

Supplementary Information: Chemically Fueled Covalent Crosslinking of Polymer Materials

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Experimental Section

General

Unless otherwise noted, all starting materials, reagents, and solvents were purchased from commercial sources and used without further purification. Polymer characterization was done using ^1H NMR spectroscopy in the solution phase, using a Bruker Avance 500 MHz spectrometer. MALDI-TOF data acquisition was performed on a Bruker AutoFlexIII MALDI-TOF mass spectrometer using α -cyano-4-hydroxycinnamic acid (CCA) as the matrix. ESI data was obtained on an Esquire LC ion trap mass spectrometer (Bruker Daltonics, Billerica, MA, USA). The electrospray ionization source (ESI) was operated in negative ion mode. IR experiments were carried out using Perkin Elmer Spectrum One FT-IR spectrometer. Rheological time sweep experiments were carried out in a TA Instruments (New Castle, DE) Discovery HR-1 rheometer with a 20 mm parallel plate geometry at 1% applied strain, which was found to be in the linear viscoelastic region.

Synthesis

RAFT polymerization of oligo(Am)COOH

PAETC (1.99 g, 9.2 mmol), acrylamide (3.389 g, 47.6 mmol), AIBN (0.156 g, 0.95 mmol) and DMF (0.5 mL) were added to a round bottom flask containing at 1:1 methanol/water mixture (12.6 mL). The reaction was purged with nitrogen for 10 minutes, then placed in an oil bath at 65 °C for 24 h. The conversion was determined using ^1H NMR spectroscopy. The product was precipitated by adding the reaction mixture dropwise to tetrahydrofuran that was cooled in an ice bath. The obtained precipitates were dried under reduced pressure. Characterization was done

using ESI MS ($M_n = 710.55$, $M_w = 746.08$, $PD = 1.05$), and 1H NMR. 1H NMR (500 MHz; D_2O) δ 4.63-4.54 (m, 1H), 3.36-3.30 (q, $J = 7.26$; 7.66 Hz, 2H), 2.43-1.33 (m, 23H), 1.28-1.22 (m, 3H), 1.09-1.00 (m, 3H) ppm.

RAFT polymerization of poly(Am85-r-AA15)

PAETC (0.097 g, 0.461 mmol), VA-044 (0.030 g, 0.092 mmol), acrylamide (2.795 g, 39.322 mmol), acrylic acid (0.5 g, 6.939 mmol), methanol (3 g) and deionized water (4 mL) were added to a small vial capped with a rubber septum. The reaction was purged with argon for 10 minutes to remove oxygen, then placed in an oil bath at 45 °C for 24 h. The conversion was then judged to be above 95% as determined by 1H NMR spectroscopy. The crude product was precipitated by dropwise addition to the stirred acetone. The product was dried under reduced pressure for 24 h. MALDI-TOF MS was used to determine the average molecular weight ($M_n = 7718.99$, $M_w = 7997.91$, $PD = 1.04$).

RAFT polymerization of poly(AM65-r-AA35)

PAETC (0.083 g, 0.397 mmol), VA-044 (0.026 g, 0.079 mmol), acrylamide (1.832 g, 25.77 mmol), acrylic acid (1 g, 13.877 mmol), methanol (3 g) and deionized water (3 mL) were added to a small vial capped with a rubber septum. The reaction was purged with argon for 10 minutes and then placed in an oil bath at 45°C for 24 h. The conversion was judged to be above 95% as determined by 1H NMR spectroscopy. The crude product was precipitated by dropwise addition to the stirred acetone. The product was dried in a vacuum oven for 24 h. MALDI-TOF MS was used to determine the average molecular weight ($M_n = 7516.98$, $M_w = 7664.49$, $PD = 1.02$).

Methods

IR Experiment for oligo(Am)COOH

Oligo(Am)COOH (300 mg) was dissolved in DI water (0.4 mL) and EDC (58.22 mg, 0.30 mmol) was dissolved in DI water (0.2 mL). These solutions were equilibrated in an ice bath for 30 min and then combined with the aid of a mixing syringe. The reaction progress was then monitored by testing aliquots using IR spectroscopy over 2 h 40 min, subtracting water as the background.

