

Experimental

Molecular weights and PDIs were measured using gel permeation chromatography in THF (1.0 mL/min and 0.5 mL/min) and DMF (0.01 M LiCl, 0.5 mL/min) and referenced against linear polystyrene standards. The system utilized three-columns (Polymer Laboratories 300 x 7.5 mm, 2 Mixed-D, 50 Å) and a refractive index detector (Waters R4010). High temperature GPC was performed on a Polymer Laboratories PL-GPC 200 equipped with a Wyatt Minidawn multiple angle laser light scattering (MALLS) detector using trichlorobenzene (135 °C) at a flow rate of 1.1 mL/min. NMR spectra were collected on a Bruker DPX 300 spectrometer (referenced to CDCl₃): ¹H at 300 MHz and ¹³C at 75 MHz. DSC experiments were performed on a TA instruments Q1000 at a heating rate of 10 °C/min.

Cyclooctene, cyclooctadiene, succinic anhydride (99%), lithium aluminum hydride (95%), and bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride were purchased from Alfa Aesar. *m*-Chloroperoxybenzoic acid (MCPBA) (77%), 4-dimethylaminopyridine (DMAP) (99%), 1,3-dicyclohexylcarbodiimide (DCC) (99%), and ethyl vinyl ether (99%) were purchased from Aldrich. 1,3-bis-(2,4,6-trimethylphenyl)-2-(imidazolidinylidene)dichloro(phenylmethylene) (tricyclohexylphosphine) ruthenium was purchased from Strem Chemical. Polyethylene glycol monomethyl ether (mPEG) 750 was purchased from Polysciences, Inc and purified by column chromatography (in CH₂Cl₂/Acetone/MeOH mixtures) before use. mPEG 1000 was purchased from Shearwater Polymer, Inc. and used without further purification.

Preparation of succinic acid mono-cyclooct-4-enyl ester (2). 3.00 g (2.38 mmol) of 5-hydroxy-cyclooctene (1),¹³ 2.38 g (2.38 mmol) of succinic anhydride, and 50 mg (0.41 mmol) of 4-dimethylaminopyridine (DMAP) were stirred in refluxing toluene (20 mL) for 16 hours. The solution was cooled to room temperature, washed with 1 M HCl_{aq}, and concentrated to yield a white solid. This solid was dissolved in ethanol and precipitated into water. This was brought to 70 °C, then precipitated into ice-cold water. The solid was collected, and dried under vacuum to afford 4.58 g (85 %) of **2**: m.p. 55-57 °C; ¹H NMR (CDCl₃) δ 10.75 (br s, 1H), 5.65 (m, 2H), 4.85 (m, 1H), 2.55-2.67 (m, 4H), 1.57-2.4 (m, 10H) ppm; ¹³C NMR (CDCl₃) δ 178.9 (acid), 171.9 (ester), 130.2, 123.0,

76.7, 34.0, 33.9, 29.6, 29.4, 25.9, 22.2, 22.7 ppm; IR (KBr) 3018, 2938, 2866, 1728 (ester), 1704 (acid), 1447, 1408, 1355, 1255, 1236, 1213, 1171 cm^{-1} .

