

Supporting Information

Polyacrylates Networks Synthesized by Endlinking of 3-armed Precursor via Radical Addition Coupling Reaction

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1. Experimental Section

1.1 Materials

Methyl acrylate (MA), *tert*-butyl acrylate (*t*BA) and styrene (St) were dried and distilled under reduced pressure before use and stored under -5 °C. α -Methyl styrene (AMS) was purified by passing through a alkaline alumina column. Tetrahydrofuran (THF) was distilled from sodium benzophenone. CuBr (98%, Aldrich) was purified using a modified literature procedure¹. Copper powder (3.25-4.75 μ m, 99%, Alfa), 1,1,1-tris(hydroxymethyl)propane (TMP, 98%, Aladdin), 1,1-diphenylethylene (DPE, 98%, Alfa), 2-bromoisobutyryl bromide (BiBB, 97%, Alfa), N,N,N',N',N''-pentamethyl diethylenetriamine (PMDETA, 98%, Alfa), ethyl 2-bromopropionate (EBP, 99%, Alfa), 1,3,5-benzenetriol (99%, TCI) and all other reagents were used as received without further purification.

1.2 Characterization

Number average molecular weight (M_n) and molecular weight distributions were determined by gel permeation chromatograph (GPC) on a Water1515 equipped with two PL g d 5 μ m MIXED-C columns against linear polystyrene standards and THF as the eluent at a flow rate of 1.0 mL/min at 40 °C. ¹H NMR spectra were recorded at room temperature by a Bruker (400 MHz) spectrometer using tetramethylsilane as the internal standard, CDCl₃ and D₂O as the solvent.

1.3 Synthesis of Trifunctional Initiator



In a three-neck flask, TMP (2.7 g, 20 mmol) and triethylamine (9 mL, 65 mmol) were mixed in anhydrous CH₂Cl₂ (50 mL) at 0 °C. A 50 mL CH₂Cl₂ solution of 2-bromoisobutyryl bromide (10 mL, 80 mmol) was added dropwise over 2 h. Then the reaction solution was warmed to room temperature. It was stirred for another 24 h. The reaction mixture was washed with 1 M HCl solution (3×50 mL), saturated NaHCO₃ solution (3×50 mL) and saturated NaCl solution (3×50 mL). The combined organic extracts were dried over anhydrous MgSO₄. The solvent was removed under the vacuum, and the crude product was recrystallized twice from methanol, and finally dried under the vacuum at 40 °C to yield a white lamellar crystal. Yield, 78 %. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 4.19 (6H,

s, $\text{CH}_2\text{-O-C=O}$), 1.94 (18H, s, $\text{O=C-C}(\text{CH}_3)_2$ -), 1.65 (2H, q, $\text{CH}_3\text{-CH}_2$ -), 0.94 (3H, t, $\text{CH}_3\text{-CH}_2$ -).

1,3,5-tris(2'-Bromo-isobutyryloxy)benzene (initiator B), phenol-based trifunctional initiator, was prepared according to the reported method.²

1.4 Synthesis of Prepolymer

1.4.1 Synthesis of Poly(methyl acrylate) (PMA) by ATRP

EBP (285 μL , 2.2 mmol), PMDETA (46 μL , 0.22 mmol) and MA (4 mL, 44.4 mmol) were added to a Schlenk flask equipped with a stir bar. After three freeze-pump-thaw cycles, CuBr (32 mg, 0.22 mmol) was added under N_2 . The flask was heated at 60 °C for 20 min. The flask was immersed in liquid nitrogen and the solution was diluted with CH_2Cl_2 and purified by passing through a neutral alumina column. The solvent and monomer were then removed by evaporation, and the polymer was redissolved in CH_2Cl_2 and then precipitated by cold methanol/water (v/v, 1/1). It was finally dried under vacuum at 40 °C and analyzed by GPC and NMR. $M_{n, \text{GPC}} = 1240$ g/mol, PDI = 1.20. $M_{n, \text{NMR}} = 1270$ g/mol and terminal group functionality was 95.0 % analyzed by ^1H NMR.

