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Supporting Information

Radical Coupling Polymerization (RCP) for Synthesis of Various Polymers

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1. Experimental section

1.1 Materials

Tetrahydrofuran (THF) was distilled from sodium. Anisole was washed with 2M NaOH three times, then washed twice with water, dried over $CaCl_2$, filtered, and finally distilled under vacuum. Dimethyl sulfoxide (DMSO) was distilled under vacuum. Dichloromethane (CH_2Cl_2) was distilled over calcium hydride before use. Copper powder (0.50-1.5 μm, Alfa, 99.9%) was treated with hydrochloric acid and washed successively with water, acetone, and methylene chloride. N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, Alfa, 98%), tris(2-(dimethylamino)ethyl)amine (Me_6TREN, Alfa, >99%), ethylene glycol (Sinopharm Chemical Reagent, SCR), 4-methylbenzoic acid(Alfa, 98%), 4-ethylbenzoic acid (J&K Chemistry), 4-ethylbenzenesulfonyl chloride (J&K Chemistry) and ethylbenzene (SCR, >98.5%) were used as received. Tris[(2-pyridyl)methyl]amine (TPMA)[1] and 2-methyl-2-nitrosopropane (MNP) dimer [2] was synthesized according to previously reported procedures.

1.2 Characterization methods

Number average molecular weights (M_n) and molecular weight distributions were determined by gel permeation chromatograph (GPC) on a Waters 1515 equipped with two PLgel 5 μm MIXED-C columns using polystyrene standards and THF as the eluent at a flow rate of 1.0 mL/min at 40 °C. ^{1}H NMR and ^{13}C NMR spectra were collected with a Bruker 400 MHz ^{1}H NMR using $CDCl_3$ as a solvent. Elemental analyses were performed on a Flash EA1112 (Thermo Finnigan). Infrared spectrum was recorded on a Bruker VECTOR 220 spectrometer using KBr pressed disks. GC-MS (m/z) were performed using a GCT Premier GC-TOFMA.

1.3 Synthesis of monomers

1.3.1 *Synthesis of 1,4-bis(1-bromoethyl)benzene* (*BBEB*)

11.7 g of N-bromosuccinimide (NBS, 66 mmol), 0.3 g of benzoyl peroxide, 4.7 mL of 1,4-diethylbenzene (30 mmol) and 50 mL of CCl_4 were placed in 100 mL three-neck round-bottom flask equipped with a reflux condenser. The solution was bubbled with N_2 for 10 minutes then refluxed for 4 hours. The suspension obtained was filtered and concentrated. The crude product was purified by recrystallization from n-hexane to give white crystal (60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 7.41 (s, 4H, Ar***H***), 5.22-5.17 (q, 2H, ArC***H***BrCH$_3$), 2.04-2.03 (d, 6H, 2CHBrC***H***$_3$). ^{13}C NMR(400 MHz, $CDCl_3$): 143.31, 48.86, 26.75. Anal. Calcd. (%): C, 41.13; H, 4.14; Found (%): C, 40.97; H, 4.12. GC-MS (m/z): 291.9 $[M]^+$, 211.1 $[M-Br]^+$, 132.2 $[M-2Br]^+$, 117.2 $[M-2Br-CH_2]^+$.

1.3.2 *Synthesis of 1,4-bis(bromomethyl)benzene* (*BBMB*)

BBMB was prepared from 1,4-dimethyl-benzene as described above. The crude product was purified by recrystallization from methanol to give white crystal (60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 7.37 (s, 4H, Ar***H***), 4.49 (s, 4H, ArC***H***$_2$Br). ^{13}C NMR(400 MHz, $CDCl_3$): 138.02, 129.69, 32.85. Anal. Calcd. (%): C, 36.40; H, 3.05; Found (%): C, 36.67; H, 3.03. GC-MS (m/z): 263.9[M]$^+$, 183.0 [M-Br]$^+$, 104.0 [M-2Br]$^+$.

1.3.3 *Synthesis of bis(4-bromomethylphenyl) ether (BMPE)*

BMPE was prepared from p-tolyl ether as described above (47% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 7.38-7.34 (d, 4H, Ar***H***), 6.99-6.95 (d, 4H, Ar***H***), 4.51 (s, 4H, ArC***H***$_2$Br). ^{13}C NMR(400 MHz, $CDCl_3$): 156.94, 132.95, 130.73, 119.18, 33.23. Anal. Calcd.(%): C, 47.23; H, 3.40; Found (%): C, 47.22; H, 3.41. GC-MS (m/z): 355.9[M]$^+$, 275.1 [M-Br]$^+$, 196.2 [M-2Br]$^+$.

1.3.4 *Synthesis of methyl 2,5-bis(bromomethyl)benzoate (MBMB)*

3.0 g of 2,5-dimethylbenzoic acid (20mmol), 50 mL of methanol (12mol) and 0.3 mL of concentrated sulphuric acid were placed in 100 mL round-bottom flask equipped with a reflux condenser. The mixture was refluxed for 6 hours and washed with saturated aqueous solution of $NaHCO_3$ and water. The organic layer was dried over magnesium sulfate, filtered, and then dried under vacuum. Methyl 2,5-dimethylbenzoate was obtained and used without further purification. MBMB was prepared by bromination of methyl 2,5-dimethylbenzoate with NBS as described above (28% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 8.00 (m, 1H, Ar***H***), 7.54-7.51 (m, 1H, Ar***H***), 7.46-7.43 (m, 1H, Ar***H***), 4.94 (s, 2H, C***H***$_2$Br), 4.48 (s, 2H, C***H***$_2$Br), 3.96 (s, 3H, OC***H***$_3$). ^{13}C NMR(400 MHz, $CDCl_3$): 166.42, 139.39, 138.34, 132.99, 132.32, 131.87, 129.45, 52.47, 31.85, 30.90. Anal. Calcd. (%): C, 37.30; H, 3.13; Found (%): C, 37.09; H, 3.14. GC-MS (m/z): 321.9 [M]$^+$, 240.9 [M-Br]$^+$, 162.1 [M-2Br]$^+$, 147.1 [M-2Br-Me]$^+$, 131.1 [M-2Br-OMe]$^+$.