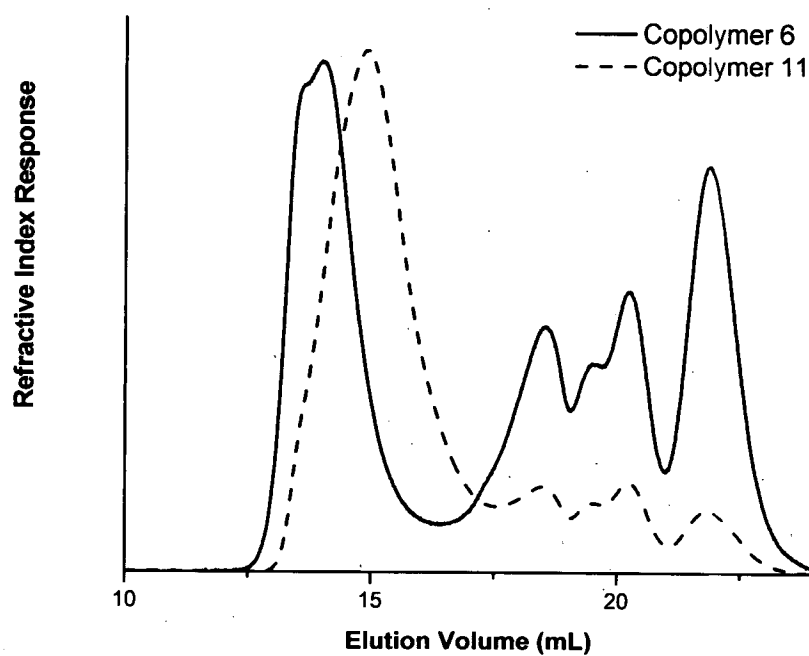
Esterification of 2 with mPEG 1000. 2.0 g (8.8 mmol) of **2**, 8.8 g (8.8 mmol) of poly(ethylene glycol) monomethyl ether (ca. 1000 a.m.u), and 106 mg (0.88 mmol) DMAP were stirred in dry CH_2Cl_2 (15 mL) under $\text{N}_{2(\text{g})}$. Separately, 2.2 g (10.6 mmol) DCC was diluted with 1.4 g (17.6 mmol) pyridine and CH_2Cl_2 (15 mL); this solution was then added by syringe to the reaction mixture and stirred for 12 hours at room temperature under $\text{N}_{2(\text{g})}$. Upon completion, the mixture was washed with 1 M HCl_{aq} and concentrated. The product was dissolved in a hexane/ethyl acetate mixture and twice extracted with water. The aqueous phase was extracted with CH_2Cl_2 , concentrated, and dissolved in toluene. This solution was washed twice with a sat. NaCl_{aq} and dried using MgSO_4 . Toluene was removed by evaporation, and the product was dissolved in a minimal amount of diethyl ether and precipitated into cold hexane. The product was collected and dried under vacuum overnight to yield 8.1 g (76 %) of **5**: m.p. 42-43 °C; ^1H NMR (CDCl_3) δ 5.65 (m, 2H), 4.83 (m, 1H), 4.22 (t, 2H), 3.5-3.7 (complex, br m, ~90H), 3.38 (s, 3H), 2.55-2.67 (m, 4H), 1.57-2.4 (m, 10H) ppm; ^{13}C NMR (CDCl_3) δ 172.4 (ester), 171.6 (ester), 129.8, 129.6, 76.8, 72.0, 70.6, 69.1, 63.9, 59.1, 33.7, 33.6, 29.5, 29.2, 25.6, 24.9, 22.3 ppm.

Example Copolymerization using Macromonomer 4 (Table 2, entry 8). 0.50 g (0.52 mmol) of macromonomer **4** was weighed into a small tube and degassed under vacuum while stirring at 45 °C. 58 mg (0.52 mmol) of cyclooctene was injected into the vessel under $\text{N}_{2(\text{g})}$. 3.52 mg (4.14 μmol) of catalyst **II** was weighed into a small vial, degassed, and diluted with 1.04 mL of dry dichloromethane under $\text{N}_{2(\text{g})}$. The catalyst solution was introduced by syringe, and the mixture was stirred at 45 °C. Upon vitrification, the reaction was terminated using ethyl vinyl ether, and a small amount of CH_2Cl_2 (~1 mL) was added to improve stirring. The contents were then precipitated into cold hexane, filtered, and dried under vacuum to yield 0.42 g (84%) of the copolymer. ^1H NMR (CDCl_3) δ 5.34 (br, olefin 2H), 4.86 (br s, 1H), 4.22 (t, 2H), 3.5-3.7 (complex, br m), 3.36 (s, 3H), 2.61 (br m, 4H), 2.32 (br s), 1.94 (br s), 1.50 (br s), 1.26 ppm (br s); ^{13}C NMR (CDCl_3) δ 172.7 (ester), 172.3 (ester), 130.0, 130.8, 129.3, 74.7, 72.3, 70.9, 69.4, 64.2, 59.4, 34.4, 33.0, 30.0, 29.7, 29.5, 28.8, 25.6 ppm. IR (NaCl plate) 2922, 2867,

1733 (ester), 1456, 1349, 1300, 1250, 1111, 1040, 968, 860 cm^{-1} . GPC (DMF w/ 0.01% LiCl vs. linear polystyrene standards) $M_n = 330,000$ g/mol, $M_w = 515,000$ g/mol, PDI = 1.56.