1.4.2 Synthesis of 3-armed Poly(methyl acrylate) (tPMA) by ATRP

TBiBB (Initiator B, 578 mg, 1.0 mmol), PMDETA (41.8 μL , 0.2 mmol) and MA (5.7 mL, 90 mmol) were added to a Schlenk flask. After three freeze-pump-thaw cycles, CuBr (28.7 mg, 0.2 mmol) was added under N_2 . The flask was heated at 60 °C. After 3 h, the flask was immersed in liquid nitrogen. The solution was diluted with CH_2Cl_2 and purified by passing through a neutral alumina column. The solvent and monomer were then removed by evaporation, and the polymer was redissolved in CH_2Cl_2 and then precipitated by cold methanol/water (v/v, 1/1). After drying under vacuum at 40 °C, pure polymer was obtained. $M_{n, \text{GPC}} = 4070$ g/mol, PDI = 1.09, $M_{n, \text{NMR}} = 4830$ g/mol and terminal group functionality was 93.0 % analyzed by ^1H NMR.

1.4.3 Synthesis of 3-armed Poly(*tert*-butyl acrylate) (tPtBA) by ATRP

TBBMP (Initiator A, 407 mg, 0.7 mmol), PMDETA (29.2 μL , 0.14 mmol), *tert*-butyl acrylate (9.3 mL, 63 mmol) and 3 mL of acetone were added to a Schlenk flask. After three freeze-pump-thaw cycles, CuBr (20.1 mg, 0.14 mmol) was added under N_2 . The flask was heated at 60 °C. After 6 h, the flask was immersed in liquid nitrogen. The solution was diluted with CH_2Cl_2 and purified by passing through a neutral alumina column. The solvent and monomer were then removed by evaporation, and the polymer was redissolved in CH_2Cl_2 and then precipitated by cold methanol/water (v/v, 1/1). After drying under vacuum at 40 °C pure polymer was obtained. $M_{n, \text{GPC}} = 6900$ g/mol, PDI = 1.06, $M_{n, \text{NMR}} = 4770$ g/mol.

1.5 Radical Addition Coupling Reaction of Linear PMA

PMA-Br ($M_{n, \text{NMR}} = 1270$ g/mol, 114 mg, 0.09 mmol), PMDETA (22.6 μL , 0.108 mmol), α -methyl styrene (5.3 mg, 0.045 mmol) and 1.5 mL of THF were added to a Schlenk flask. After three freeze-pump-thaw cycles, Cu (6.9 mg, 0.108 mmol) was added under N_2 . The flask was heated at 50 $^\circ\text{C}$. After certain reaction time, the flask was immersed in liquid nitrogen. The solution was diluted with CH_2Cl_2 and purified by passing through a neutral alumina column. The polymer solution was concentrated and then dried under vacuum at 40 $^\circ\text{C}$. $M_{n, \text{GPC}} = 1850$ g/mol, PDI = 1.34.

RAC of DPE and styrene was carried out by the same procedure of α -methyl styrene.

1.6 Synthesis of Crosslinked PMA and Crosslinked PtBA

tPMA ($M_{n, \text{NMR}} = 4830$ g/mol, 145 mg, 0.03 mmol), PMDETA (22.6 μL , 0.108 mmol), α -methyl styrene (5.3 mg, 0.045 mmol) and 1.5 mL of THF were added to a Schlenk flask. After three freeze-pump-thaw cycles, Cu (6.9 mg, 0.108 mmol) was added under N_2 . The flask was heated at 50 $^\circ\text{C}$. After certain reaction time, the flask was immersed in liquid nitrogen. The product was firstly extracted with ethanol and THF until the gel was colorless. The sol part was obtained by removal of copper complex from the extracts by passing through a neutral alumina column. Both sol and gel parts were finally dried under vacuum at 40 $^\circ\text{C}$.

Crosslinked PtBA was synthesized by the same procedure of crosslinked PMA.