1.3.5 *Synthesis of ethylene bis(4-bromomethyl)benzoate (EBMB)*

4-(bromomethyl)benzoic acid was prepared by bromination of 4-methylbenzoic acid with NBS as described above. 4.3 g of 4-(bromomethyl)benzoic acid (20 mmol) and 8.8 mL of $SOCl_2$ (120 mmol) were refluxed for 1.5 hours. HCl and SO_2 evolved were neutralized with saturated solution of NaOH. 4-(bromomethyl)benzoyl chloride was obtained after the excessive $SOCl_2$ was removed under reduced pressure and dissolved in 20 mL of dry CH_2Cl_2. The mixture was cooled to 0 ℃ and a solution of 0.62 g of ethylene glycol (10mmol) and 1.6mL of pyridine (20 mmol) in 30 mL of dry CH_2Cl_2 was added dropwise. The temperature was allowed to rise to room temperature and stirred overnight. Then the solution was washed with 1 M HCl three times, followed by saturated $NaHCO_3$ solution, water and brine. The organic layer was dried over magnesium sulfate, filtered, and then concentrated. The crude product was purified by recrystallization from methanol to give white crystal (66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 8.04-8.01 (d, 4H, Ar***H***), 7.48-7.45 (d, 4H, Ar***H***), 4.66 (s, 4H, O(C$\boldsymbol{H}_2$)$_2$O), 4.50 (s, 4H, C$\boldsymbol{H}_2$Br). ^{13}C NMR(400 MHz, $CDCl_3$): 165.80, 142.94, 130.23, 129.68, 129.12, 62.83, 32.17. Anal. Calcd. (%): C, 47.40; H, 3.54; Found (%): C, 47.83; H, 3.48. GC-MS (m/z): 455.9 $[M]^+$, 377.1 $[M\text{-}Br]^+$, 163.1 $[M\text{-}2Br\text{-}PhCOO\text{-}CH_2]^+$

1.3.6 *Synthesis of ethylene bis(4-(1-bromoethyl))benzoate (EBEB)*

3.0 g of 4-ethylbenzoic acid (20 mmol) and 4.0 mL of $SOCl_2$ (55 mmol) were refluxed for 2 hours. HCl and SO_2 evolved were neutralized with saturated solution of NaOH. 4-ethylbenzoyl chloride was obtained after the excessive $SOCl_2$ was removed under reduced pressure. The 4-ethylbenzoyl chloride was dissolved in 20 mL of CH_2Cl_2. The mixture was cooled to 0 ℃ and a solution of 0.62 g of ethylene glycol (10 mmol) and 1.6 mL of pyridine (20 mmol) in 30 mL of dry CH_2Cl_2 was added dropwise. The temperature was allowed to rise to room temperature and stirred overnight. Then the solution was washed with 1 M HCl three times, followed by saturated $NaHCO_3$ solution, water and brine. The organic layer was dried over magnesium sulfate, filtered, and dried under vacuum. The obtained ethylene-bis(4-ethylbenzoate) was used without further purification in the next step. EBEB was prepared by bromination of ethylene- bis(4-ethylbenzoate) with NBS as described above (23% yield). ^{1}H NMR (400MHz, $CDCl_3$): 8.04-8.01 (d, 4H, Ar***H***), 7.52-7.49 (d, 4H, Ar***H***), 5.23-5.16 (t, 2H, ArC***H***BrCH$_3$), 4.66 (s, 4H, O(C$\boldsymbol{H}_2$)$_2$O), 2.05-2.03 (d, 6H, ArCHBrC$\boldsymbol{H}_3$). Anal. Calcd.(%): C, 49.61; H, 4.16; Found (%): C, 48.96; H, 4.15.

1.3.7 *Synthesis of bis(4-(1-bromoethyl)phenyl) sulfone (BEPS)*

2.1 g of 4-ethylbenzene sulfonyl chloride (10 mmol), 4 mL of ethylbenzene (33 mmol) and 1.33 g of anhydrous $AlCl_3$ (10mmol) in 100 mL three-neck round-bottom flask were stirred at room temperature. After 3 hours, 30 mL of ice-water was poured into reaction mixture and the aqueous layer was extracted with ether (2×40 mL). The combined organic layers were dried over magnesium sulfate, filtered, and dried under vacuum to give the crude product as white solid. The crude product was purified by recrystallization from methanol to give bis((4-ethyl)phenyl) sulfone (49% yield) as white crystal. BEPS was prepared by bromination of bis(4-ethylphenyl) sulfone with NBS as described above. The crude product was purified by recrystallization from CCl_4 (58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 7.93-7.89 (d, 4H, Ar***H***), 7.58-7.54 (d, 4H, Ar***H***), 5.18-5.11 (q, 2H, ArC***H***BrCH$_3$), 2.02-2.00 (d, 6H, ArCHBrC$\boldsymbol{H}_3$). ^{13}C NMR (400 MHz, $CDCl_3$): 148.68, 141.03, 128.24, 127.89, 46.98, 26.52. Anal. Calcd.(%): C, 44.47; H, 3.73; Found (%): C, 43.83; H, 3.87. GC-MS (m/z): 352.9 $[M-Br]^+$, 273.1 $[M-2Br]^+$.

1.4 Procedure for the Radical Coupling Polymerization

Method A is used for ligand TPMA and method B for ligands PMDETA and Me_6TREN.

Method A: In a typical procedure, for example, 29.2 mg of BBEB (0.1 mmol), 58.0 mg of TPMA (0.2 mmol) and 14.1 mg of copper powder (0.22 mmol) were added to an ampule equipped with a stir bar. The ampule was degassed, backfilled four times with N_2, and then left under N_2. Deoxygenated 1 mL of THF was then added. The ampule was heated at 60 ℃ for 2 hours. The ampule was immersed in liquid nitrogen and the mixture was diluted with THF and purified by passing through a neutral alumina column. The solution was concentrated, precipitated with methanol and dried under vacuum at 40 ℃ to yield polymer. The yield was determined gravimetrically and the conversion was calculated by $W_{polymer}/(W_{monomer}$*weigh fraction of carbon and hydrogen of monomer).

Method B: In a typical procedure, for example, 29.2 mg of BBEB (0.1 mmol), 14.1 mg of copper powder (0.22 mmol) were added to an ampule equipped with a stir bar. The ampule was degassed, backfilled four times with N_2, and then left under N_2. Deoxygenated 42 μL of PMDETA (0.2 mmol) and 1 mL of THF were then added. The ampule was heated at 60 ℃ for 2 hours. The ampule was immersed in liquid nitrogen and the mixture was diluted with THF and purified by passing through a neutral alumina column. The solution was concentrated, precipitated with methanol and dried under vacuum at 40 ℃ to yield polymer. The yield was determined gravimetrically and the conversion was calculated by $W_{polymer}/(W_{monomer}$*weigh fraction of carbon and hydrogen of monomer).

