

Supporting Information

The Formation of Core Cross-Linked Star Polymers Containing Cores Cross-Linked by Dynamic Covalent Imine Bonds

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Experimental Section:

All chemicals were purchased from Sigma-Aldrich or Alfa Aesar and were used as received without further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 and 75 MHz, respectively, with the residual solvent signal as an internal standard. FTIR spectroscopy was performed on a Varian 800 FTIR instrument (Varian Inc.). High-resolution mass spectrometry was performed on a Waters LCT premier mass spectrometer (Waters Inc.). Gel permeation chromatography (GPC) was conducted on a Varian ProStar instrument (Varian Inc.) equipped with a Varian 325 UV-vis dual wavelength detector (254 nm), a Dawn Heleos II multi-angle laser light scattering detector (Wyatt Technology Corp.), a Viscotek 3580 differential RI detector, and a pair of PL gel 5 μm Mixed D 300 × 7.5 mm columns with guard column (Polymer Laboratories Inc.) in series. Near monodisperse polystyrene standards (Polymer Laboratories) were used for calibration. Data collection was performed with Galaxie software (Varian Inc.) and chromatograms analyzed with the Cirrus software (Varian Inc.) and Astra software (Wyatt Technology Corp.). MALDI-TOF analysis was performed on a Bruker Microflex (Bruker Daltonics). Samples for analysis were prepared by mixing solutions of dithranol (20 mg/mL) and AgTFA (10 mg/mL) with solutions of the polymer sample (10 mg/mL) in amounts of 100 μL: 40 μL: 20 μL respectively. 0.6 μL of solution was spotted onto the MALDI plate for analysis. Calibration was carried out against near monodisperse polystyrene standards. Data collection was performed with Flexcontrol and analysis of spectra was performed using Flexanalysis software.

4-Vinylbenzaldehyde^[1]:

A solution of 4-vinylbenzyl chloride (20.01 g, 130.2 mmol) and sodium acetate (12.9 g, 157.1 mmol) in (CH₃)₂SO (60 mL) was heated at 45 °C whilst stirring under N₂ for 24 h. The reaction mixture was transferred to a separating funnel and H₂O (100 mL) added. The product was extracted into EtOAc (3 × 100 mL). The organic extracts were combined and dried over MgSO₄, filtered and evaporated to dryness to afford crude 4-vinylbenzylacetate as a pale yellow oil (24.81 g, 99%), which was dried under high vacuum. 20 % NaOH_(aq) (50 mL) was added to a stirred solution of crude 4-vinylbenzylacetate (24.81 g, 140.8 mmol) in EtOH (50 mL). The reaction mixture was heated at reflux for 4 h then transferred into a separating funnel with EtOAc (100 mL). The aqueous layer was washed with EtOAc (2 × 100 mL), and the organic extracts were combined and dried over MgSO₄, filtered and evaporated to dryness to afford crude 4-vinylbenzalcohol as a brown oil (26.36 g, 100%) which was dried under high vacuum. A solution of (COCl)₂ (8.55 g, 67.4 mmol) in CH₂Cl₂ (50 mL) was cooled to -78 °C whilst stirring under N₂. A solution of (CH₃)₂SO (10.67 g, 134.8 mmol) in CH₂Cl₂ (50 mL) was added dropwise over 15 min, and then a solution of crude 4-vinylbenzylalcohol (8.22 g, 61.3 mmol) in CH₂Cl₂ (50 mL) was added dropwise over 30 min. NEt₃ (19.84 g, 196.0 mmol) was added to the reaction mixture and the solution was allowed to reach room temperature. The reaction mixture was left to stir under N₂ for 16 h, then transferred into a separating funnel with HCl_(aq) (1 M, 100 mL) and H₂O (100 mL). The organic layer was collected and dried over MgSO₄, filtered and evaporated to dryness to afford crude brown oil (8.09 g, 100 %). The crude product was purified by vacuum distillation to afford 4-vinylbenzaldehyde as a clear oil (4.2 g, 52%). ¹H NMR (CDCl₃): δ 5.44 (d, 1H, J = 10.8 Hz), 5.92 (d, 1H, J = 17.4 Hz), 6.76 (dd, 1H, J = 10.8 Hz, J = 17.4 Hz), 7.55 (d, 2H, J = 8.4 Hz), 7.84 (d, 2H, J = 8.4 Hz), 9.99 (s, 1H).