1.7 Alcoholization of tPMA and Treatment of Gel and Sol Part of PMA

1.7.1 Alcoholization of tPMA

tPMA (112 mg, 0.023 mmol) and NaOH (4.2 mg, 0.10 mmol) were dissolved in 15 mL THF and 10 mL methanol. The solution was heated at 60 $^\circ\text{C}$ for 2 hours and the solvent was evaporated. The resulted product was extracted with 30 mL THF and the cleaved polymer was obtained by evaporation of solvent. Pure polymer was obtained after drying under vacuum at 40 $^\circ\text{C}$. $M_{n, \text{GPC}} = 1210$ g/mol, PDI = 1.26.

1.7.2 Treatment of gel and sol part of crosslinked PMA

The gel (99.4 mg) was swelled in 15 mL THF and 10 mL methanol, and then NaOH (4.0 mg, 0.10 mmol) was added as the alkaline catalyst. The solution was heated at 60 $^\circ\text{C}$ for 2 hours and the solvent was evaporated. The resulted product was extracted with 30 mL THF and the cleaved polymer was obtained by evaporation of solvent. Pure polymer was obtained after drying under

vacuum at 40 °C. The molecular weight distribution of cleaved gel was measured by GPC. The GPC curve of cleaved product was simulated with two Gaussian distribution functions with same standard deviation.

The sol part was treated with the same procedure.

1.8 Hydrolysis of tPtBA and Crosslinked PtBA

1.8.1 Hydrolysis of t-PtBA

tPtBA (98.9 mg) was dissolved in 2 mL THF, followed by the addition of trifluoroacetic acid (TFA, 2 mL). The mixture was stirred at room temperature for 30 min. The solvent was evaporated from the resulting mixture, and the residual solid was washed with petroleum ether (3×20 mL) followed by drying under vacuum at 40 °C to give pure polymer.

1.8.2 Partial hydrolysis of crosslinked PtBA

The gel (35.4 mg) of crosslinked PtBA was swelled in 2 mL THF and 2 mL trifluoroacetic acid (TFA) with stirring at room temperature. After 24 h, the reaction mixture was washed by dichloromethane (3×20 mL) and finally dried to obtain white shrunk gel. Swelling ratio was measured in THF, distilled water and methanol, respectively.

1.8.3 Total hydrolysis and cleavage of crosslinked PtBA

The gel (25.8 mg) of crosslinked PtBA was swelled in 10 mL water and 20 mL methanol, then NaOH (500 mg, 12.5 mmol) was added as the alkaline catalyst. The solution was heated at 60 °C for 24 hours and the solvent was evaporated. The reaction mixture was washed by ethanol (3×30 mL) and finally dried to give pure polymer. The molecular weight distribution of cleaved gel was measured by GPC. The GPC curve of cleaved product was simulated with two Gaussian distribution functions with same standard deviation.

1.9 Swelling Ratio Measurement

Partial hydrolyzed PtBA gel (25.8 mg) was immersed in 15 mL distilled water and kept in the liquid at the room temperature. The sample was taken out at certain intervals of time, dried superficially with filter paper, weighed and placed back in the same solution until a constant weight. If assuming ideal mixing, the mass swelling ratio Q_m and the volume swelling ratio Q_v were measured using the following formula

$$Q_m = (W_s - W_d)/W_d \quad (1)$$

$$Q_v = [(W_s - W_d)/\rho_s + W_d/\rho_d]/(W_d/\rho_d) \quad (2)$$

Where W_s and W_d are the mass of swelled sample and dried sample, ρ_s and ρ_d are the densities of the polymer and water, respectively. The same procedure was applied to measure swelling ratio for THF and methanol. THF ($\rho_s = 0.89 \text{ g/cm}^3$), methanol ($\rho_s = 0.79 \text{ g/cm}^3$), distilled water ($\rho_s = 1.0 \text{ g/cm}^3$), PAA ($\rho_s = 1.22 \text{ g/cm}^3$).