1.5 Procedure for the Radical Addition Coupling Polymerization

In a typical procedure, for example, 26.4 mg of BBMB (0.1 mmol), 58.0 mg of TPMA (0.2 mmol), 8.7 mg of MNP (0.1 mmol) and 14.1 mg of copper powder (0.22 mmol) were added to an ampule equipped with a stir bar. The ampule was degassed, backfilled four times with N_2, and then left under N_2. Deoxygenated 1 mL of THF was then added. The ampule was heated at 60 ℃ for 4 hours. The ampule was immersed in liquid nitrogen and the mixture was diluted with THF and purified by passing through a neutral alumina column. The solution was concentrated, precipitated with methanol and dried under vacuum at 40 ℃ to yield polymer. The yield was determined gravimetrically.

2 Spectra of monomers and polymers

2.1 NMR and MS spectra of monomers

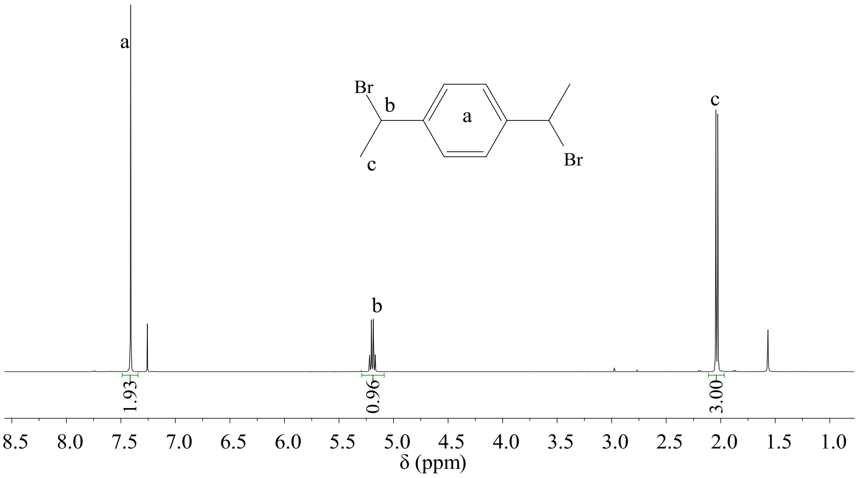

Fig. S1 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of BBEB

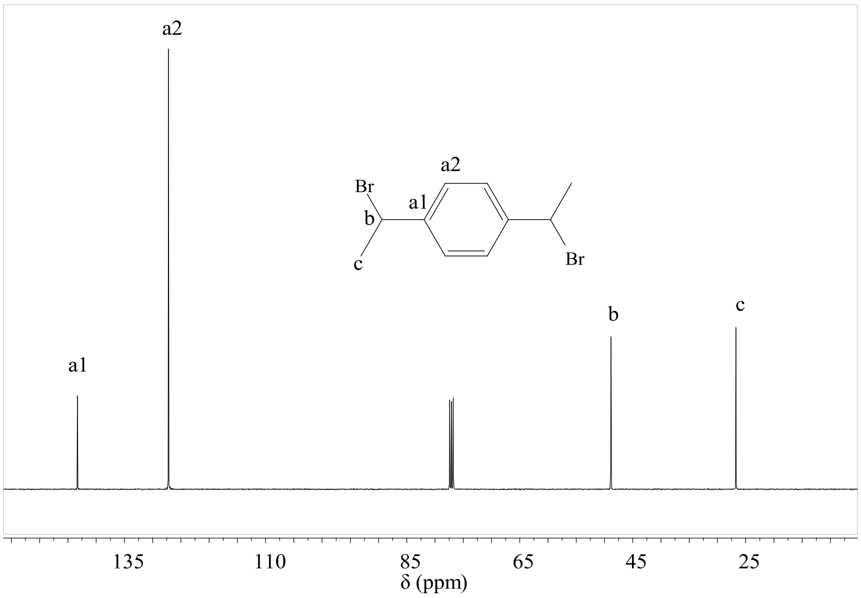

Fig. S2 ^{13}C NMR (400 MHz, CDCl$_3$) spectrum of BBEB

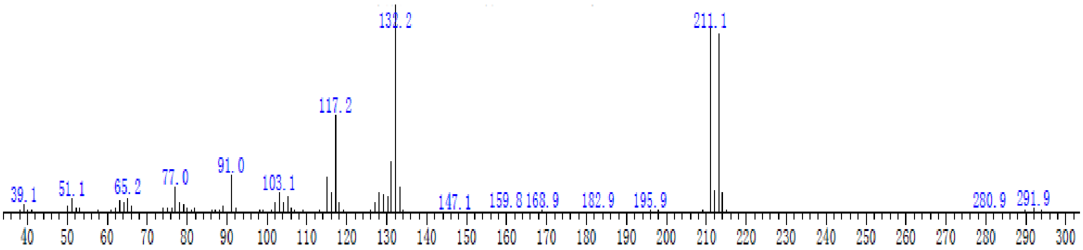

Fig. S3 GC-MS spectrum of BBEB

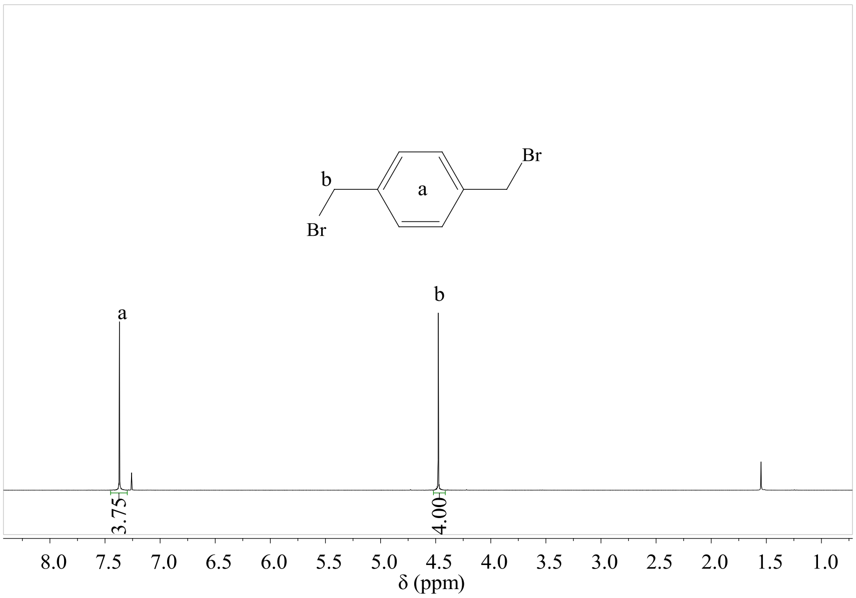

Fig. S4 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of BBMB

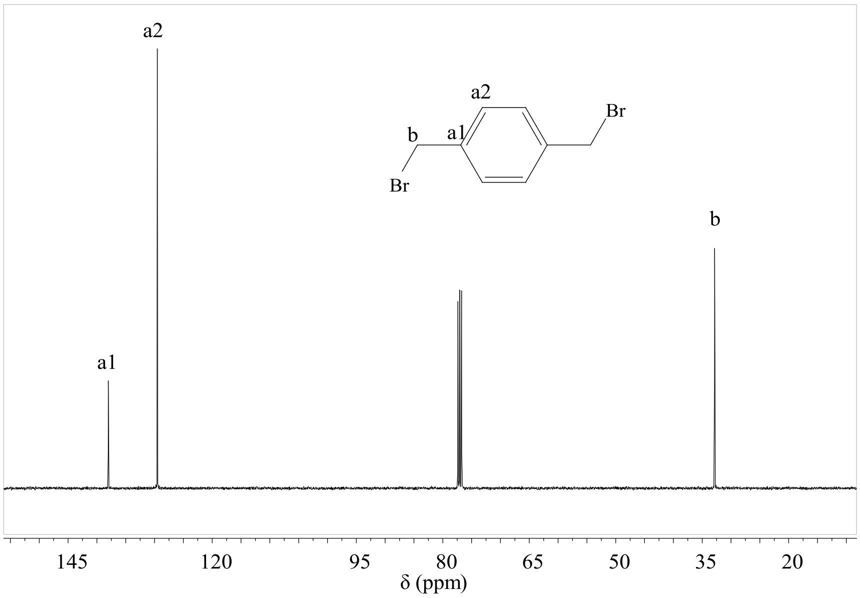