N-Boc-4-aminostyrene^[2]:

A solution of 4-aminostyrene (4.49 g, 37.6 mmol) and di-*tert*-butyl dicarbonate (9.87 g, 45.2 mmol) in THF (100 mL) was heated at reflux under N₂ for 16 h. After evaporation to dryness crude material was transferred to a separating funnel in H₂O (50 mL) and the product was extracted with CH₂Cl₂ (3 × 50 mL). The organic extracts were combined and dried over Na₂SO₄, filtered, and evaporated to dryness to obtain a crude solid which was purified by column chromatography [SiO₂, Hexane-EtOAc (9:1)] to afford N-Boc-4-aminostyrene as a white solid (6.64 g, 80.3 %). ¹H NMR (CDCl₃): δ 1.52 (s, 9H), 5.15 (d, 1H, J = 9.9 Hz), 5.65 (d, 1H, J = 16.5 Hz), 6.53 (s, 1H), 6.65 (dd, 1H, J = 9.9 Hz, J = 16.5 Hz), 7.33 (s, 4H).

Aldehyde-Functionalized Copolymer (**P1**):

S-1-dodecyl-*S'*-(α,α -dimethyl- α'' -acetic acid)trithiocarbonate (DDMAT) (1 eq, 57.5 mg, 0.158 mmol) and AIBN (0.2 eq, 5.2 mg, 31.6 μ M) were added to a small schlenk tube. Styrene (65 eq, 1.07 g, 10.3 mmol) and 4-vinylbenzaldehyde (65 eq, 1.37 g, 10.3 mmol) was then added followed by dioxane (2.5 mL). The reaction mixture was degassed five times, and then the vessel was backfilled with N₂, purged with N₂, and allowed to warm to room temperature. The reaction mixture was then placed in an oil bath at 70 °C, and the polymerization was quenched after 21 h and solvent was removed on the rotary evaporator. The resulting yellow oil was dissolved in a minimal amount of THF and added dropwise to a large excess of ice-cold hexane. The polymer precipitate was then isolated by filtration and dried under high vacuum. Polymer **P1** was obtained as a pale yellow solid (1.77 g, 91%). ¹H NMR (CDCl₃): δ 0.84 (br, SC₁₁H₂₂CH₃, of the chain terminus), 1.42 (br, CHCH₂, polymer backbone), 1.61 (br, CHCH₂, polymer backbone), 3.29 (br, SCH₂C₁₁H₂₃, of the chain terminus), 6.51 (br, Ar, polymer backbone), 7.03 (br, Ar, polymer backbone), 7.50 (br, Ar, polymer backbone), 9.89 (br, CHO, polymer backbone).

The composition of **P1** can be determined simply by comparing the integration of the aldehyde protons with the total integration of the aromatic protons. The monomer composition was determined to be 1:1 styrene:vinylbenzaldehyde.

N-Boc-Protected Amine-Functionalized Copolymer (**P2a**):

