

**Supporting Information for**

**Formation of Nanoparticles by Intramolecular Cross-linking:  
Following the Reaction Progress of Single Polymer Chains by  
Atomic Force Microscopy**

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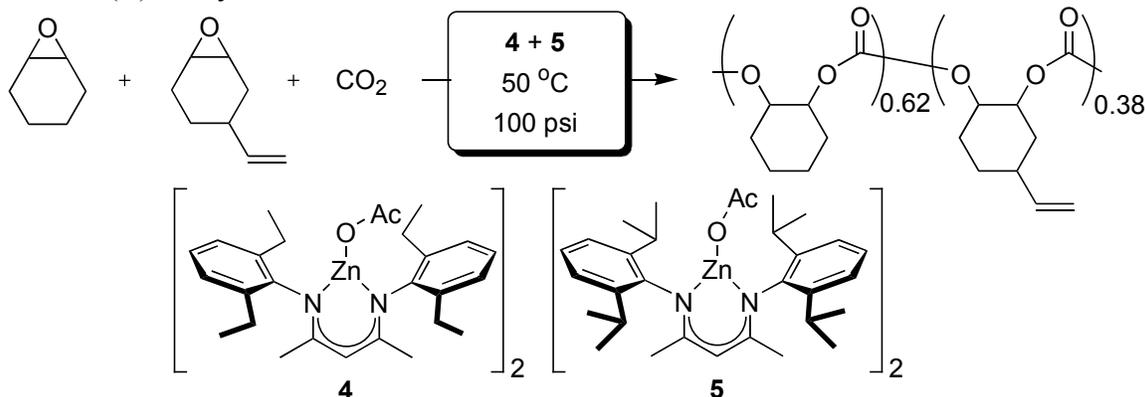
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**General Methods.** All manipulations of air- and /or water-sensitive compounds were carried out under dry nitrogen using a Braun UniLab drybox or standard Schlenk line techniques. Polymer samples were dissolved in chloroform-*d* in a 5-mm O.D. tube and spectra were recorded on a Varian Mercury (300 MHz) spectrometer and referenced versus residual non-deuterated solvent shifts. Molecular weights ( $M_n$  and  $M_w$ ) and polydispersities ( $M_w/M_n$ ) were determined by gel permeation chromatography using a Waters instrument (515 HPLC pump, 717plus autosampler) equipped with Waters UV486 and Waters 2410 differential refractive index detectors, and three 5m PL Gel columns (Polymer Laboratories: 100Å, 500 Å, 1000 Å, and Mixed C porosities) in series. The GPC columns were eluted with tetrahydrofuran at 40 °C at 1 mL/min and calibrated using 23 monodisperse polystyrene standards. Polymer melting points ( $T_m$ ) and glass transition temperatures ( $T_g$ ) were measured by differential scanning calorimetry (DSC) using a TA Instruments Q1000 calorimeter equipped with an automated sampler. Analyses were performed in crimped aluminum pans under nitrogen and data were collected from the second heating run at a heating rate of 10 °C/min from -100 to 200 or 220 °C, and processed with the TA Q series software.

**Materials.** Toluene was purified over columns of alumina and copper (Q5). All chemicals were purchased from Aldrich, except where noted, and used as received. Cyclohexene oxide and vinylcyclohexene oxide were distilled from CaH<sub>2</sub> and degassed by three freeze-pump-thaw cycles. [(BDI)ZnOAc]<sub>2</sub> catalysts **4** and **5** were prepared according to literature procedures.<sup>1</sup> Linear polymers were prepared as described below.

**Scheme S1.** Terpolymerization of cyclohexene oxide, vinylcyclohexene oxide, and CO<sub>2</sub> with Zn(II) catalysts **4** and **5**.

