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 (tBA) 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 an alkaline alumina column. Tetrahydrofuran (THF) was distilled from sodium benzophenone. CuBr (98%, Aldrich) was purified using a modified literature procedure. Copper powder (3.25-4.75 μm, 99%, Alfa), 1,1,1-tris(hydroxymethyl)propane (TMP, 98%, Aladdin), 1,1-diphenylethylene (DPE, 98%, Alfa), 2-bromoisoobutyryl 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 gel 5 μm MIXED-C columns against linear polystyrene standards and THF as the eluent at a flow rate of 1.0 mL/min at 40 °C. $^1$H NMR spectra were recorded at room temperature by a Bruker (400 MHz) spectrometer using tetramethylsilane as the internal standard, CDCl$_3$ and D$_2$O 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 CH$_2$Cl$_2$ (50 mL) at 0 °C. A 50 mL CH$_2$Cl$_2$ solution of 2-bromoisoobutyryl 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 NaHCO$_3$ solution (3×50 mL) and saturated NaCl solution (3×50 mL). The combined organic extracts were dried over anhydrous MgSO$_4$. 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 %. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 4.19 (6H,
s, \(\text{CH}_2\text{-O-C}=\text{O}\)), 1.94 (18H, s, \(\text{O=C-C(CH}_3\text{)}_2\text{)}) , 1.65 (2H, q, \text{CH}_3\text{-CH}_2\text{-}), 0.94 (3H, t, \text{CH}_3\text{-CH}_2\text{-}).

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 \(\mu\text{L}, 2.2\text{ mmol}), \text{PMDETA (46 } \mu\text{L, 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\(_2\text{Cl}_2\) and purified by passing through a neutral alumina column. The solvent and monomer were then removed by evaporation, and the polymer was re-dissolved in CH\(_2\text{Cl}_2\) 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. \(M_\text{n, GPC} = 1240\text{ g/mol}, PDI = 1.20\). \(M_\text{n, NMR} = 1270\text{ g/mol}\) and terminal group functionality was 95.0 % analyzed by \(^1\text{H 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 \(\mu\text{L, 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\(_2\text{Cl}_2\) and purified by passing through a neutral alumina column. The solvent and monomer were then removed by evaporation, and the polymer was re-dissolved in CH\(_2\text{Cl}_2\) and then precipitated by cold methanol/water (v/v, 1/1). After drying under vacuum at 40 °C, pure polymer was obtained. \(M_\text{n, GPC} = 4070\text{ g/mol}, PDI = 1.09\), \(M_\text{n, NMR} = 4830\text{ g/mol}\) and terminal group functionality was 93.0 % analyzed by \(^1\text{H NMR}.

1.4.3 Synthesis of 3-armed Poly(\text{tert}-butyl acrylate) (tPrBA) by ATRP

TBBMP (Initiator A, 407 mg, 0.7 mmol), PMDETA (29.2 \(\mu\text{L, 0.14 mmol}), \text{\text{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\(_2\text{Cl}_2\) and purified by passing through a neutral alumina column. The solvent and monomer were then removed by evaporation, and the polymer was re-dissolved in CH\(_2\text{Cl}_2\) and then precipitated by cold methanol/water (v/v, 1/1). After drying under vacuum at 40 °C pure polymer was obtained. \(M_\text{n, GPC} = 6900\text{ g/mol}, PDI = 1.06\), \(M_\text{n, NMR} = 4770\text{ g/mol}\).
1.5 Radical Addition Coupling Reaction of Linear PMA

PMA-Br \( (M_{n, NMR} = 1270 \text{ g/mol}, 114 \text{ mg}, 0.09 \text{ mmol}) \), PMDETA \( (22.6 \mu\text{L}, 0.108 \text{ mmol}) \), \( \alpha \)-methyl styrene \( (5.3 \text{ mg}, 0.045 \text{ mmol}) \) and 1.5 mL of THF were added to a Schlenk flask. After three freeze-pump-thaw cycles, Cu \( (6.9 \text{ mg}, 0.108 \text{ mmol}) \) 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\(_2\)Cl\(_2\) and purified by passing through a neutral alumina column. The polymer solution was concentrated and then dried under vacuum at 40 \({}^\circ\text{C}\). \( M_{n, GPC} = 1850 \text{ g/mol}, \text{PDI} = 1.34 \).

RAC of DPE and styrene was carried out by the same procedure of \( \alpha \)-methyl styrene.

1.6 Synthesis of Crosslinked PMA and Crosslinked PrBA

tPMA \( (M_{n, NMR} = 4830 \text{ g/mol}, 145 \text{ mg}, 0.03 \text{ mmol}) \), PMDETA \( (22.6 \mu\text{L}, 0.108 \text{ mmol}) \), \( \alpha \)-methyl styrene \( (5.3 \text{ mg}, 0.045 \text{ mmol}) \) and 1.5 mL of THF were added to a Schlenk flask. After three freeze-pump-thaw cycles, Cu \( (6.9 \text{ mg}, 0.108 \text{ mmol}) \) 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 PrBA was synthesized by the same procedure of crosslinked PMA.

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

1.7.1 Alcoholyzation of tPMA
tPMA \( (112 \text{ mg}, 0.023 \text{ mmol}) \) and NaOH \( (4.2 \text{ mg}, 0.10 \text{ mmol}) \) 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 \({}^\circ\text{C}\). \( M_{n, GPC} = 1210 \text{ g/mol}, \text{PDI} = 1.26 \).

1.7.2 Treatment of gel and sol part of crosslinked PMA
The gel \( (99.4 \text{ mg}) \) was swelled in 15 mL THF and 10 mL methanol, and then NaOH \( (4.0 \text{ mg}, 0.10 \text{ mmol}) \) 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 tPrBA and Crosslinked PrBA

1.8.1 Hydrolysis of t-PrBA
tPrBA (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 PrBA
The gel (35.4 mg) of crosslinked PrBA 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 shrinked gel. Swelling ratio was measured in THF, distilled water and methanol, respectively.

1.8.3 Total hydrolysis and cleavage of crosslinked PrBA
The gel (25.8 mg) of crosslinked PrBA 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 PrBA 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

\[
Q_m = \frac{(W_s - W_d)}{W_d} \quad (1)
\]

\[
Q_v = \frac{[(W_s - W_d)/\rho_s + W_d/\rho_d]}{(W_d/\rho_d)} \quad (2)
\]
Where $W_s$ and $W_d$ are the mass of swelled sample and dried sample, $\rho_s$ and $\rho_d$ 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
(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. S9 GPC curves of cleaved sol (left) and gel (right) part of product obtained at 81 min and fitting results

Fig. S10 GPC curves of cleaved sol (left) and gel (right) parts of product obtained at 96 min and fitting results
Fig. S11 GPC curve of 3-armed PtBA prepared by ATRP
Fig. S12 $^1$H-NMR spectrum (CDCl$_3$, 400 MHz) of 3-armed tPrBA and partial hydrolyzed tPrBA

Fig. S13 $^1$H-NMR spectrum (D$_2$O, 400 MHz) hydrolysis and cleaved gel part of crosslinked PrBA (* ethanol)