References

- (1) M. H. Acar, K. Matyjaszewski, *Macromol. Chem. Phys.* **1999**, 200, 1094–1100
- (2) D. M. Haddleton, C. Waterson, *Macromolecules* **1999**, 32, 8732-8739

2. Figures

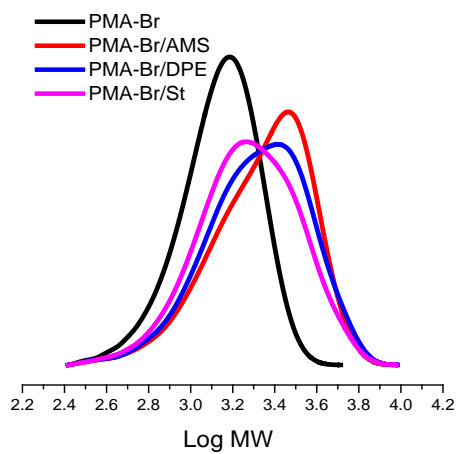


Fig. S1 GPC curves of PMA-Br and RAC of PMA-Br with three different alkenes

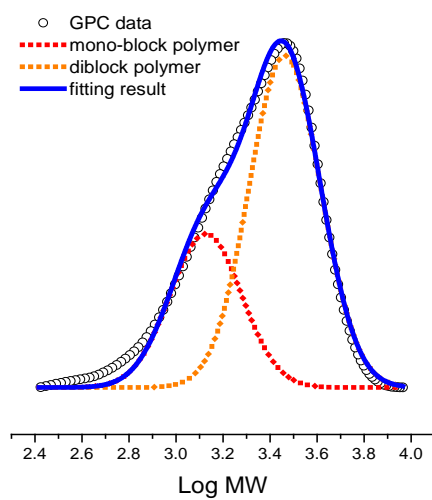


Fig. S2 GPC curve of RAC of PMA-Br with AMS and fitting result

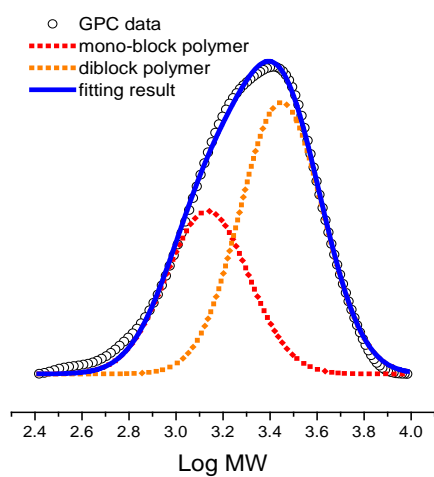


Fig. S3 GPC curve of RAC of PMA-Br with DPE and fitting result

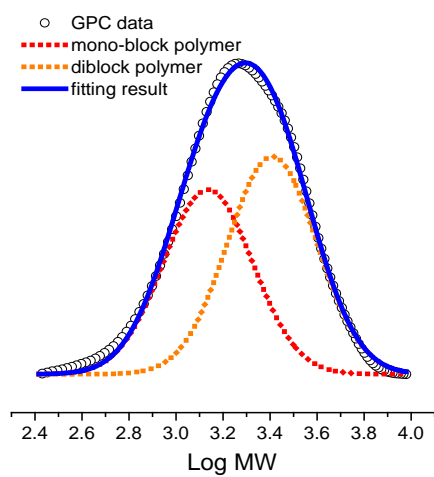