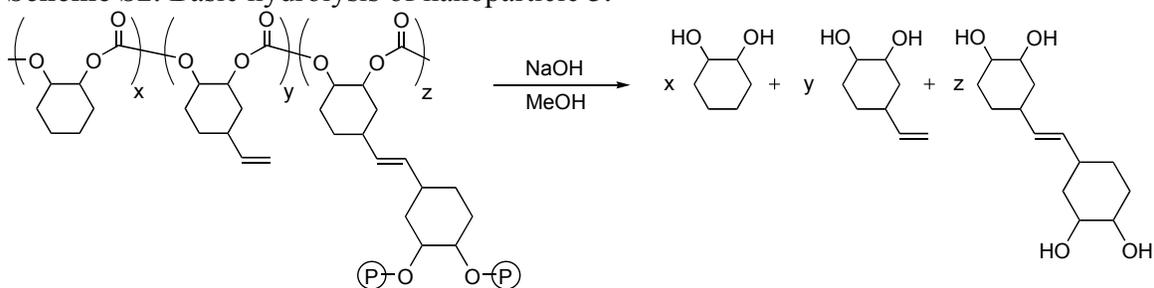


**Terpolymerization of Cyclohexene Oxide, Vinylcyclohexene Oxide, and CO<sub>2</sub>.** A combination of Zn(II) catalysts **4** and **5** were used, which resulted in approximately double the activity of either catalyst independently.<sup>1</sup> Cyclohexene oxide (36.8 mL, 0.364 mol), vinylcyclohexene oxide (20.4 mL, 0.156 mol) catalyst **4** (0.126 g, 0.260 mmol), catalyst **5** (0.141 g, 0.260 mmol) and toluene (50 mL) were combined in a 6 oz. Parr reactor. The reactor was heated to 50 °C and CO<sub>2</sub> (100 psi) was added. After 3.5 h, the reaction was quenched and precipitated by venting CO<sub>2</sub> and pouring into MeOH. The resulting polymer **1**, (48.3 g,  $M_n = 54,100$  g/mol,  $M_w/M_n = 1.20$ ) had 38 mol % vinyl-containing units.

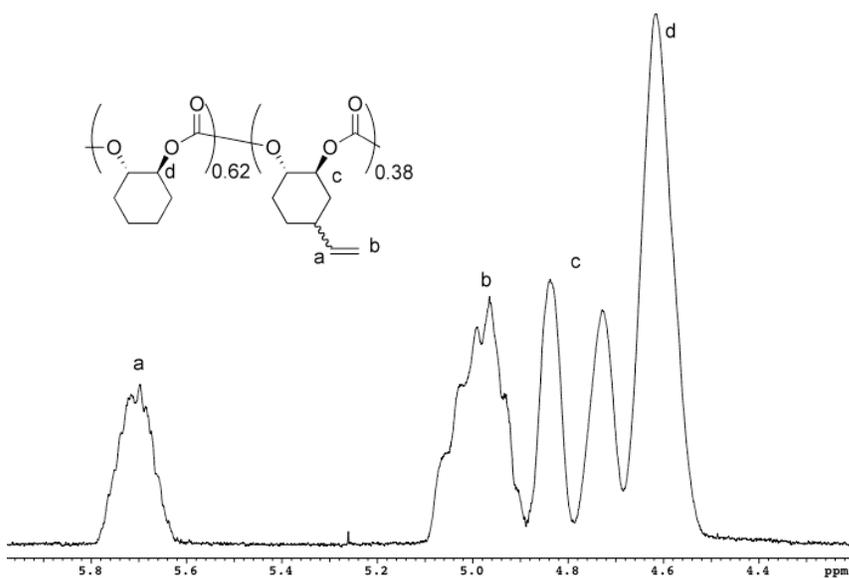
**Intramolecular Cross-linking of Poly(CHC-co-VCHC).** Polymer **1** (0.25 g, 0.65 mmol vinyl-containing units) was dissolved in toluene (250 mL). A solution of **2** (0.011 g,  $13.0 \times 10^{-6}$  mol) in toluene (5 mL) was added. The reaction was quenched with ethyl vinyl ether (10 mL) after the appropriate time. Solvents were removed in vacuo, and the product **3** was dissolved in toluene (4 mL) and passed over a short column of silica gel to remove residual catalyst **2**. The nanoparticle **3** was then precipitated by adding to MeOH.

<sup>1</sup> Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2003**, *125*, 11911-11924.