Vial test for poly(Am85-r-AA15)

Polymer poly(Am85-r-AA15) (400 mg) was dissolved in DI water (0.6 mL) and EDC (79.9 mg, 0.42 mmol) was dissolved in DI water (0.2 mL). Both solutions were equilibrated at 4 °C for 30 minutes in a cold room. The solutions were mixed together using a mixing syringe and the changes were observed visually over the time.

Vial test for poly(AM65-r-AA35)

Polymer poly(AM65-r-AA35) (200 mg) was dissolved in DI water (0.3 mL) and EDC (46.6 mg, 0.24 mmol) was dissolved in DI water (0.1 mL). Both solutions were equilibrated at 4 °C for 30 minutes in a cold room. They were mixed together using a mixing syringe and the changes were observed visually over the time.

Rheology measurements of poly(Am85-r-AA15)

Poly(Am85-r-AA15) (0.8 g) was dissolved in deionized water (1.2 mL) and sonicated to get a homogeneous solution. EDC (0.1596 g, 0.83 mmol) was dissolved in deionized water (0.4 mL). The polymer solution (0.3 mL) was loaded on the Peltier plate of the rheometer using a 1 mL syringe and the prepared EDC solution (0.1 mL) was injected on the top of polymer solution layer. Mixing was achieved through rheometer oscillation. The storage and loss modulus during the gelation and hydrolysis processes were monitored during time sweep measurements at 4 °C using an angular frequency of 1 Hz or 10 Hz.

Rheology measurements of poly(AM65-r-AA35)

Poly(AM65-r-AA35) (0.8g) in deionized water (1.2 mL) and dissolved EDC (0.3728 g, 1.94 mmol) in deionized water (0.4 mL). The polymer solution (0.3 mL) was loaded on the Peltier plate of the rheometer using a 1 mL syringe and the prepared EDC solution (0.1 mL) was injected on the top of polymer solution layer. Mixing was achieved through rheometer oscillation. The storage and loss modulus during the gelation and hydrolysis processes were monitored during time sweep measurements at 4 °C using an angular frequency of 1 Hz or 10 Hz.

Figures

ESI-MS data

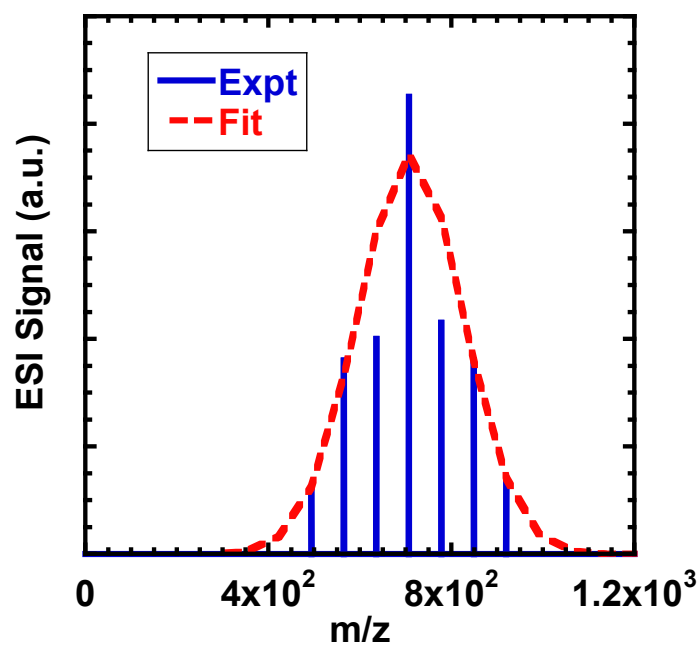
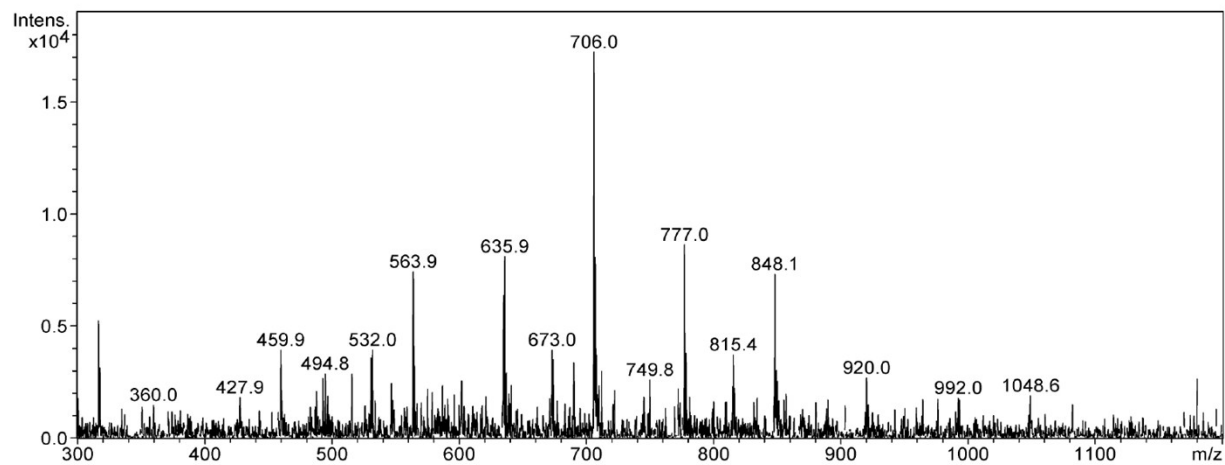