Fig. S4 GPC curve of RAC of PMA-Br with styrene and fitting result

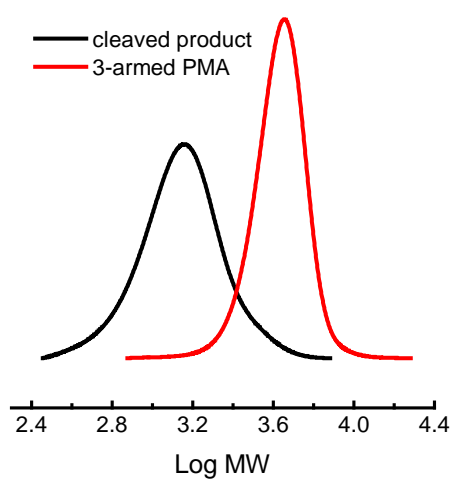


Fig. S5 GPC curves of 3-armed PMA prepared by ATRP and its cleaved product

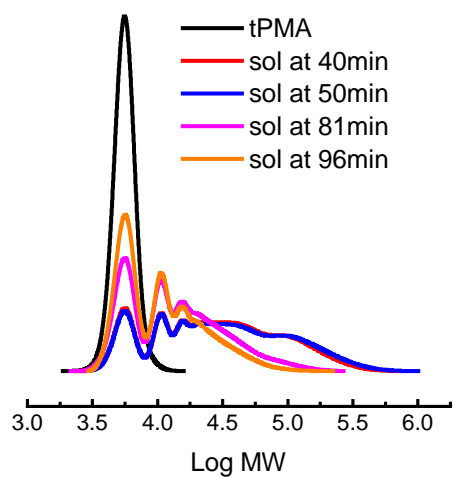


Fig. S6 GPC curves of sol part of product obtained at various times

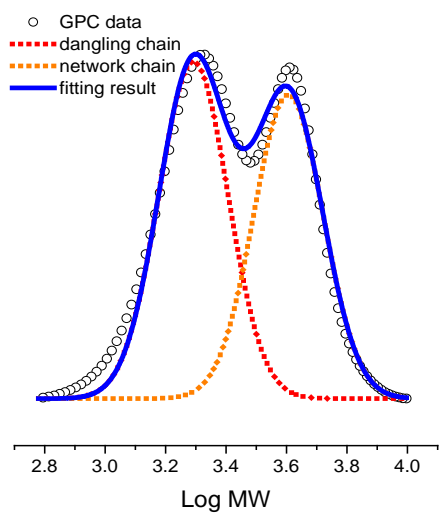


Fig. S7 GPC curve of cleaved sol part of product obtained at 40 min and fitting result

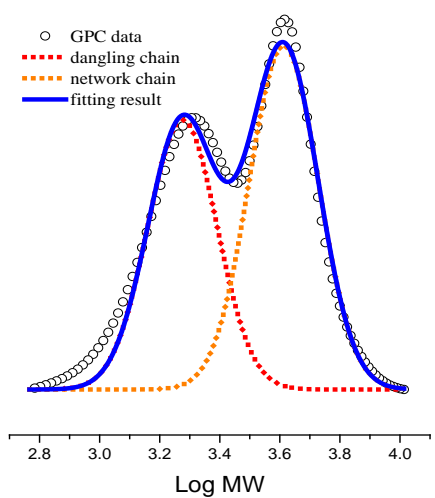


Fig. S8 GPC curve of cleaved sol part of product obtained at 50 min and fitting result