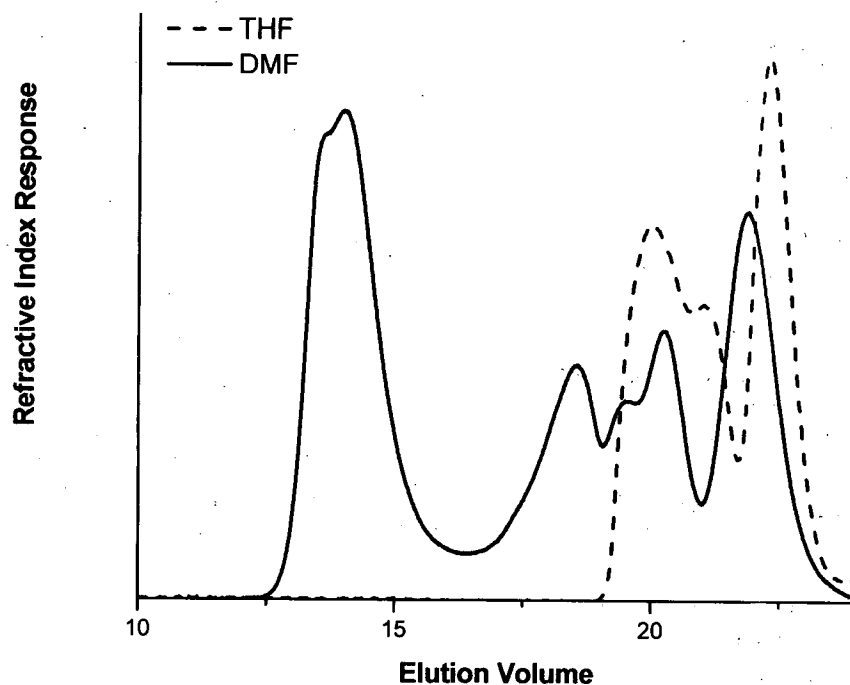
Hydrogenation of Unsaturated Graft Copolymers. Hydrogenated copolymers were synthesized according to published procedures^{13,21} in 90% yield. Precipitation of copolymers **6a** - **8a** were performed in cold hexane. Precipitation of **9a** was performed in cold methanol. Hydrogenated copolymer **7a**: ^1H NMR (CDCl_3) δ 4.86 (broad s, 1H), 4.24 (t, 2H), 3.5-3.7 (complex, br m), 3.38 (s, 3H), 2.61 (br m, 4H), 1.65 (br s), 1.50 (br s), 1.26 ppm (br s); ^{13}C NMR (CDCl_3) δ 172.7 (ester), 172.3 (ester), 75.2, 72.2, 70.8, 69.4, 64.0, 59.4, 30.0, 25.6 ppm. IR (NaCl plate) 2919, 2852, 1733 (ester), 1464, 1349, 1299, 1250, 1139, 1110, 1040, 957, 858 cm^{-1} .

Supporting Figure 1



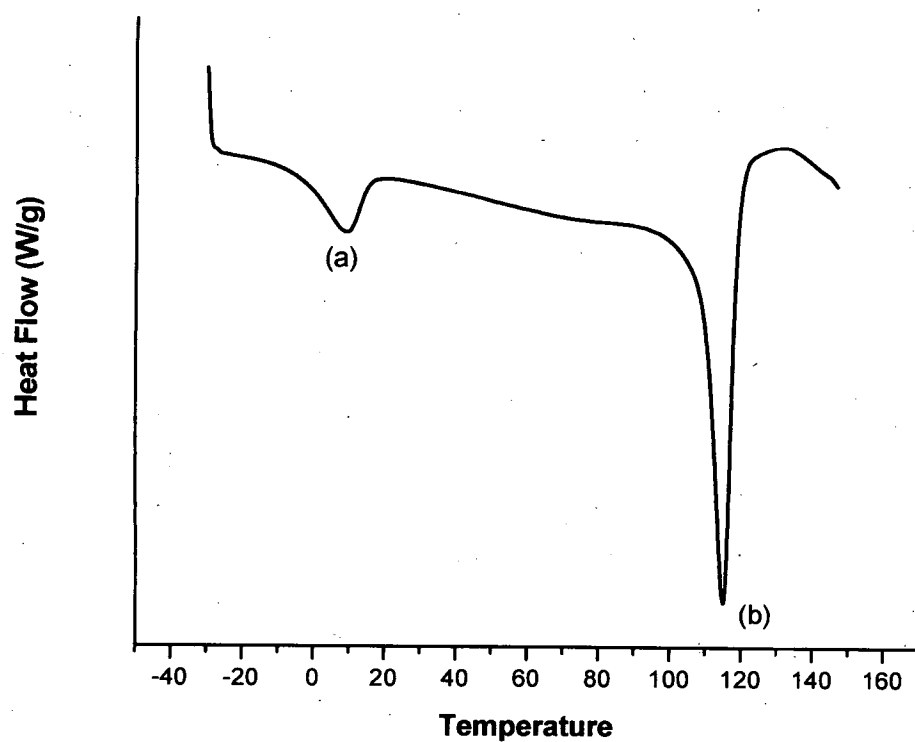
Supporting Figure 1. GPC chromatograms of copolymers 6 and 11 synthesized with different concentrations of catalyst I (500-to-1 and 100-to-1, respectively)