S-1-dodecyl-*S'*-(α,α -dimethyl- α'' -acetic acid)trithiocarbonate (DDMAT) (1 eq, 52.1 mg, 0.143 mmol) and AIBN (0.2 eq, 4.7 mg, 28.6 μ M) were added to a small schlenk tube. Styrene (75 eq, 1.12 g, 10.7 mmol) and *N*-boc-4-aminostyrene (75 eq, 2.35 g, 10.7 mmol) were then added followed by dioxane (3 mL). The reaction mixture was degassed five times and then the vessel was backfilled with N₂, purged with N₂, and allowed to warm to room temperature. The reaction mixture was then placed in an oil bath at 70 °C, and the polymerization was quenched after 22 h and solvent was removed on the rotary evaporator. The resulting yellow oil was dissolved in a minimal amount of THF and added dropwise to a large excess of ice-cold hexane. The polymer precipitate was then isolated by filtration and dried under high vacuum. Polymer **P2a** was obtained as a pale yellow solid (1.18 g, 62%). ¹H NMR (CDCl₃): δ 0.89 (br, SC₁₁H₂₂CH₃, of the chain terminus), 1.38 (br, CHCH₂, polymer backbone), 1.55 (br, C(CH₃)₃), 1.76 (br, CHCH₂, polymer backbone), 3.29 (br, SCH₂C₁₁H₂₃, of the chain terminus), 6.53 (br, Ar, polymer backbone), 7.05 (br, Ar, polymer backbone). The composition of **P1** can be determined simply by comparing the integration of the *Boc* protons at δ = 1.55 ppm with the total integration of the aromatic protons. The monomer composition was determined to be 1:1 styrene:*N*-Boc-4-aminostyrene.

Amine-Functionalized Polymer (**P2b**):

TFA (1 mL) Was added to a stirred solution of **P2a** (0.1 g, 7.53 μ M) in CH₂Cl₂ (1 mL) at room temperature. After 1 h the reaction mixture was evaporated to dryness to afford a crude yellow oil which was dissolved in minimal amount of THF and added dropwise to a large excess of ice-cold hexane. The polymer precipitate was then isolated by filtration and dried under high vacuum. Polymer **P2b** was obtained as a pale yellow solid (0.09 g, 87%). ¹H NMR (THF-*d*⁸): δ 0.85 (br, SC₁₁H₂₂CH₃, of the chain terminus), 1.45 (br, CHCH₂, polymer backbone), 1.79 (br, CHCH₂, polymer backbone), 3.29 (br, SCH₂C₁₁H₂₃, of the chain terminus), 6.56 (br, Ar, polymer backbone), 7.02 (br, Ar, polymer backbone), 7.44 (br, Ar, polymer backbone).

Aldehyde-Functionalized Diblock Copolymer (**P3**):

P1 (1 eq, 1.02 g, 85 μ M) and AIBN (0.2 eq, 2.8 mg, 17 μ M) were added to a small schlenk tube. Styrene (300 eq, 2.66 g, 25.5 mmol) was then added followed by dioxane (3 mL) and the reaction mixture was degassed five times. The vessel was backfilled with N₂, purged with N₂, and allowed to warm to room temperature. The reaction mixture was then placed in an oil bath at 70 °C, and the polymerization was quenched after 24 h and solvent was removed on the rotary evaporator. The resulting yellow oil was dissolved in a minimal amount of THF and added dropwise to a large excess of ice-cold methanol. The polymer precipitate was then isolated by filtration and dried under high vacuum. Polymer **P3** was obtained as a pale yellow solid (3.03 g, 96%). ¹H NMR (CDCl₃): δ 0.89 (br, SC₁₁H₂₂CH₃, of the chain terminus), 1.43 (br, CHCH₂, polymer backbone), 1.86 (br, CHCH₂, polymer backbone), 6.57 (br, Ar, polymer backbone), 7.05 (br, Ar, polymer backbone), 7.52 (br, Ar, polymer backbone), 9.89 (br, CHO, polymer backbone).