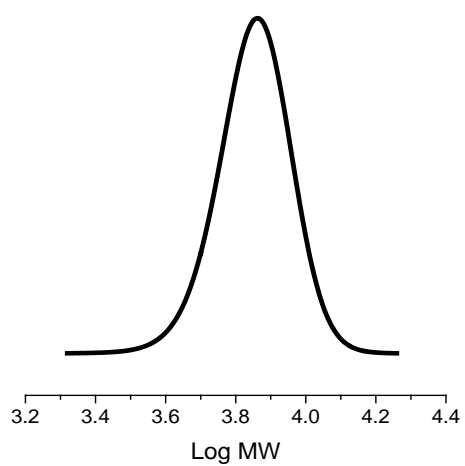


Fig. S11 GPC curve of 3-armed *Pt*BA prepared by ATRP

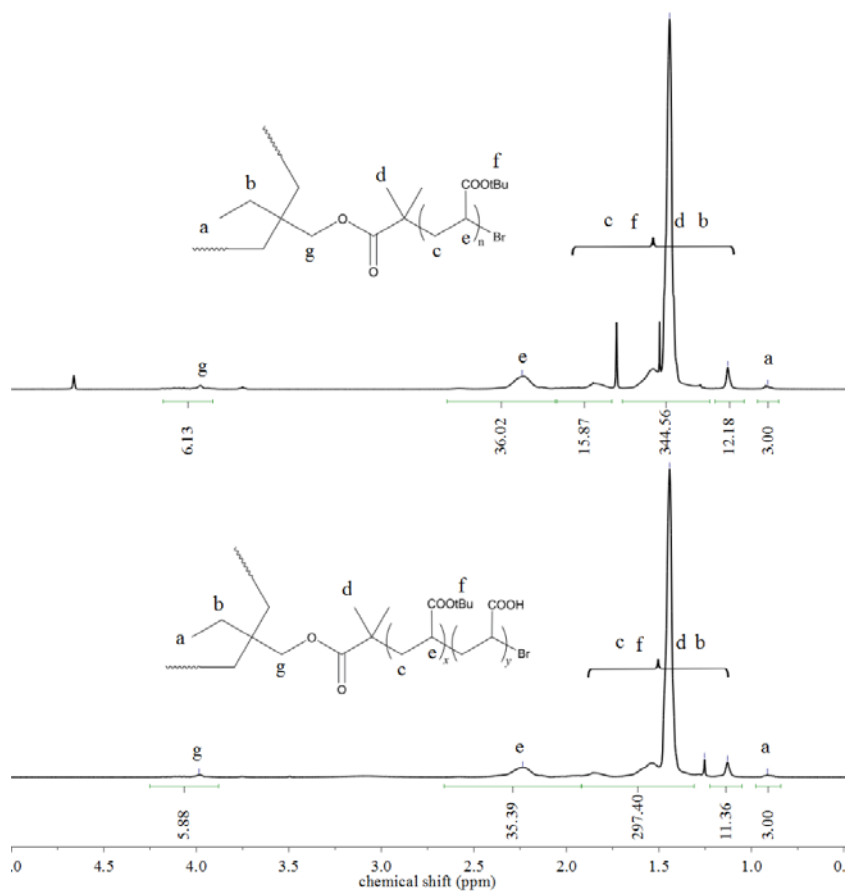


Fig. S12 $^1\text{H-NMR}$ spectrum (CDCl_3 , 400 MHz) of 3-armed tPtBA and partial hydrolyzed tPtBA

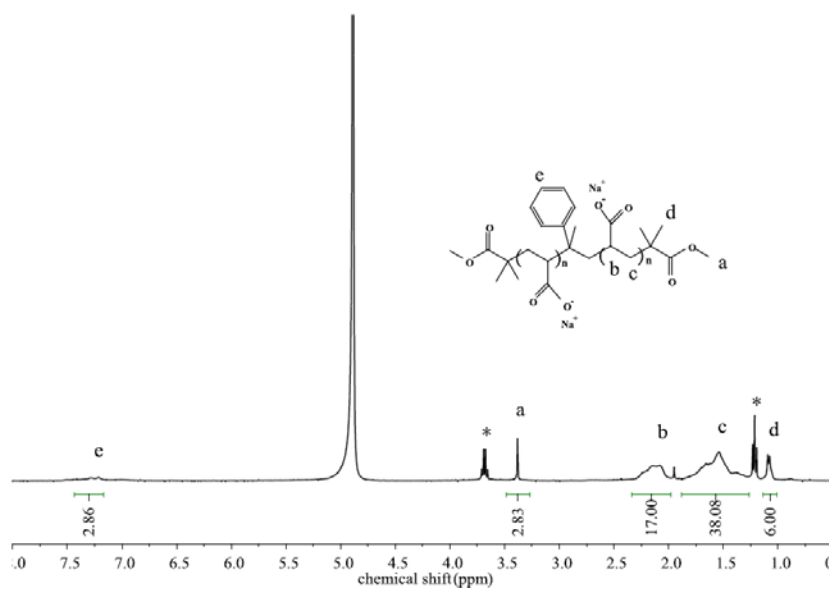


Fig. S13 $^1\text{H-NMR}$ spectrum (D_2O , 400 MHz) hydrolysis and cleaved gel part of crosslinked PtBA (* ethanol)