Electronic Supplementary Material (ESI) for Polymer Chemistry

Synthesis and Characterization of 4-Vinylimidazole ABA Triblock Copolymers Utilizing a Difunctional RAFT Chain Transfer Agent

Michael H. Allen, Jr.[a], Sean T. Hemp[a], Musan Zhang[a], Mingqiang Zhang[a], Adam E. Smith[b], Robert B. Moore[a], and Timothy E. Long[a,*]

Supporting Information

Triblock Copolymer	25 °C	60 °C	80 °C	100 °C
Poly(4VIM$_{35}$-*b*-DEGMEMA$_{134}$-*b*-4VIM$_{35}$)	32,500	32,900	34,300	40,500
Poly(4VIM$_{53}$-*b*-DEGMEMA$_{134}$-*b*-4VIM$_{53}$)	35,800	35,300	46,400	47,000
Poly(4VIM$_{89}$-*b*-DEGMEMA$_{134}$-*b*-4VIM$_{89}$)	42,500	58,600	67,200	67,200

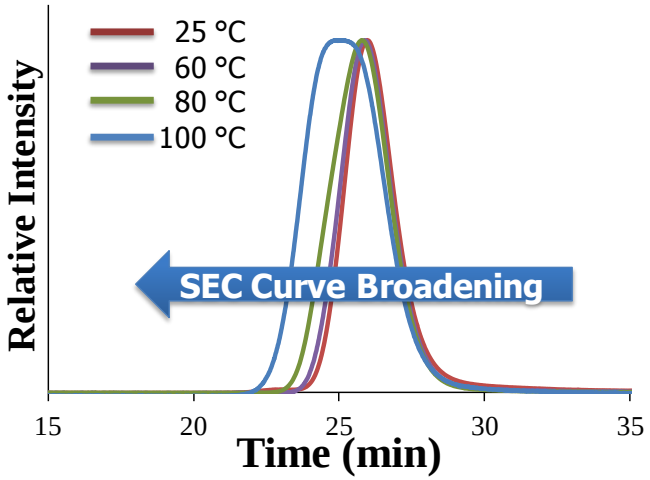


Figure S1. Aqueous SEC of poly(4VIM-b-DEGMEMA-b-4VIM) triblock copolymers after annealing for 24 h at various temperatures. SEC curve broadening occurred suggesting a post-polymerization reaction for extended times at elevated temperatures.