Amine-Functionalized Diblock Copolymer (**P4**):

P2a (1 eq, 1.05 g, 79 μ M) and AIBN (0.2 eq, 2.6 mg, 15.8 μ M) were added to a small schlenk tube. Styrene (400 eq, 3.29 g, 31.6 mmol) was then added followed by dioxane (4 mL) and the reaction mixture was degassed five times. The vessel was backfilled with N₂, purged with N₂, and allowed to warm to room temperature. The reaction mixture was then placed in an oil bath at 70 °C, and the polymerization was quenched after 25.5 h and solvent was removed on the rotary evaporator. The resulting yellow oil was dissolved in a minimal amount of THF and added dropwise to a large

excess of ice-cold methanol. The polymer precipitate was then isolated by filtration and dried under high vacuum. The pale yellow solid obtained was dissolved in CH_2Cl_2 (3 mL) and TFA (3 mL) was added, solution was left to stir at room temperature. The reaction mixture was evaporated to dryness after 1 h, and the resulting crude yellow oil was dissolved in minimal amount of THF and added dropwise to a large excess of ice-cold hexane. The polymer precipitate was then isolated by filtration and dried under high vacuum. Polymer **P4** was obtained as a pale yellow solid (1.11 g, 47%). ^1H NMR (CDCl_3): δ 0.89 (br, $\text{SC}_{11}\text{H}_{22}\text{CH}_3$, of the chain terminus), 1.44 (br, CHCH_2 , polymer backbone), 1.87 (br, CHCH_2 , polymer backbone), 3.29 (br, $\text{SCH}_2\text{C}_{11}\text{H}_{23}$, of the chain terminus), 6.59 (br, Ar, polymer backbone), 7.05 (br, Ar, polymer backbone).

Procedure for Macroscopic Gelation between **P1** and **P2b**:

Solutions of **P1** (0.5 and 5 wt %) in THF with TFA (10 eq) were prepared and allowed to stir at room temperature for 10 min to allow complete dissolution of the polymer sample. Solutions of **P2b** (0.5 and 5 wt %) were prepared in THF with TFA (10 eq) under identical conditions. Equal volumes of these corresponding solutions were mixed and gelation was observed in both cases after 15 min and 2h respectively.

General Procedure for the Preparation of CCS Polymers (**1** – **6**):

Solutions of the aldehyde functional diblock copolymer component **P3** (0.5 – 5 wt %) were prepared in THF with TFA (10 eq). Solutions of the amine functional diblock copolymer component **P4** (0.5 – 5 wt %) were also prepared under identical conditions. Equal volumes of corresponding solutions of the same concentration were combined with rapid stirring and left to equilibrate at room temperature for 16 h before GPC–MALLS analysis. GPC Analysis of all crude reaction mixtures reveals no evidence for any unreacted reactive polymers, indicating that the cross-linking reaction proceeds with 100% conversion.

Procedure for the Disassembly of CCS Polymers:

A sample of CCS polymers (2 mL, containing 2 wt % of polymer building blocks) was isolated. To this solution a large excess of propylamine (10 eq per aldehyde functional group) was added. The reaction mixture was left to stir overnight at room temperature before GPC analysis.

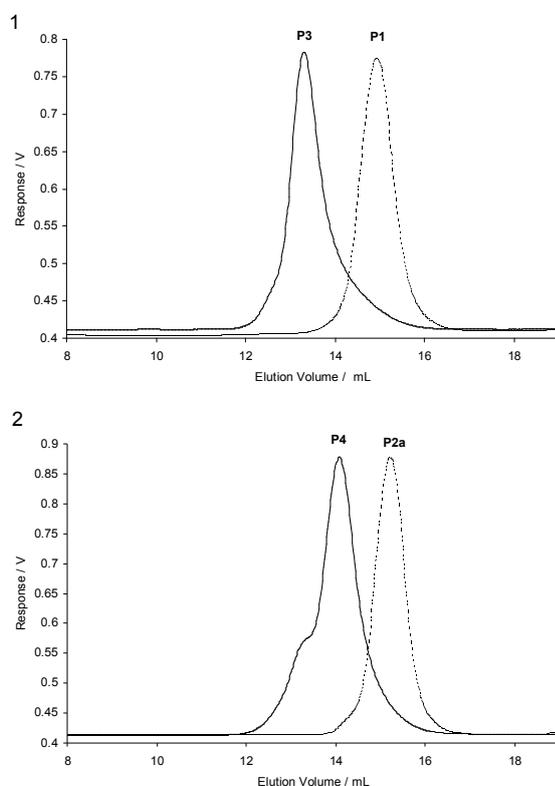


Figure A. 1) dRI GPC traces (THF 1.0 mL/ min) of **P1** and resulting diblock copolymer **P3** after chain extension, 2) dRI GPC traces (THF 1.0 mL/ min) of **P2a** and resulting diblock copolymer **P4** after chain extension. These chromatograms show the successful and complete chain extension of the macroinitiators **P1** and **P2a**.