Figure S1: ESI-MS data for oligo(Am)COOH

MALDI-TOF data

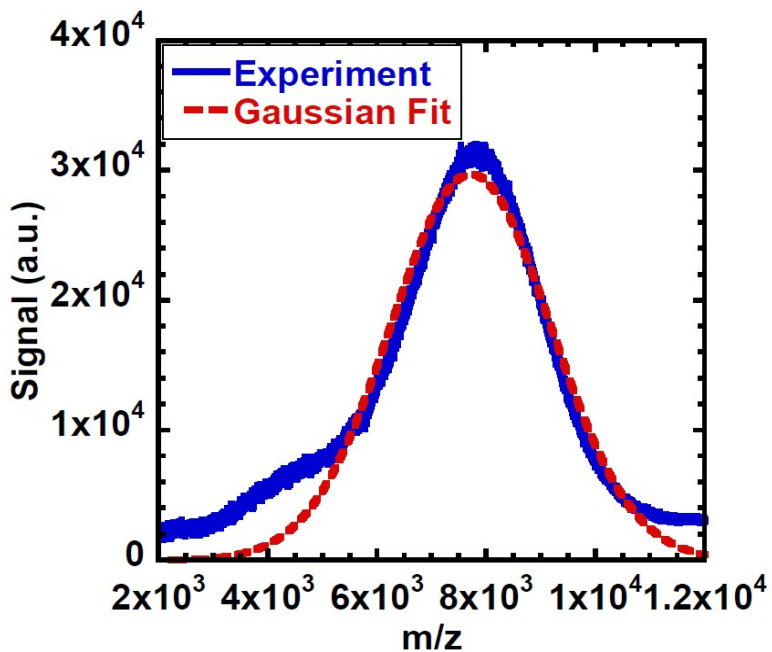


Figure S2: MALDI-TOF MS data with Gaussian Fit for poly(Am85-r-AA15)

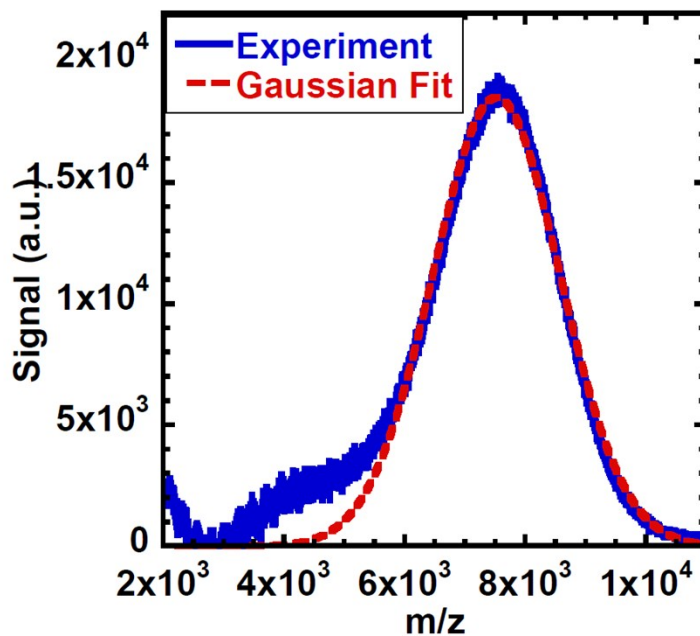


Figure S3: MALDI-TOF MS data with Gaussian Fit for poly(Am65-r-AA35)