Fig. S5 ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of BBMB

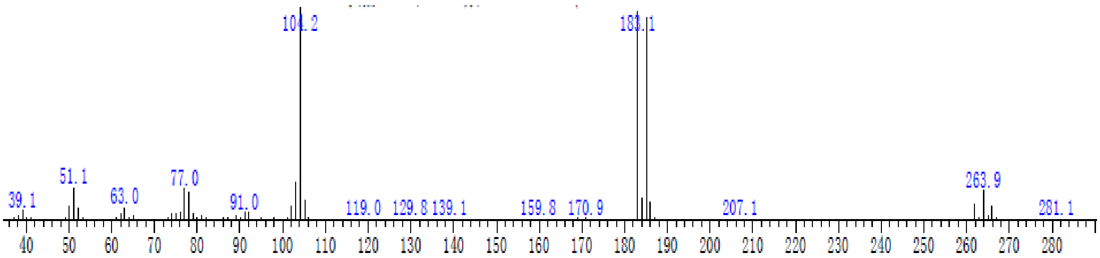

Fig. S6 GC-MS spectrum of BBMB

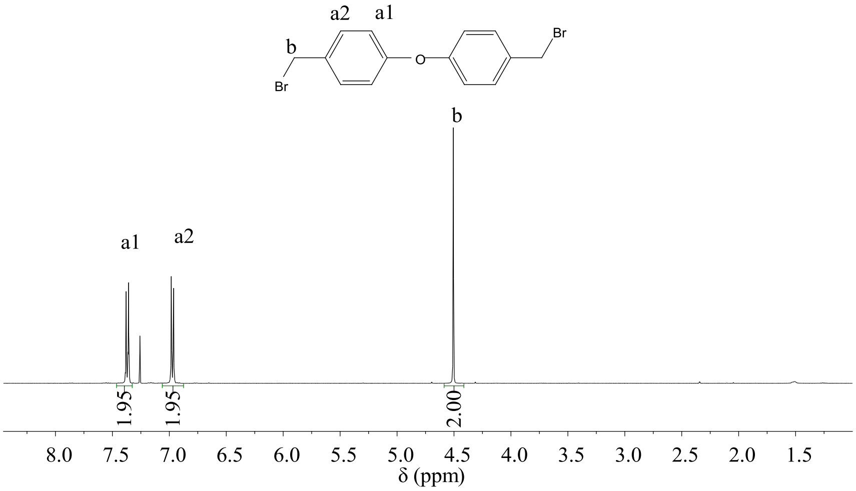

Fig. S7 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of BMPE

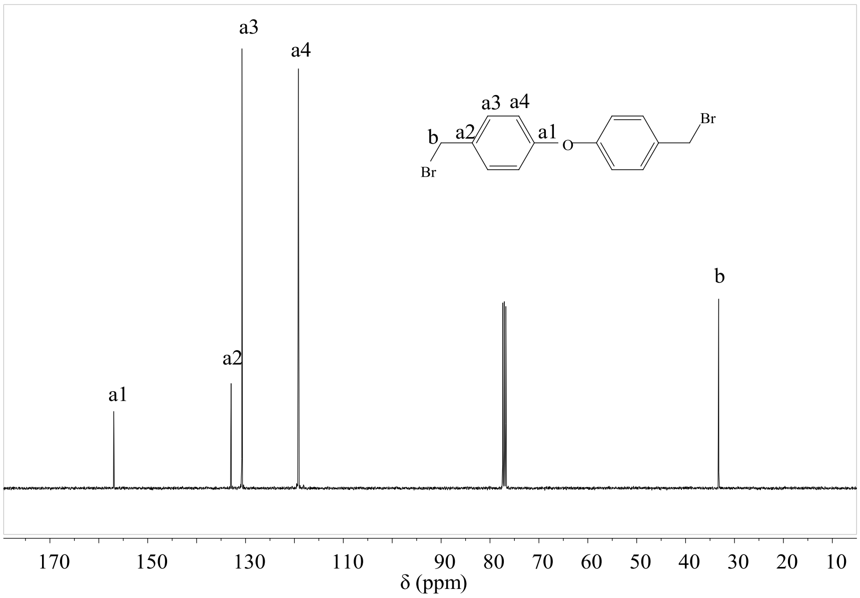

Fig. S8 ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of BMPE

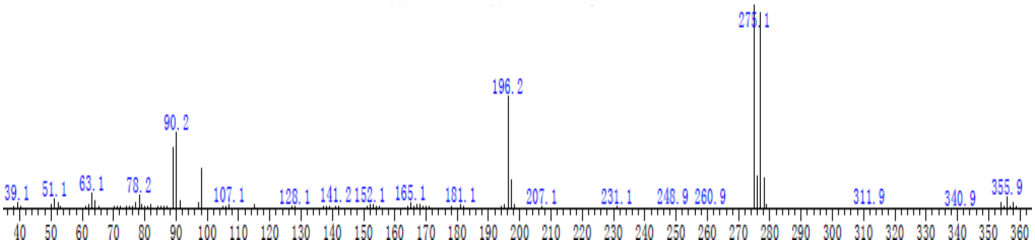

Fig. S9 GC-MS spectrum of BMPE

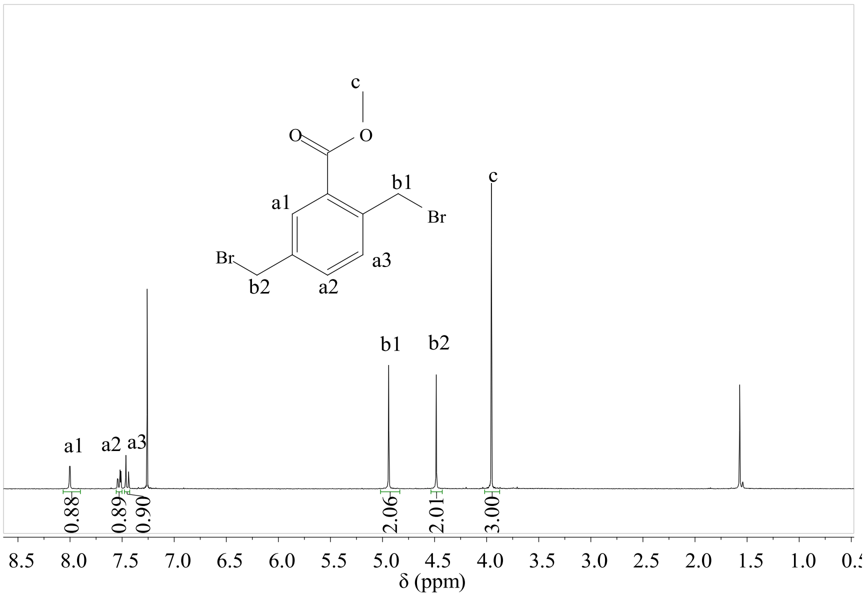

Fig. S10 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of MBMB

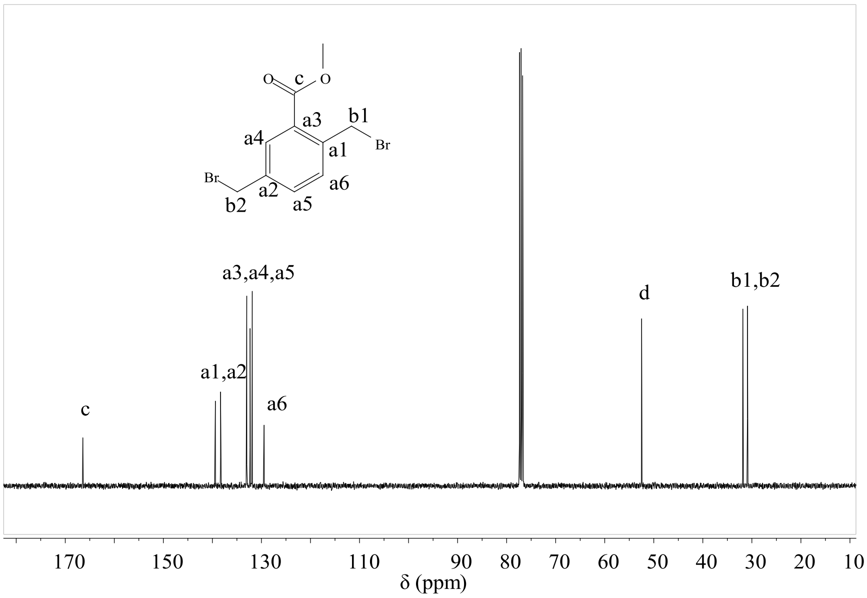

