

Supporting Information

The Convergent Synthesis of Star Polymers from RAFT-Prepared Precursors via A Macromolecular Thiol-Ene Click Reaction

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Experimental procedures

All materials were purchased from Aldrich at the highest available purity and used as received unless stated otherwise. Trimethylolpropane triacrylate was donated by Sartomer. *N,N*-Diethylacrylamide was purchased from PolySciences and purified by vacuum distillation. *N*-Isopropylacrylamide was purified by recrystallization from hexane. *n*-Butyl acrylate was purified by passage over a column of basic alumina. 1-Cyano-1-methylethyl dithiobenzoate (CPDB) was prepared according to a literature procedure (Moad, G.; Chiefari, J.; Chong, Y. K.; Krstina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993-1001.) AIBN was recrystallized from methanol and stored in a freezer prior to use.

RAFT homopolymerization of *N,N*-diethylacrylamide (DEAm)

A mixture of DEAm (11.0 g, 86.5 mmol), CPDB (569 mg, 2.57 mmol), AIBN (84.4 mg, 0.514 mmol), and DMF (11.0 g) were added to a Schlenk flask equipped with a magnetic stirring bar. The mixture was stirred for at least 30 min in an ice bath to ensure complete dissolution of all components. The flask was then purged by repeatedly evacuating and refilling with N₂ at least 3 times and subsequently immersed in a preheated oil bath at 70 °C. After 11 hours the reaction was quenched by rapid cooling in liquid N₂ and exposure to air. The polymer was isolated by precipitation into a large excess of hexanes and 9.53 g polymer was recovered by freeze-drying. The polymer was analyzed via ¹H NMR spectroscopy, organic size exclusion chromatography (SEC).

Preparation of 3-arm stars (1.5:1 molar ratio of –SH:ene)

Poly(*N,N*-diethylacrylamide) (0.78g) was dissolved in THF (2.0 g) in a scintillation vial. After dissolution 14 µL of TMPTA was added followed by 29 µL of DMPP. The solution was stirred under nitrogen for 5 minutes to ensure complete homogeneity. Hexylamine (35 µL) was then added to this solution and the mixture was allowed to stir overnight.

Instrumentation

MALDI-TOF mass spectrometry was performed on a Bruker Reflex III Instrument equipped with a 337 nm N₂ laser in the reflector mode and 20kV acceleration voltage. α-Cyano-4-hydroxycinnamic acid (CHCA) was used as a matrix for molecular weight determination of the poly(*N,N*-diethylacrylamide) polymers before and after star formation.

NMR spectra were recorded on either a 300 (Bruker 300 53 mm) or 500 MHz NMR spectrometer. Specifically, in the case of the 500 MHz spectrometer:

¹³C NMR characterization: All spectra were acquired on a Varian ^{UNITY} INOVA spectrometer operating at a frequency of 125 MHz for carbon and using a standard 5mm two channel probe. A 90° pulsewidth of 5.75 µs was used. The acquisition time was 1.5 secs. with no recycle delay,

making the time between scans 1.5 secs. Proton decoupling was implemented during data acquisition to remove ^1H - ^{13}C scalar coupling. Samples were dissolved in THF, with sealed capillaries filled with DMSO- d_6 used for deuterium shimming and locking.

^1H NMR characterization: All spectra were acquired on a Varian ^{UNITY}INOVA spectrometer operating at a frequency of 499.8 MHz for proton and using a standard 5mm two channel probe. A 90° pulsewidth of 15.25 μs was used and an acquisition time of 1.9 secs. were used. Typically 64-96 scans were acquired for each sample, with a recycle delay of 4.1 secs. making the overall time between scans 6 secs. Samples were dissolved in THF, with sealed capillaries filled with DMSO- d_6 used for deuterium shimming and locking.

Organic SEC was conducted on a Waters system comprised of a Waters 515 HPLC pump, Waters 2487 Dual λ absorbance detector, Waters 2410 RI detector with a PolymerLabs PLgel 5 μm guard column and a PolymerLabs PLgel 5 μm MIXED-C column, in THF stabilized with 281 ppm BHT at a flow rate of 1.0 mL/min. The column was calibrated with a series of narrow molecular mass distribution poly(methyl methacrylate) standards.

FT-IR spectra were recorded using a modified Bruker 88 spectrometer. Samples were sandwiched between two sodium chloride salt plates at a thickness of ~20 micron. Each spectrum was collected over 32 scans. The data were analyzed with the Bruker OPUS/IR Version 4.0 software.