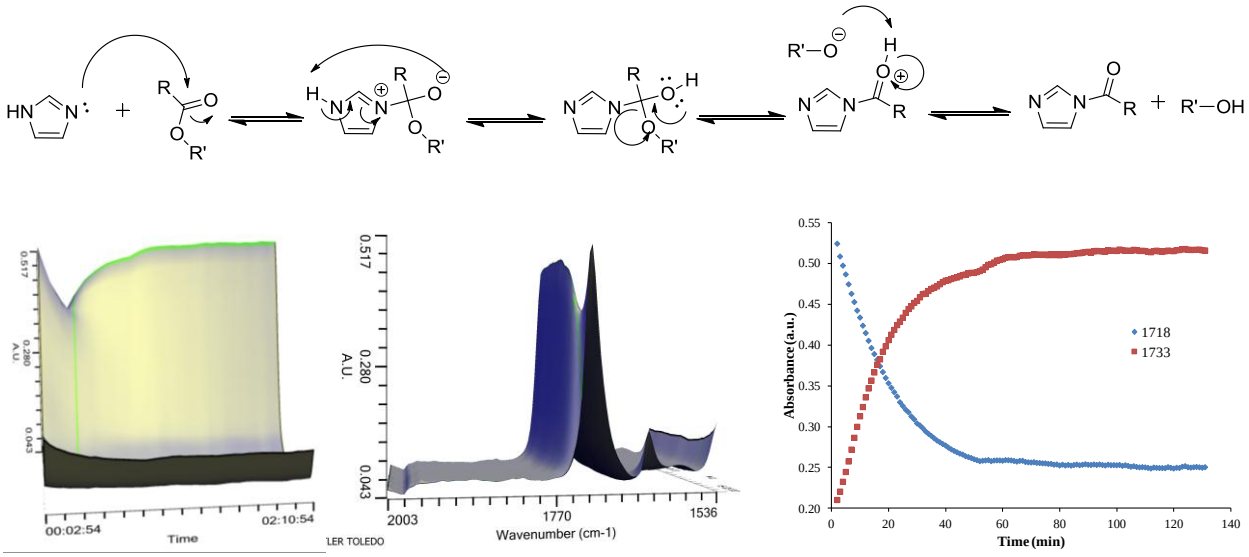
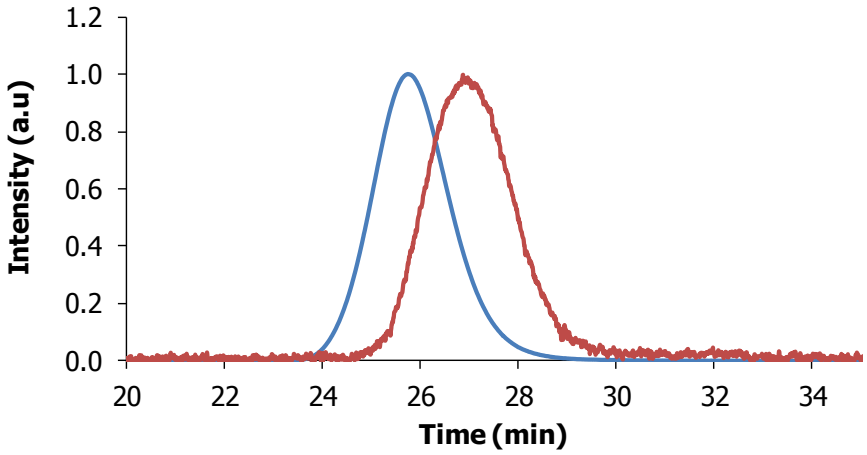


Figure S2. *In situ* FTIR of DEGMEMA in imidazole at 100 °C to probe possible reactions occurring during annealing of triblock copolymer films. Imidazole catalyzed the hydrolysis of DEGMEMA (1718 cm^{-1}) into an amide bond (1733 cm^{-1}) and di(ethylene glycol) methyl ether as evidenced in the *in situ* FTIR plots. The proposed mechanism is shown above.



Polymer	M_n g/mol	M_w g/mol	PDI
Poly(DEGMEMA) macroCTA	53,700	54,700	1.02
After 24 h in 1 M NaOH solution	25,000	25,700	1.03

Figure S3. Base stability study of poly(DEGMEMA) macroCTA synthesized with dCEP-OH to cleave the ester groups present in dCEP-OH. dCEP-NH2 shows no hydrolysis of amide groups.