Fig. S11 ^{13}C NMR (400 MHz, CDCl$_3$) spectrum of MBMB

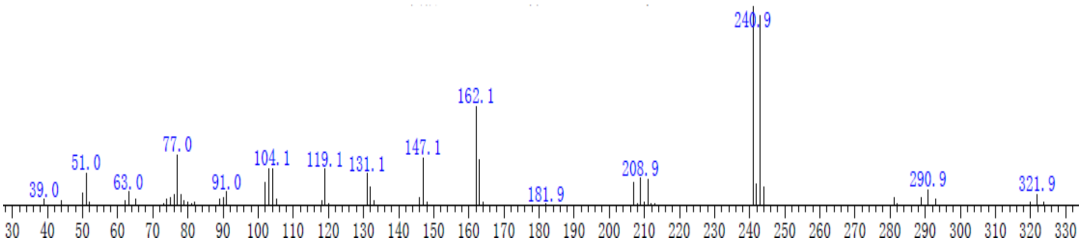

Fig. S12 GC-MS spectrum of MBMB

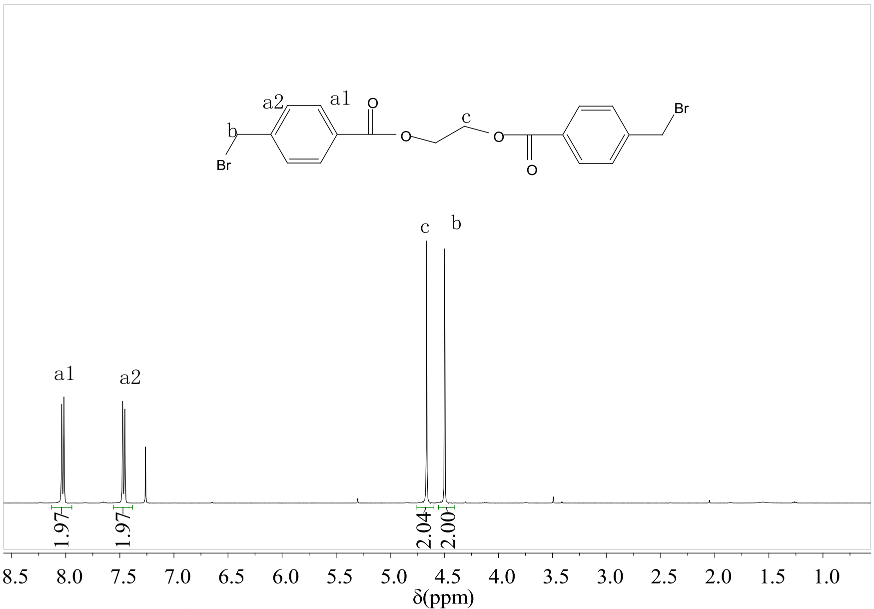

Fig. S13 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of EBMB

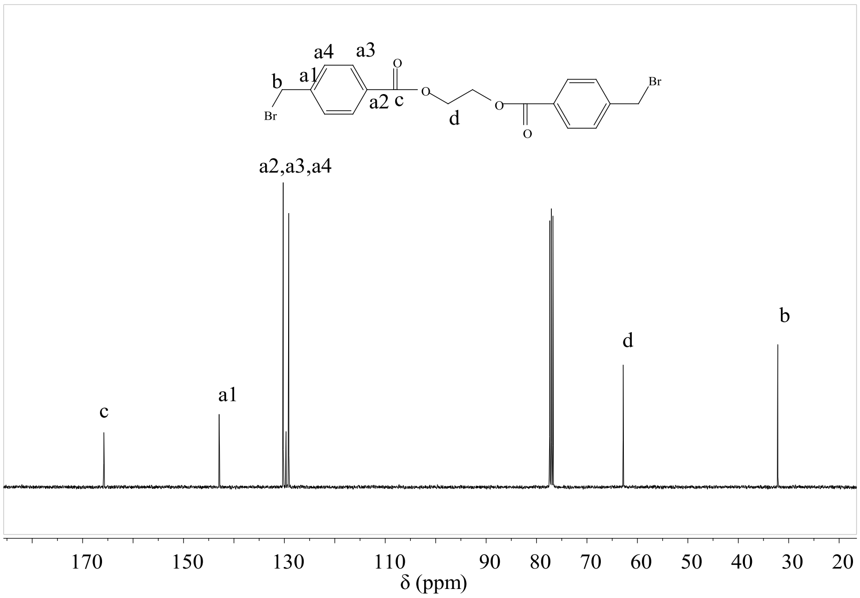

Fig. S14 ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of EBMB

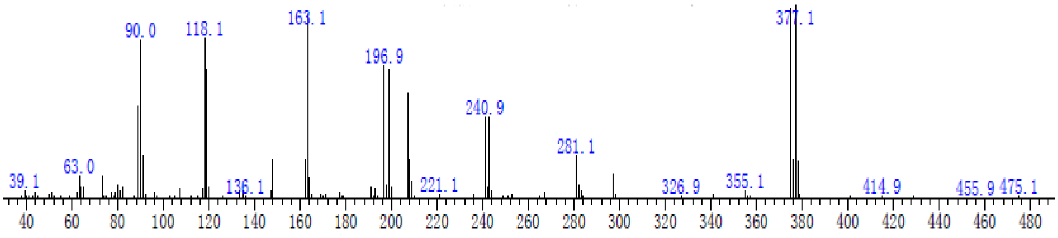

Fig. S15 GC-MS spectrum of EBMB

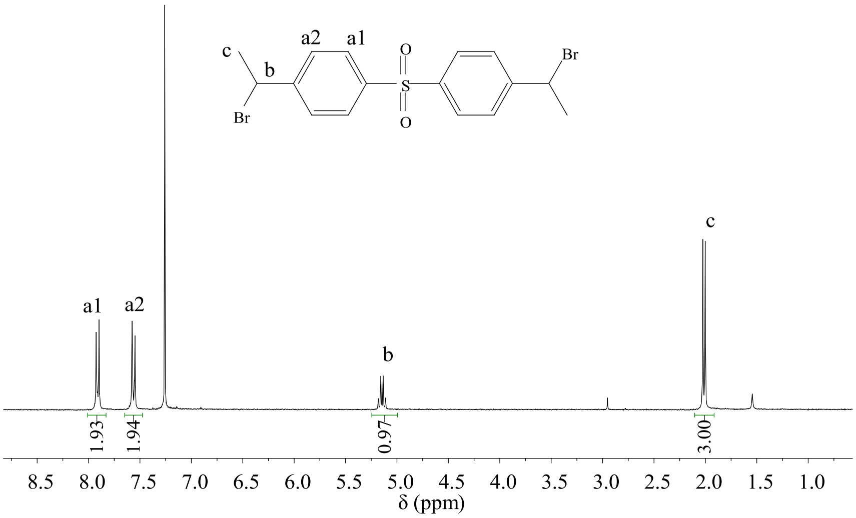

Fig. S16 ^{13}H NMR (400 MHz, $CDCl_3$) spectrum of BEPS

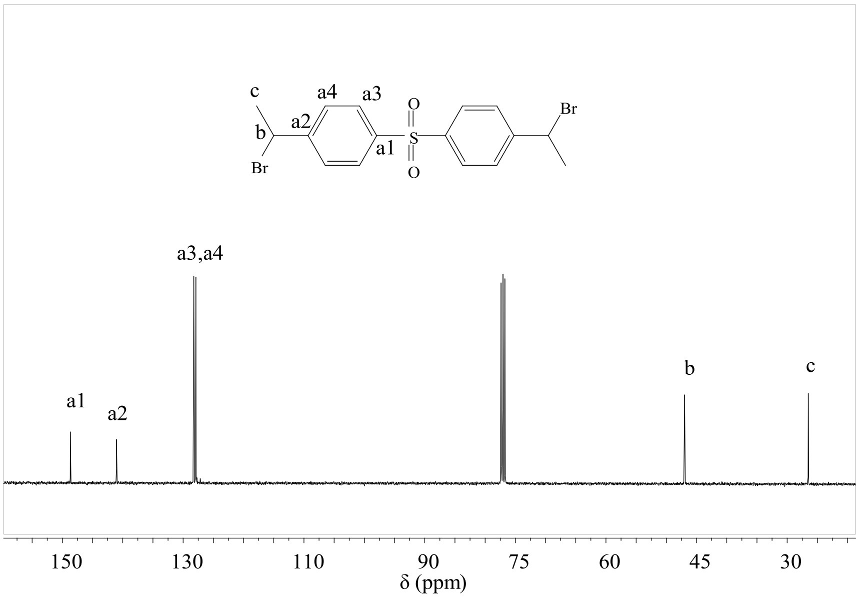

Fig. S17 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of BEPS