NMR Data

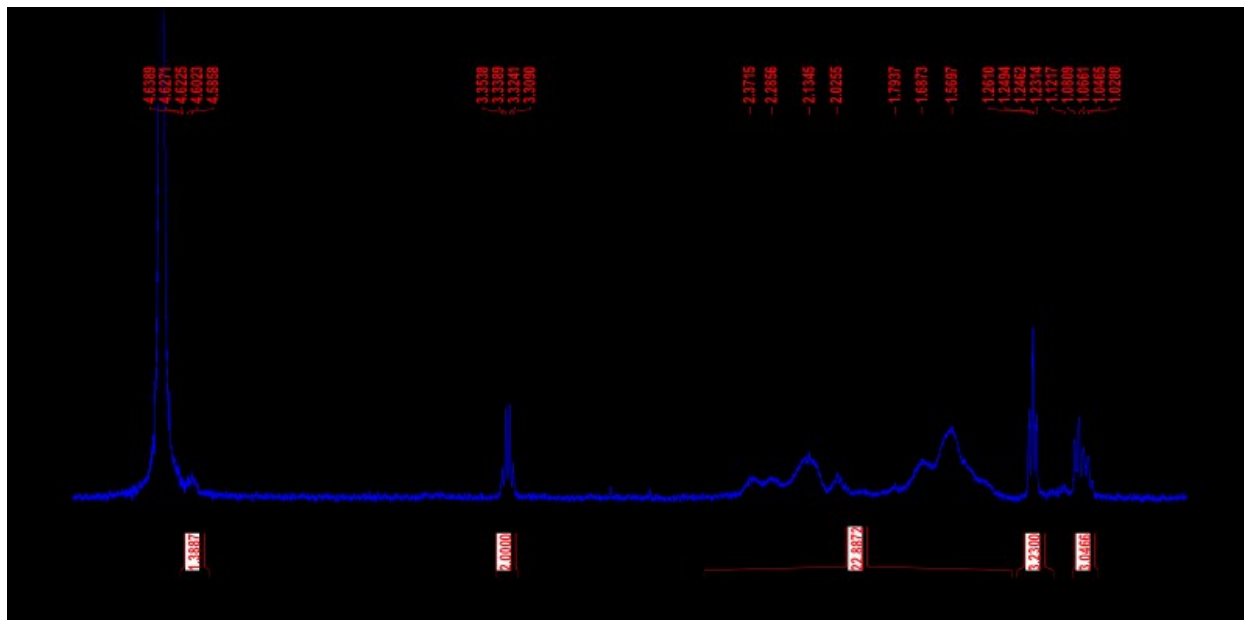


Figure S4: ¹H NMR spectrum of oligo(Am)COOH

IR experimental data

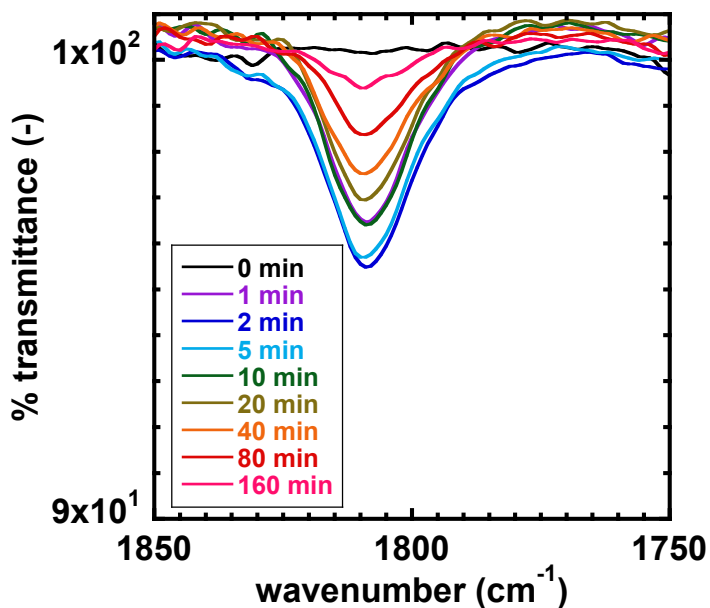


Figure S5: Magnification of anhydride stretching region for IR experiment at 0 - 5 °C using oligo(Am)COOH