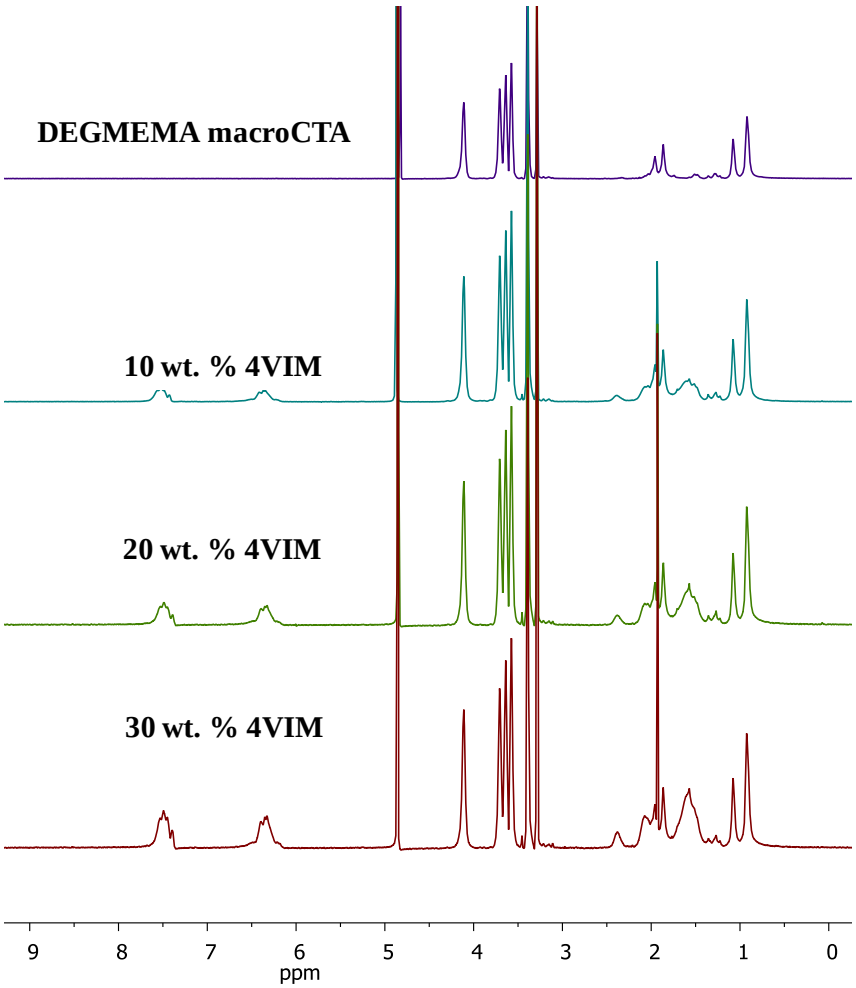


Figure S4. ^{1}H NMR spectroscopy of the DEGMEMA macroCTA and the various 4VIM-containing triblock copolymers in CD_3OD.