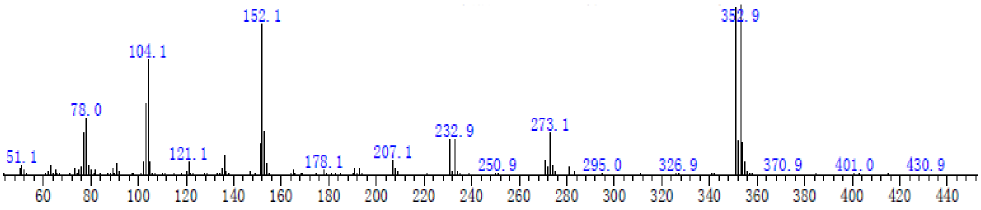

Fig. S18 GC-MS spectrum of BEPS

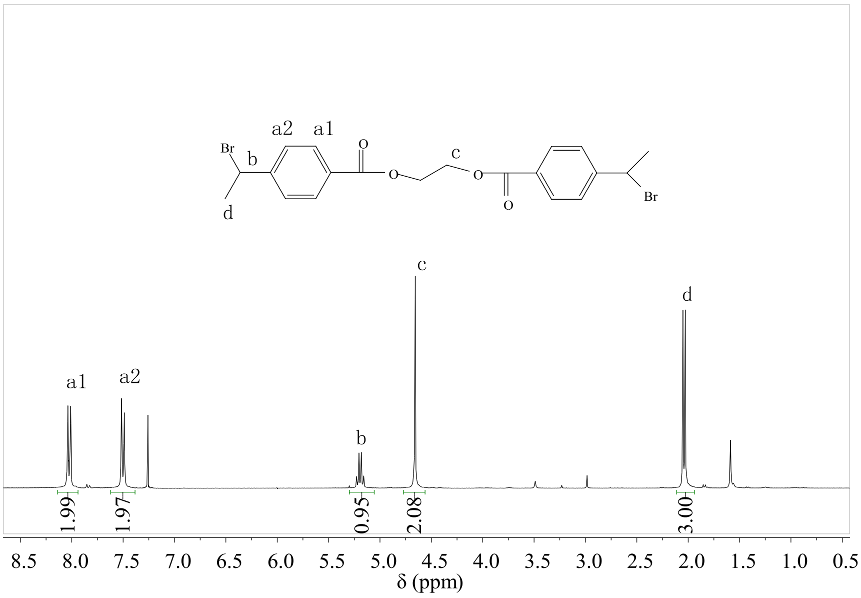

Fig. S19 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of EBEB

2.2 NMR spectra of polymers

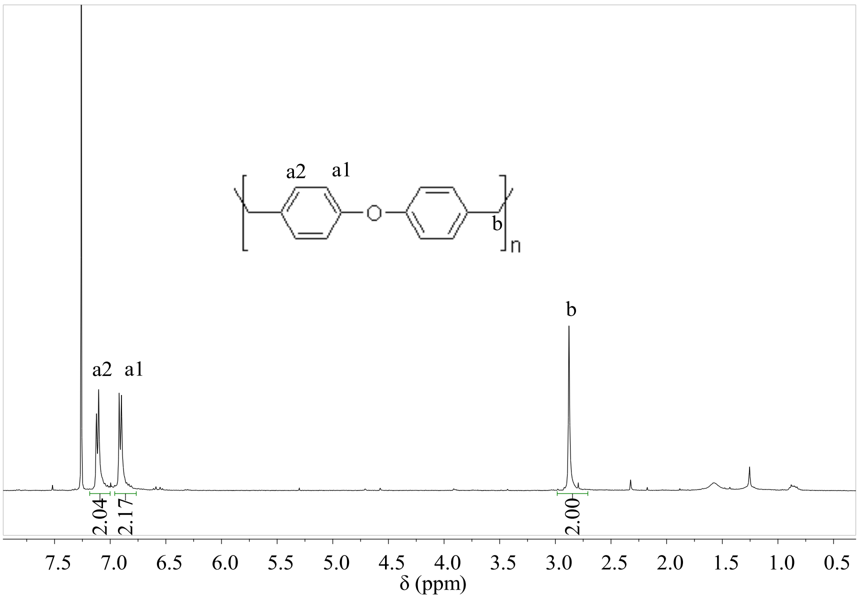

Fig. S20 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of polymer prepared by BMPE

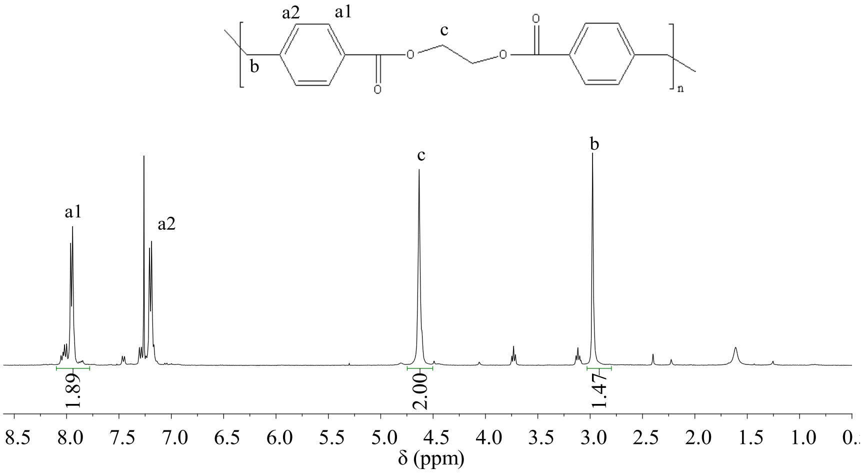

Fig. S21 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of polymer prepared by EBMB

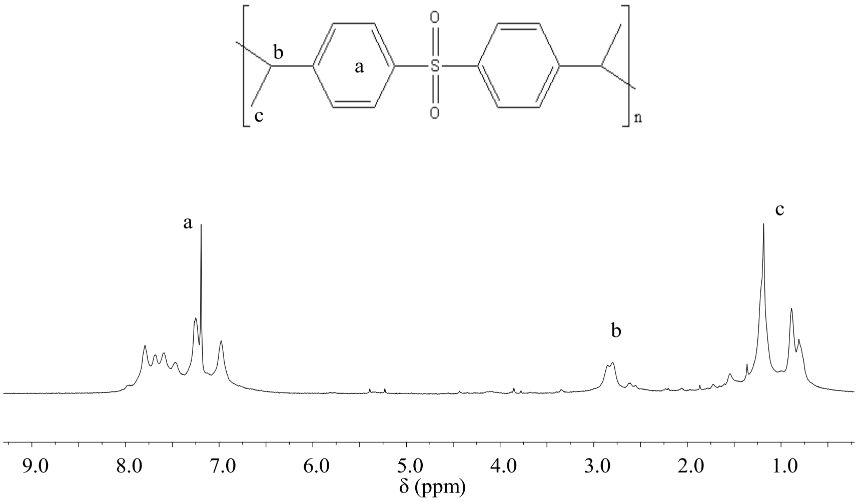

Fig. S22 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of polymer prepared by BEPS