Supporting Figure 2



Supporting Figure 2. Comparison of solvent effects on copolymer 6 (50/50 COE/Macromonomer copolymer); GPC recorded in THF and DMF

Supporting Figure 3



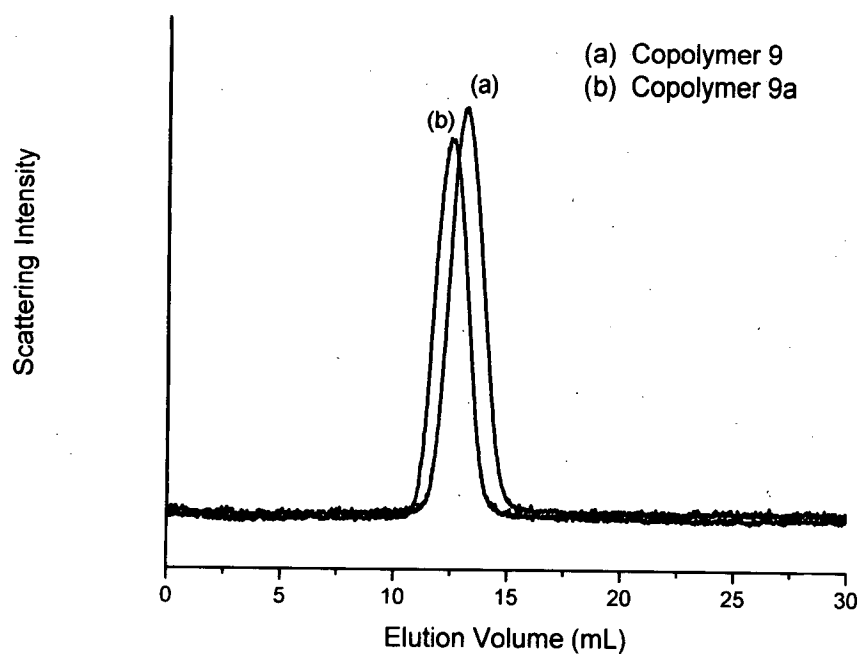
Supporting Figure 3. DSC chromatogram of copolymer 9a: (a) PEO $T_m = 8.7^\circ\text{C}$, (b) PE $T_m = 115.1^\circ\text{C}$)

The chemical structure represents a copolymer of 2-ethylhexanoic acid and 2-ethyltetrahydrofuran. The main chain consists of repeating units of 2-ethylhexanoate and 2-ethyltetrahydrofuran. The protons are labeled as follows: (a) for the methylene protons adjacent to the ester group, (b) for the methine proton adjacent to the ester group, (c) for the methylene protons adjacent to the ether oxygen, and (d) for the methylene protons in the tetrahydrofuran ring. The ¹H NMR spectrum shows peaks corresponding to these labels: (a) at ~4.8 ppm, (b) at ~2.3 ppm, (c) at ~1.8 ppm, and (d) at ~1.2 ppm.

Supporting Figure 4. ^1H NMR spectrum of hydrogenated copolymer 7a

8

Supporting Figure 5



Supporting Figure 5. GPC chromatograms of copolymer 9 before and after hydrogenation (9a) using Multiple Angle Laser Light Scattering (MALLS)