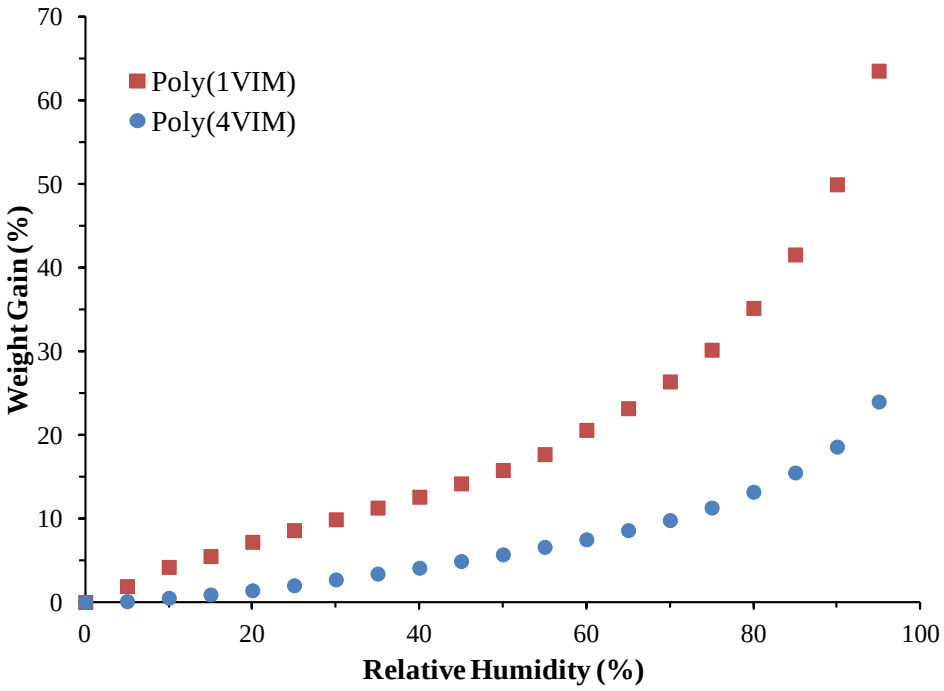
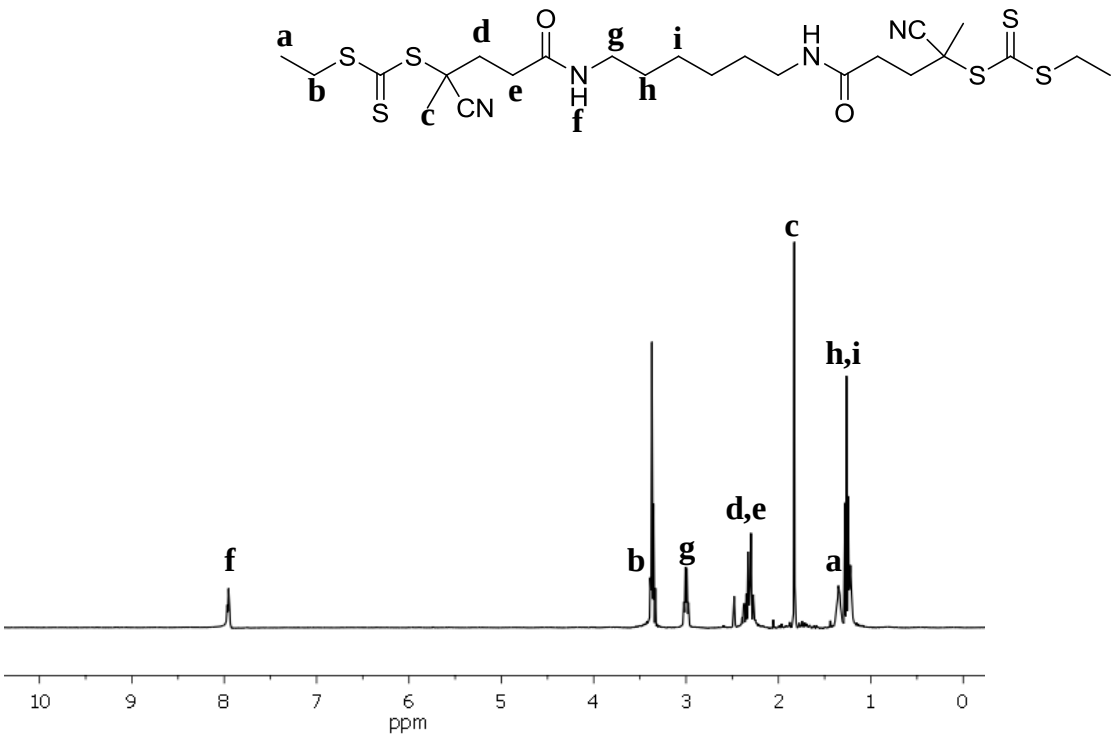


Figure S5. Water sorption analysis of poly(1VIM) and poly(4VIM) at various relative humidities.

a)



b)