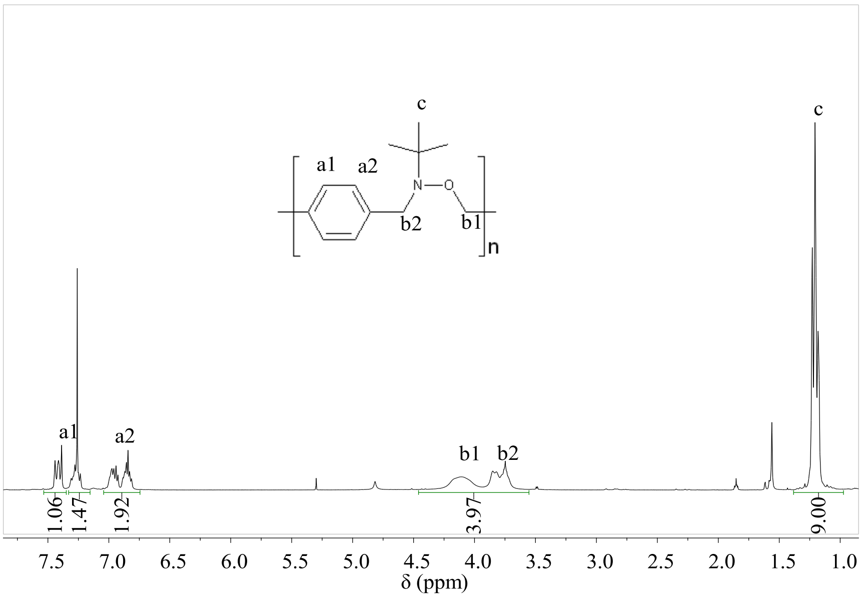

Fig. S23 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of polymer prepared by BBMB and MNP

(M_n=8900, PDI=1.60, [MNP]/ [BBMB]= $(S_{Hc}/9)/((S_{Hb1}+ S_{Hb2})/4)$=1.01)

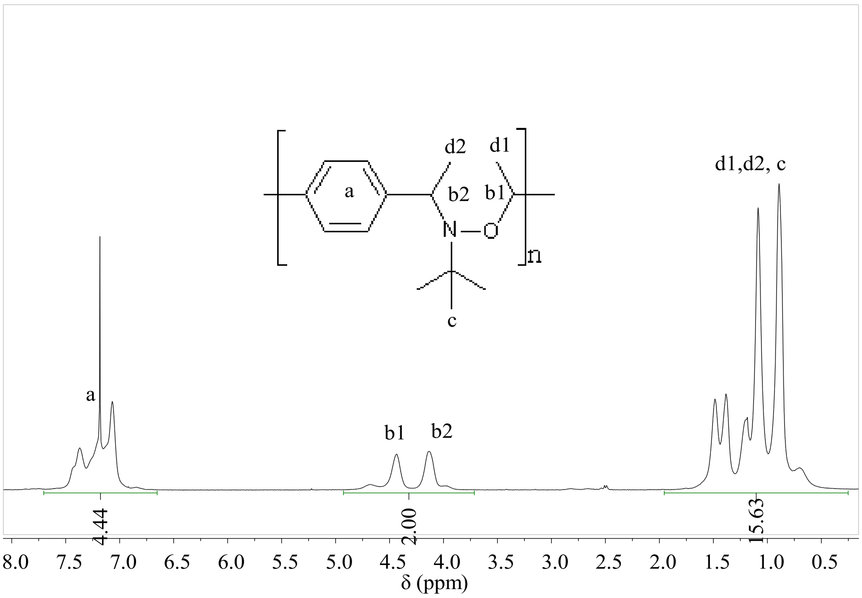

Fig. S24 ^1H NMR (400 MHz, $CDCl_3$) spectrum of polymer prepared by BBEB and MNP (M_n= 17200, PDI=2.12, [MNP]/[BBEB]= $((S_{Hd1}+S_{Hd2}+S_{Hc}) - 3*(S_{Hb1}+S_{Hb2}))/9/((S_{Hb1}+S_{Hb2})/2)$ =1.07)

2.3 IR spectrum of polymer prepared by BBMB

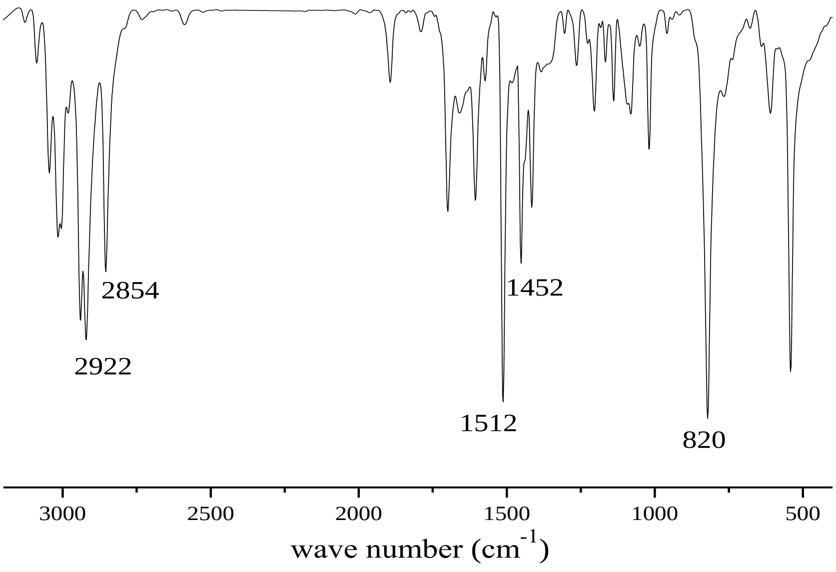

Fig. S25 Infrared spectrum of polymer prepared by BBMB

EA result: C，81.02%；H，7.10%；N，0.24%

Reference

(1) Tyeklar, Z.; Jacobson, R. R.; Wei, N.; Murthy, N. N.; Zubieta, J.; Karlin, K. D. *Journal of the American Chemical Society* **1993**, *115*, 2677.

(2) Stowell, J. C. *J Org Chem* **1971**, *36*, 3055.