Rheology Data

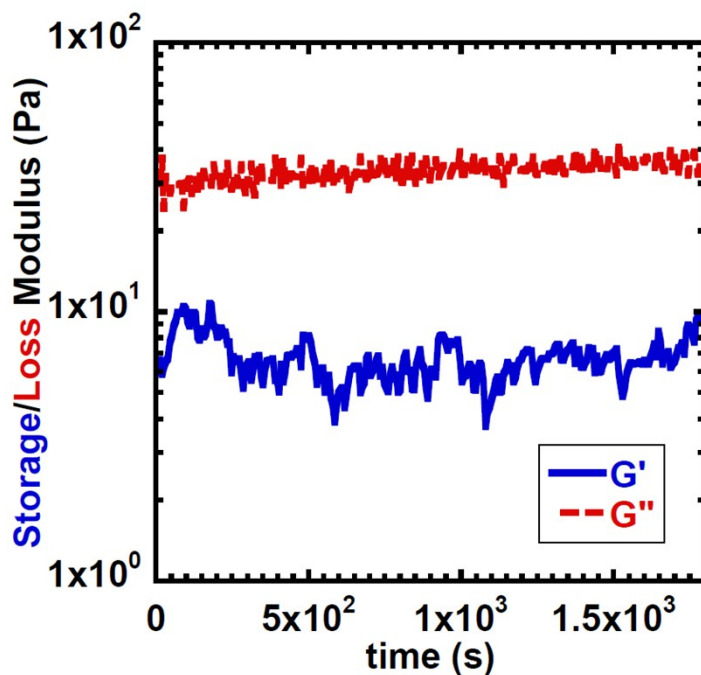


Figure S6: Time sweep at 4 °C for the poly(AM85-r-AA15) at 10 Hz in the absence of EDC

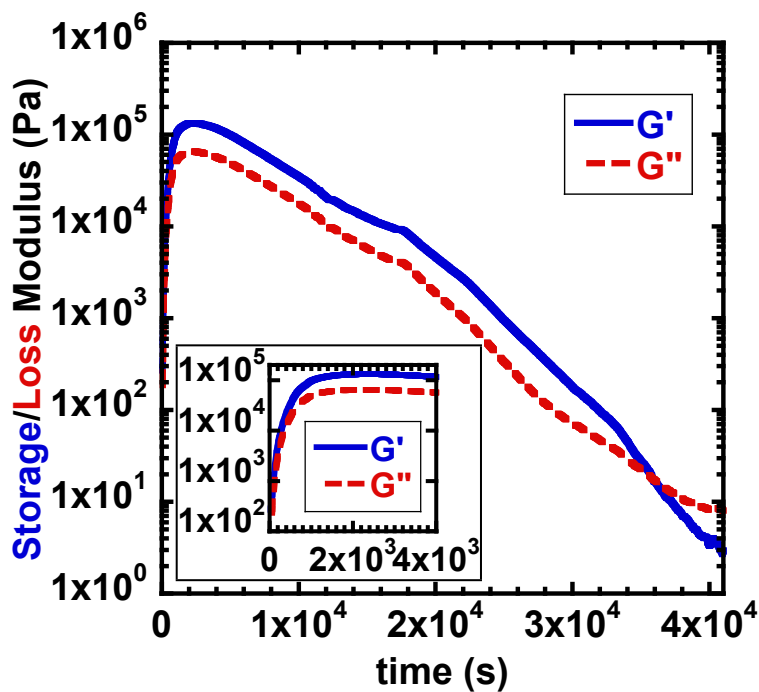


Figure S7: Time sweep at 4 °C for the poly(AM65-r-AA35) at 1 Hz.