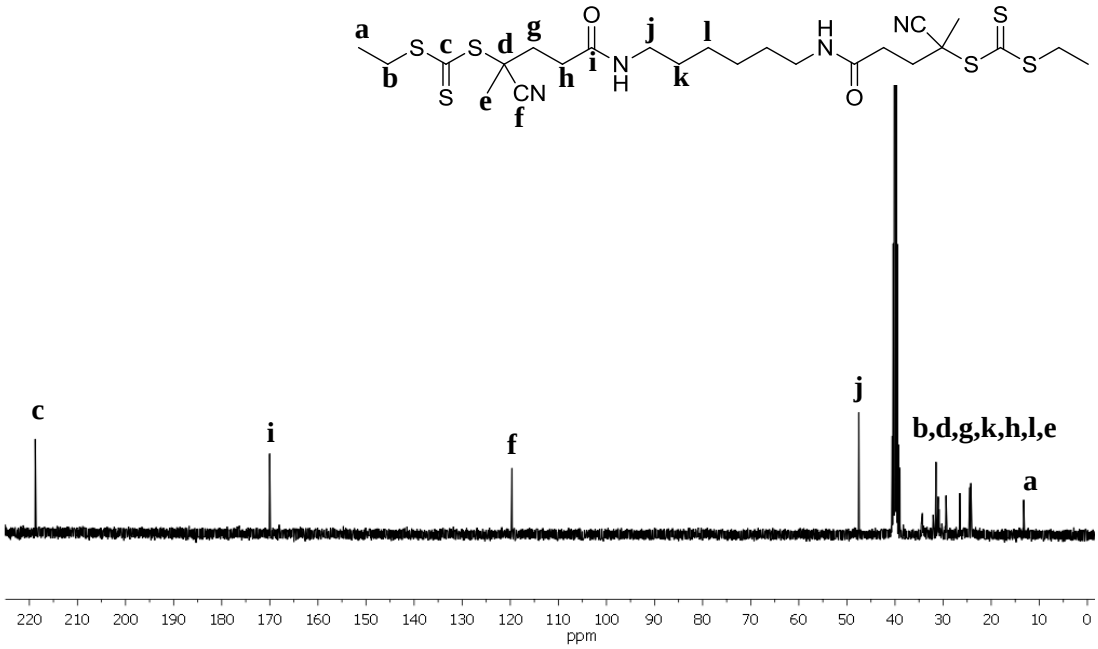


Figure S6. a) ^{1}H NMR and b) ^{13}C NMR of dCEP-NH_2 in d_6-DMSO.

a)

b)

