C}_6\text{D}_4\text{Cl}_2$, 400 MHz, 110 °C): δ 0.81-1.39 (br, CH_3 and CH_2), 1.42 (s, $\text{OC}(\text{CH}_3)_3$), 4.07 (br, CH_2CHNCOO), 5.79 (br, NHCOO); ^{13}C NMR ($o\text{-C}_6\text{D}_4\text{Cl}_2/o\text{-C}_6\text{H}_4\text{Cl}_2$, 300 MHz, 110 °C): δ 13.8-29.8 (CH_3 and CH_2), 28.3 ($\text{OC}(\text{CH}_3)_3$), 32.9 (CH_2CHNCOO), 58.2 (CH_2CHNCOO), 80.3 ($\text{OC}(\text{CH}_3)_3$), 155.3, 155.8 ($\text{COOC}(\text{CH}_3)_3$).

Synthesis of PE-g-NHNH₂.⁴ To a 25 mL two-neck round bottom flask was added PE-g-DBAD (160 mg), trifluoroacetic acid (2 mL) and tetrachloroethane (5 mL). The reaction was refluxed for 1 h at 110 °C under an N_2 atmosphere and then precipitated in 200 mL of methanol. The crude product was redissolved in toluene with a little NaOH solution added and stirring continued for 5 minutes. The mixture was then precipitated in methanol, filtered under vacuum and washed with a large amount of distilled water. The product was dried for 24 h under vacuum to obtain PE-g-NHNH₂ (128 mg). ^1H NMR ($o\text{-C}_6\text{D}_4\text{Cl}_2$, 400 MHz, 110 °C): δ 0.81-1.52 (br, CH_3 and CH_2), 1.94-2.24 (br, $\text{CH}_2\text{CHNHNH}_2$), 2.79 (br, $\text{CH}_2\text{CHNHNH}_2$); ^{13}C NMR ($o\text{-C}_6\text{D}_4\text{Cl}_2/o\text{-C}_6\text{H}_4\text{Cl}_2$, 300 MHz, 110 °C): δ 13.7-31.7 (CH_3 and CH_2), 32.8 ($\text{CH}_2\text{CHNHNH}_2$), 60.5 ($\text{CH}_2\text{CHNHNH}_2$).

Surface chemical modification of PE membrane. In a 50 mL round bottom flask,

PE membrane (160 mg, 5.71 mmol repeat units), BTCEAD (361 mg, 0.95 mmol), and NHPI (32 mg, 0.20 mmol) were added into dichloroethane (20 mL). The mixture was refluxed at 80 °C. After reacting for 24 h, the mixture was cooled to room temperature. The membrane was washed with methanol and CH₂Cl₂ three times, and then dried at 40 °C under vacuum. Similar to the procedure described above for the DBAD system.

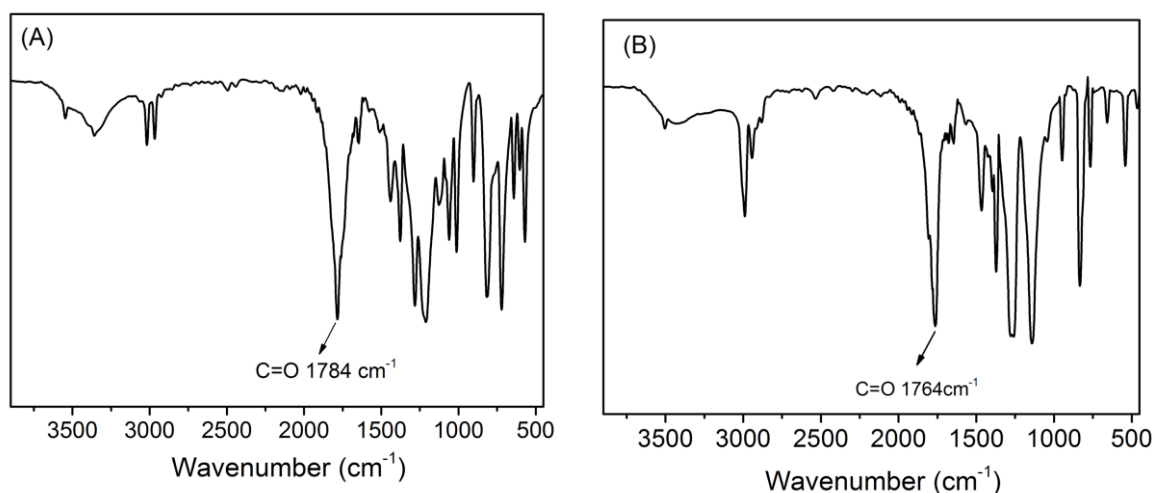


Figure S1. FT-IR spectra of (A) bis(2,2,2-trichloroethyl) azodicarboxylate (BTCEAD) and (B) di-*tert*-butyl azodicarboxylate (DBAD).