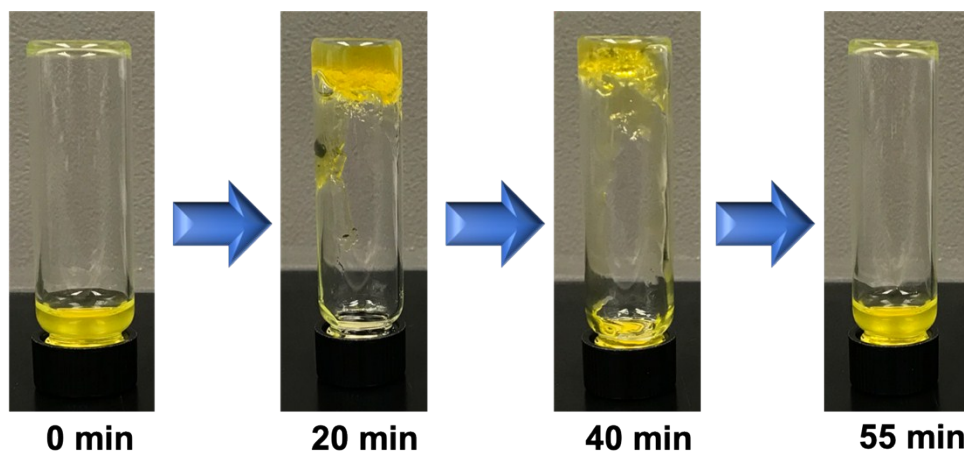


Figure S8: Inverted vial tests for poly(Am85-r-AA15) upon treatment with EDC at room temperature (20 °C)

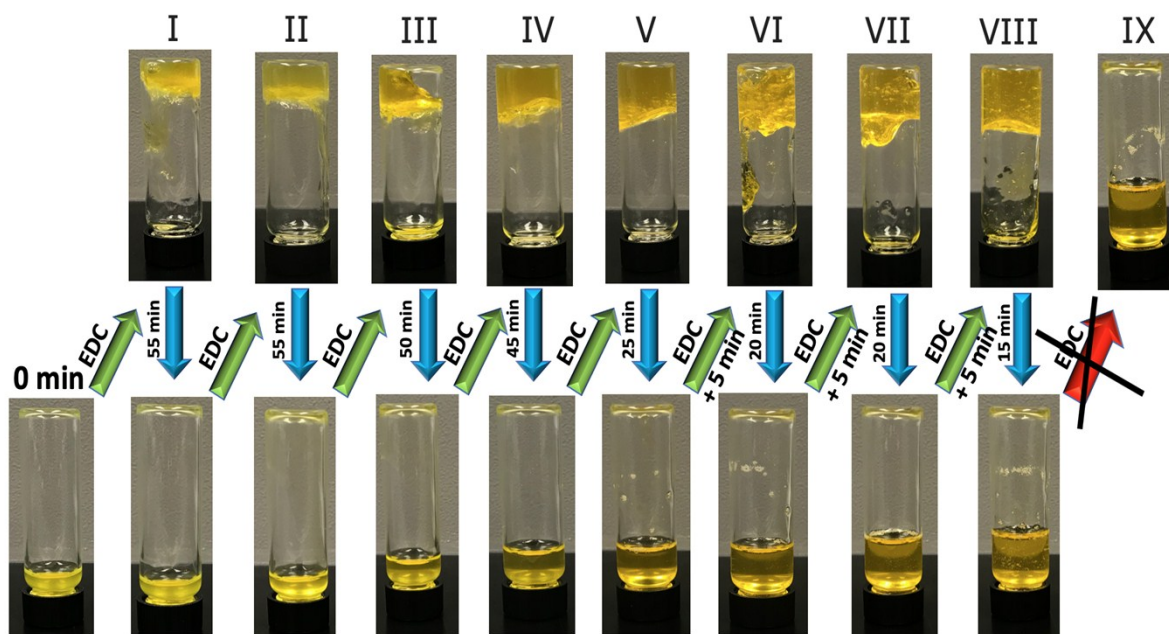


Figure S9: Repetition of inverted vial tests for poly(Am85-r-AA15) upon treatment with EDC nine times at room temperature (20 °C)