polymer	(macro) chain transfer agent	monomer(s)	initiator	temp (°C)	solvent	time (h)	M _n ^a (g mol ⁻¹)	M _n ^b (g mol ⁻¹)	M _w ^b (g mol ⁻¹)	PD ^b (M _w /M _n)	R _h ^c (nm)
P1	DDMAT (1 equiv)	4-Vinylbenzaldehyde (65 equiv) styrene (65 equiv)	AIBN (0.2 equiv)	70	dioxane	21	12200	9200	10750	1.17	2.5
P2a	DDMAT (1 equiv)	<i>N</i> -Boc-aminostyrene (75 equiv) Styrene (75 equiv)	AIBN (0.2 equiv)	70	dioxane	22	13300	7350	8300	1.13	2.4
P2b	-	-	-	-	-	-	13800	8000	9000	1.13	2.6
P3	P1 (1 equiv)	Styrene (300 equiv)	AIBN (0.2 equiv)	70	dioxane	24	37200	32000	43300	1.35	4.5
P4	P2 (1 equiv)	Styrene (400 equiv)	AIBN (0.2 equiv)	70	dioxane	25.5	30100	20250	28350	1.40	5.2

Table 1. Reaction conditions and characterization of polymers **P1** – **P4**. ^a As determined by ¹H NMR spectroscopy. ^b As determined by gel permeation chromatography in THF (1.0 mL/min) calibrated against polystyrene standards. ^c As determined by online dynamic LS measurements.