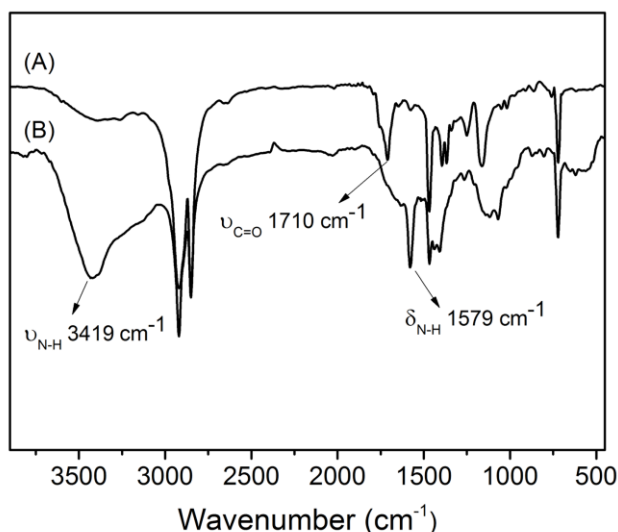


Figure S2. FT-IR spectra of (A) PE-g-DBAD (Entry 6, Table 2) and (B) PE-g-NHNH₂.

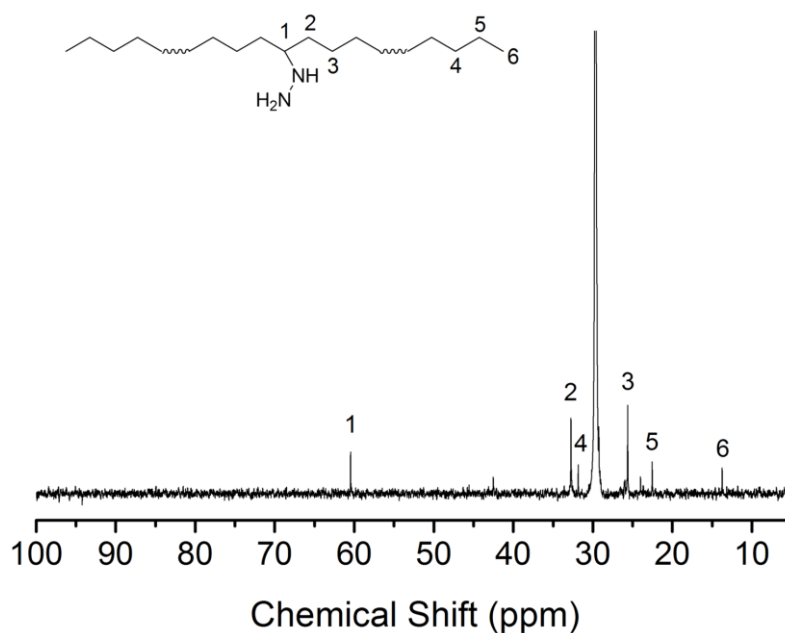


Figure S3. ^{13}C NMR ($o\text{-C}_6\text{D}_4\text{Cl}_2/o\text{-C}_6\text{H}_4\text{Cl}_2$, 300 MHz, 110 °C) spectrum of PE-*g*-NHNH₂ derived from PE-*g*-DBAD (Entry 6, Table 2).