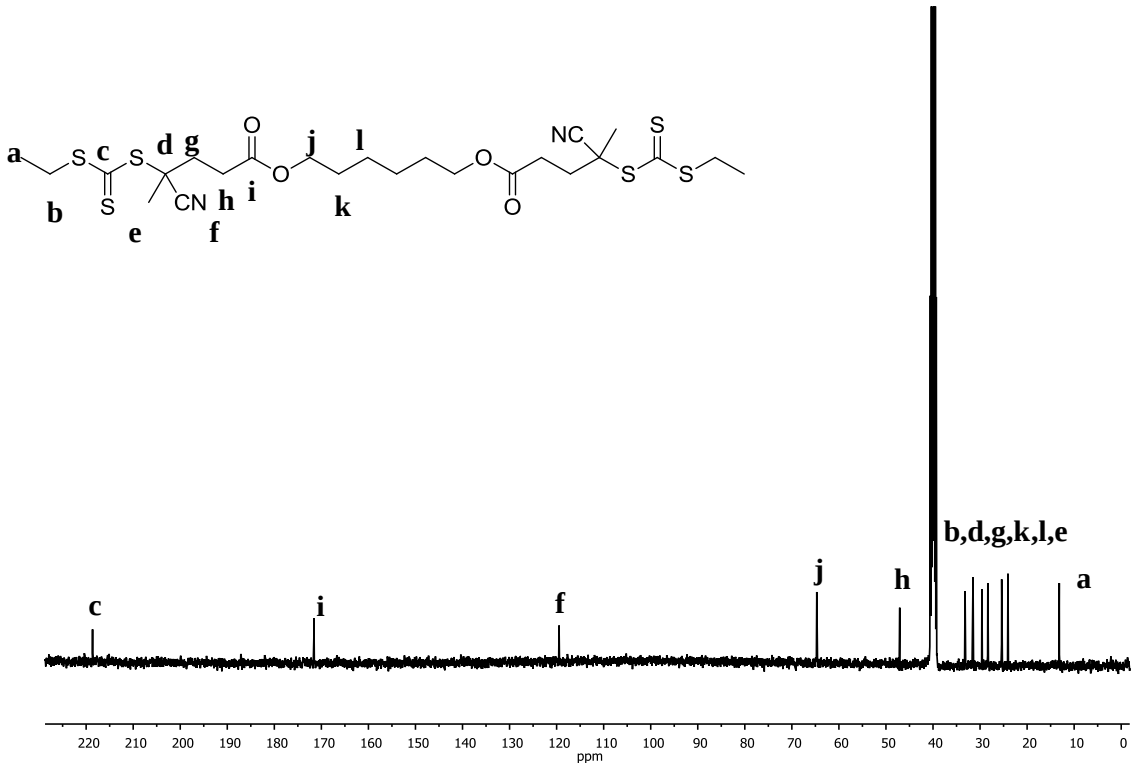


Figure S7. a) ^{1}H NMR and b) ^{13}C NMR of dCEP-OH in d_6-DMSO.

RAFT Polymerization of Additional Methacrylic Monomers with dCEP. In a representative polymerization, methyl methacrylate (1.00 g, 9.99 mmol), dCEP (15.2 mg, 25.0 μmol = 50.0 μmol TTC), V-501 (7.00 mg, 25.0 μmol, and DMF (18.85 g, 258 mmol) were added to a 50-mL, round-bottomed flask equipped with stir bar. The reaction was sparged with argon for 15 min and immersed in a thermostated oil bath at 70 °C for 6 h. Absolute molecular weights were determined with SEC using 0.05M LiBr-DMF as the mobile phase.

RAFT Polymerization of Styrene with dCEP. Styrene (3.00 g, 28.8 mmol) and dCEP (9.8 mg, 16.1 μmol = 32.2 μmol TTC) were added to a 10-mL, round-bottomed flask equipped with stir bar and sparged with argon for 5 min. The reaction was immersed in a thermostated oil bath at 140 °C for 1 h. Absolute molecular weights were determined with SEC using 0.05 M LiBr-DMF as the mobile phase.**RAFT Polymerization of Acrylic Monomers with dCEP.** In a representative polymerization, *n*BA (1.00 g, 7.80 mmol), dCEP (11.8 mg, 19.5 μmol = 39.0 μmol TTC), V-501 (2.19 mg, 7.80 μmol), and DMF (113 mg, 1.55 μmol) were added to a 10-mL, round-bottomed flask equipped with stir bar. The reaction was sparged with argon for 15 min and immersed in a thermostated oil bath at 70 °C for 1 h. Absolute molecular weights were determined with SEC using 0.05 M LiBr-DMF as the mobile phase.

RAFT Polymerization. In a representative RAFT polymerization, EG_9MEMA (4.00 g, 8.25 mmol), dCEP (100 mg, 165 μmol = 330 μmol TTC), V-501 (18.5 mg, 66.0 μmol), and DMSO (36.3 g, 465 mmol) were added to a 50-mL, round-bottomed flask equipped with a stir bar. The reaction was sparged with argon for 30 min at room temperature. The reaction was subsequently placed in a thermostated oil bath at 70 °C for 250 min. The resulting polymer was dialyzed (MWCO = 3500 g/mol) for 3 days against dI water while changing the water every 24 h. The solution was lyophilized for 48 h to obtain a pure, yellow oil. Aqueous SEC determined an

absolute M_n = 22,900 g/mol, PDI = 1.02. RAFT polymerization with CEP (86.9 mg, 330 μmol = 330 μmol TTC) under the same conditions ([EG_9MEMA]/[TTC]/[V-501] ratio = 125/5/1) produced poly(EG_9MEMA) with an M_n = 12,000 g/mol, PDI = 1.01.

Microscopy. A veeco multimode running in tapping mode with a 42 nN spring constant tip at a set point ratio of 0.82 on microtomed surfaces where the block was mounted with epoxy onto an AFM sample holder magnetic disc. Cryo ultramicrotomy was performed on a RMC Products Powertome PC ultramicrotome equipped with a CRX cryo attachment using a Diaotome MT12610 diamond blade. TEM was performed on a JEOL-JEM 1400 operated at 80 kV accelerating voltage.