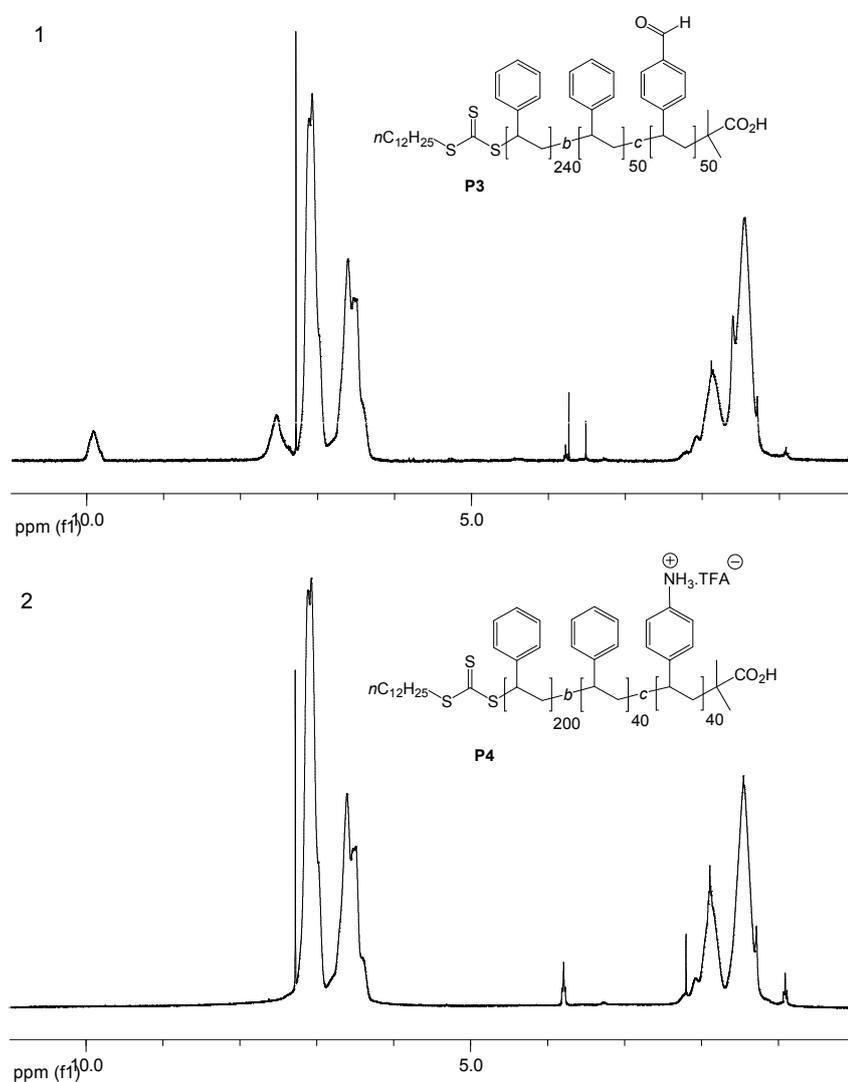


Figure B. 1) ¹H NMR spectra of aldehyde functional diblock copolymer **P3**, 2) ¹H NMR spectra of amine functional diblock copolymer **P4**.

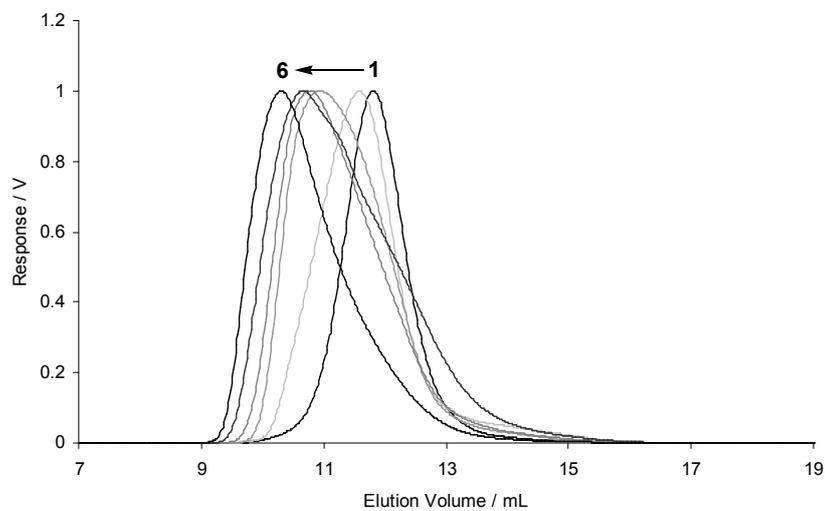


Figure 1. MALLS GPC traces of experiments 1- 6 in THF (1.0 mL/ min).

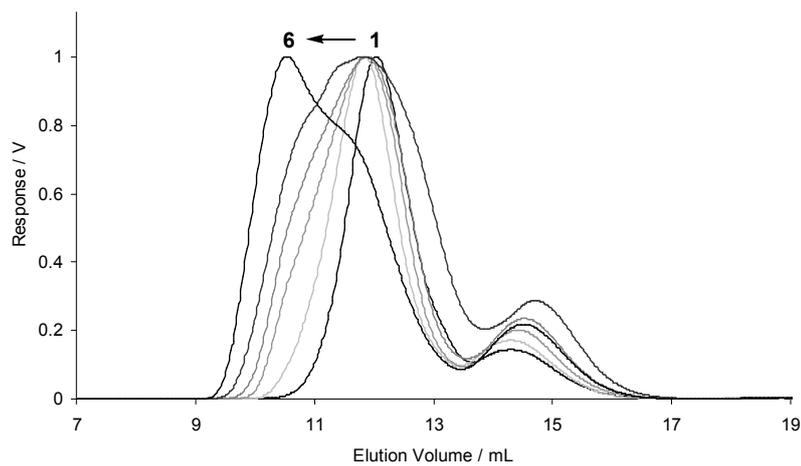


Figure 2. dRI GPC traces of experiments 1 – 6 in THF (1.0 mL/ min).