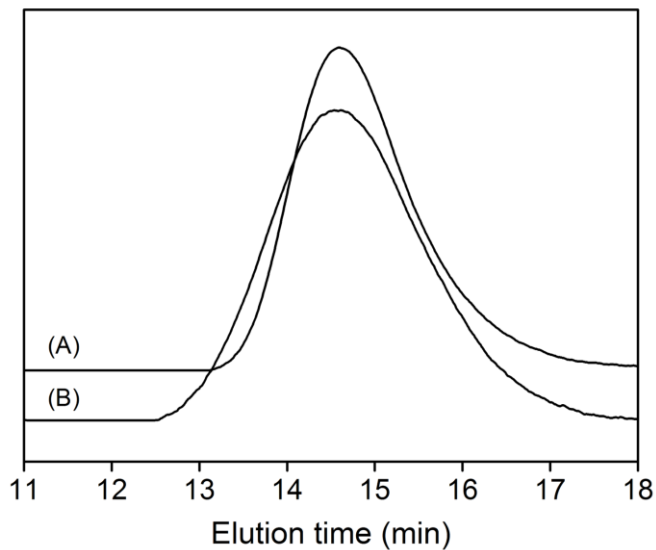


Figure S4. SEC traces of (A) PE-*g*-DBAD (Entry 6, Table 2) [M_n = 11.6 kg/mol, PDI = 2.56] and (B) PE-*g*-NHNH₂ [M_n = 11.9 kg/mol, PDI = 3.53]. M_n and PDI were based on the refractive index detector results.

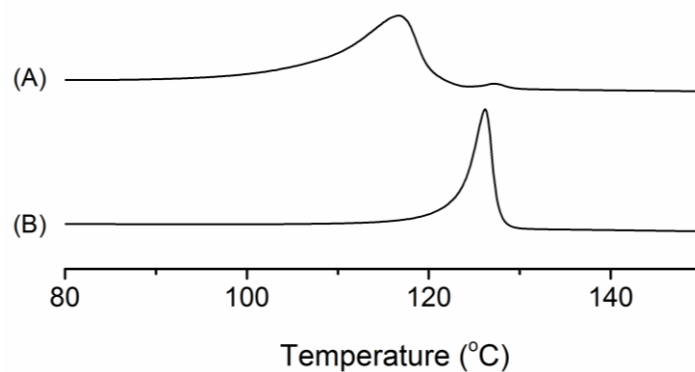


Figure S5. DSC curves of (A) PE-g-DBAD (Entry 6, Table 2) and (B) PE-g-NHNH₂.

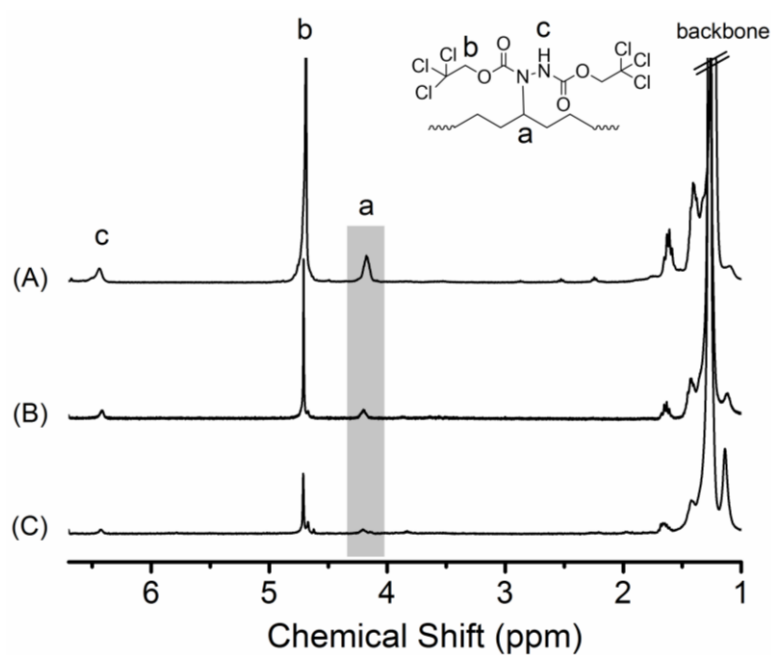


Figure S6. ¹H NMR spectra of (A) PE-g-BTCEAD (Entry 9, Table 1), (B) PE-g-BTCEAD (Entry 6, Table 1) and (C) PE-g-BTCEAD (Entry 3, Table 1) in *o*-C₆D₄Cl₂ at 110 °C.