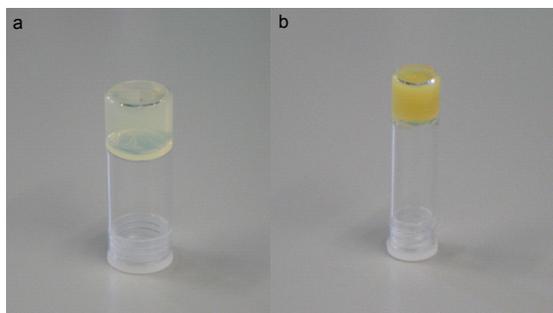


Figure 3. a) Gelation of **P1** and **P2b** in THF (0.5 wt %), b) Gelation of **P1** and **P2b** in THF (5 wt %).

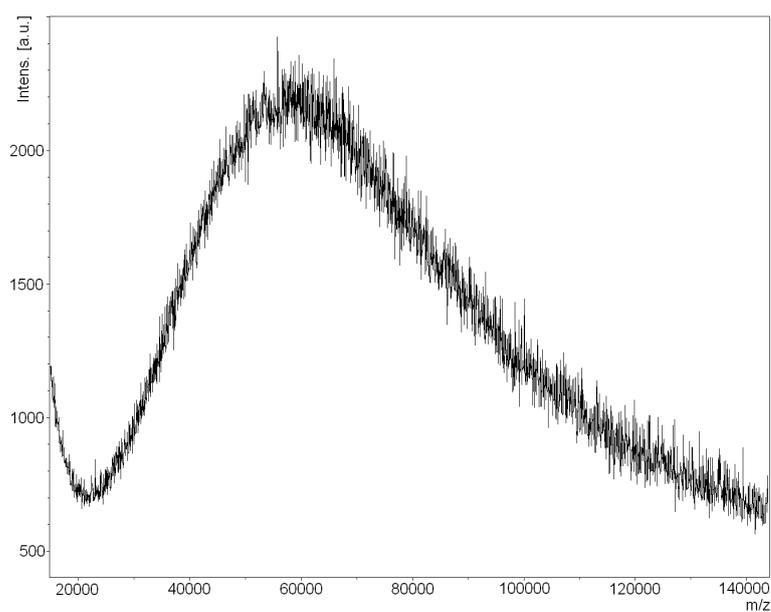


Figure 4. MALDI-TOF mass spectra of 2-arm core cross-linked star polymer.

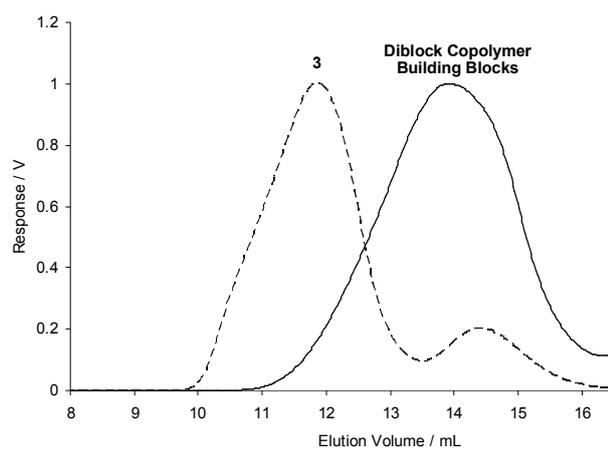


Figure 5. dRI GPC traces indicating the decomposition of the CCS polymers prepared in Table 1 experiment 3 (dashed line) into block copolymers (solid line) after the addition of propylamine.

References:

- 1 R. Manzotti, T. S. Reger and K. D. Janda, *Tetrahedron Lett*, 2000, **41**, 8417.
- 2 J. Jiang and S. Thayumanavan, *Macromolecules*, 2005, **38**, 5886.