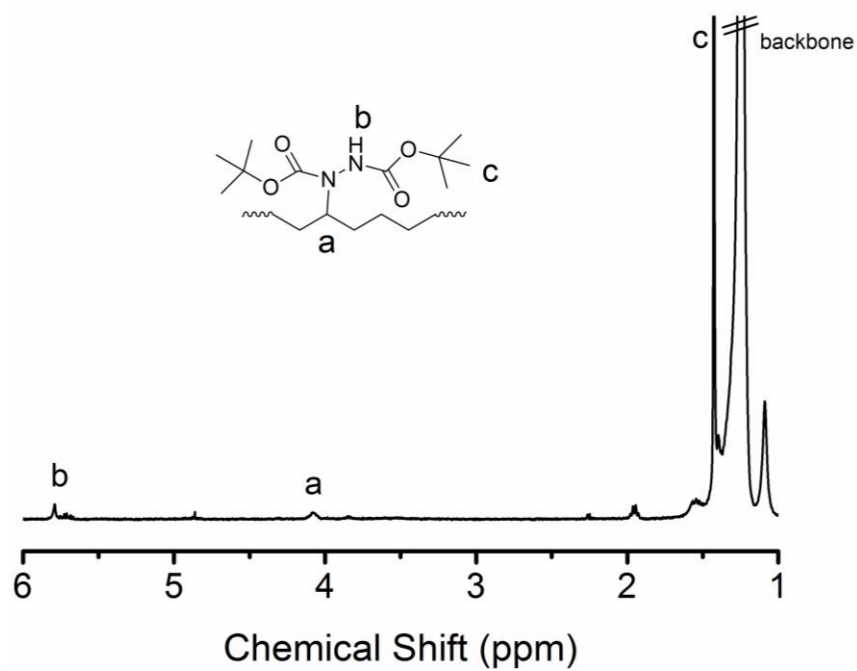


Figure S7. ^1H NMR spectrum of PE-g-DBAD (Entry 4, Table 2) in $o\text{-C}_6\text{D}_4\text{Cl}_2$ at 110 $^\circ\text{C}$.

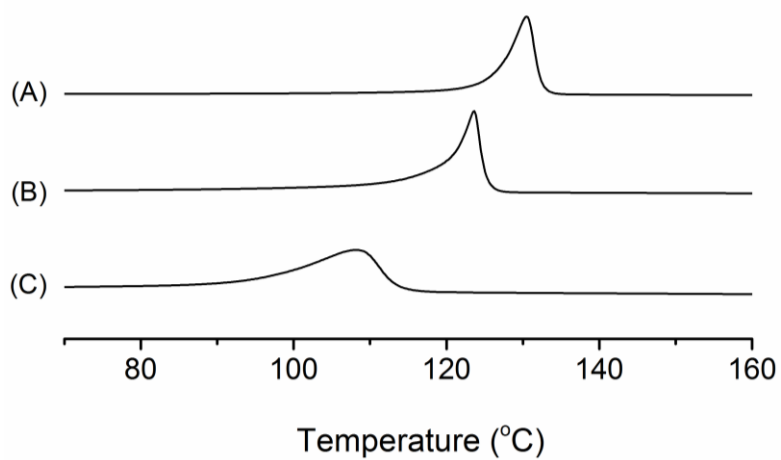


Figure S8. DSC curves of (A) original PE, (B) PE-g-DBAD (Entry 3, Table 2) and (C) PE-g-BTCEAD (Entry 7, Table 1).

Table S1. SEC and DSC characterization results of modified PE.

polymer	M_n^a (kg/mol)	PDI ^a	T_m^b (°C)	X_c^b (%)
Entry 3, Table 1	9.6	1.73	121	36
Entry 6, Table 1	10.9	1.60	119	29
Entry 7, Table 1	12.7	1.62	108	18
Entry 8, Table 1	16.9	1.70	90	9
Entry 9, Table 1	19.6	1.55	80	-
Entry 10, Table 1	18.2	1.54	78	-
Entry 2, Table 2	7.0	1.92	124	50
Entry 3, Table 2	8.5	1.73	123	47
Entry 4, Table 2	9.4	1.80	119	38
Entry 5, Table 2	10.7	1.77	114	33
Entry 7, Table 2	10.4	1.81	107, 119	30

^a Determined by high temperature SEC with standard polystyrene as calibration;

^b Calculated from DSC tests.

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- [3] Amaoka, Y.; Kamijo, S.; Hoshikawa, T.; Inoue, M. *J. Org. Chem.* **2012**, *77*, 9959.
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