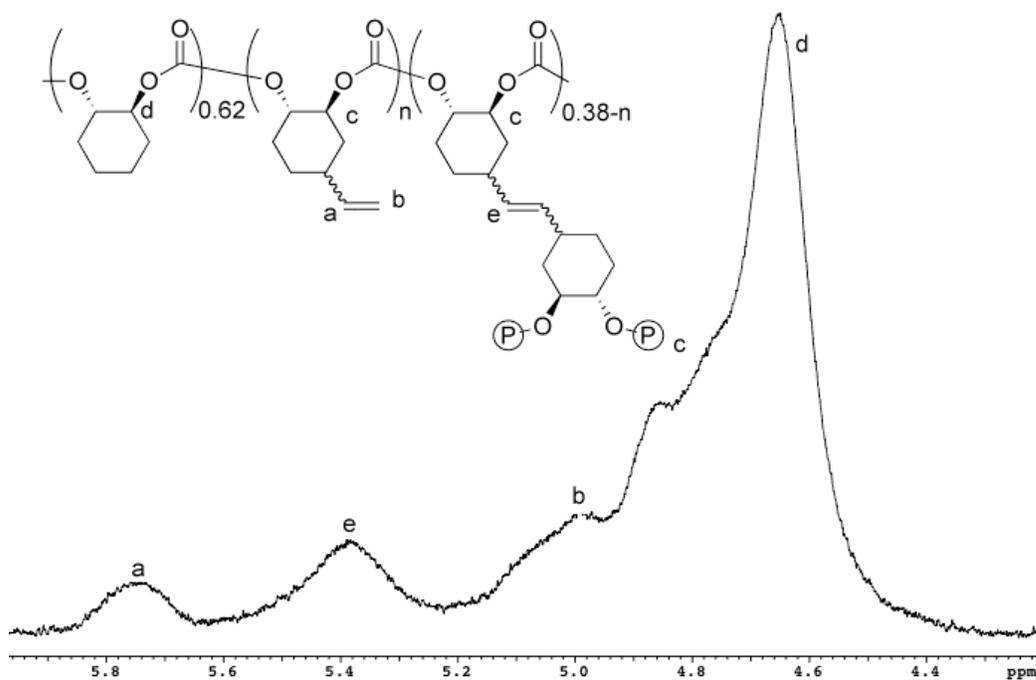
**Scheme S2.** Basic hydrolysis of nanoparticle **3**.



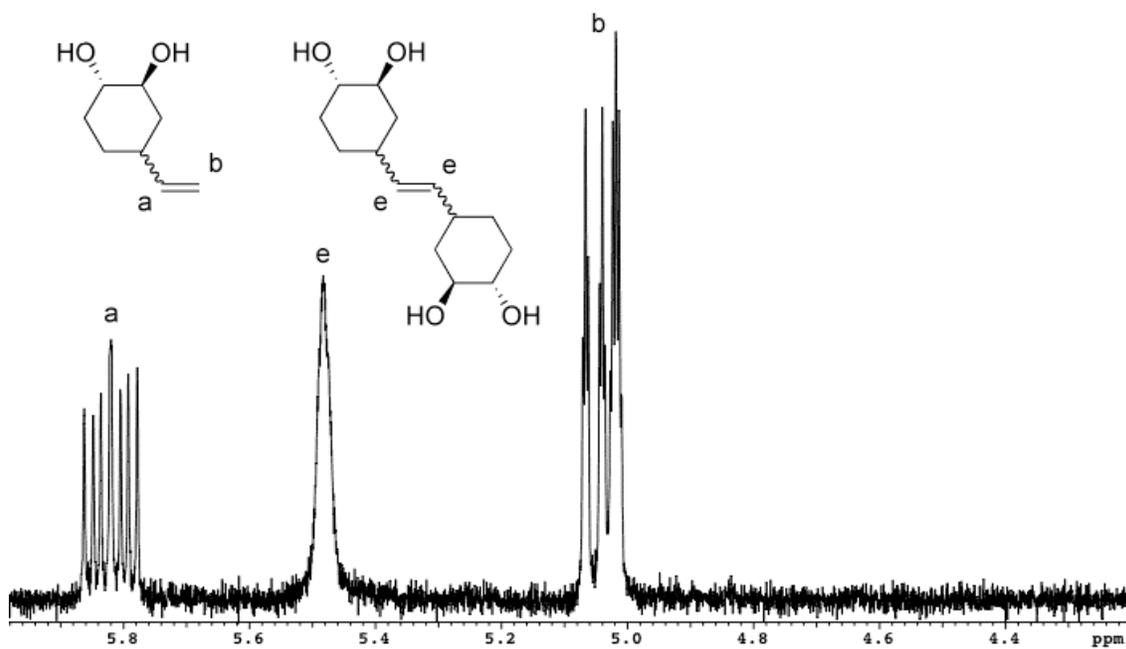
**Basic Hydrolysis of Nanoparticle 3.** Nanoparticle **3** (Table 1, entry 2; 50 mg, 0.32 mmol vinyl containing units) and NaOH (95 mg, 2.4 mmol) were combined in MeOH (10 mL) and heated to reflux for 6 h. Glacial acetic acid (0.5 mL) was added to quench the reaction, and all volatiles were removed in vacuo. Chloroform-*d* was added to a 5 mg sample of the solid residue and shaken for 30 min. The solution was filtered and analyzed by  $^1\text{H}$  NMR spectroscopy, revealing 54 % cross-linking.



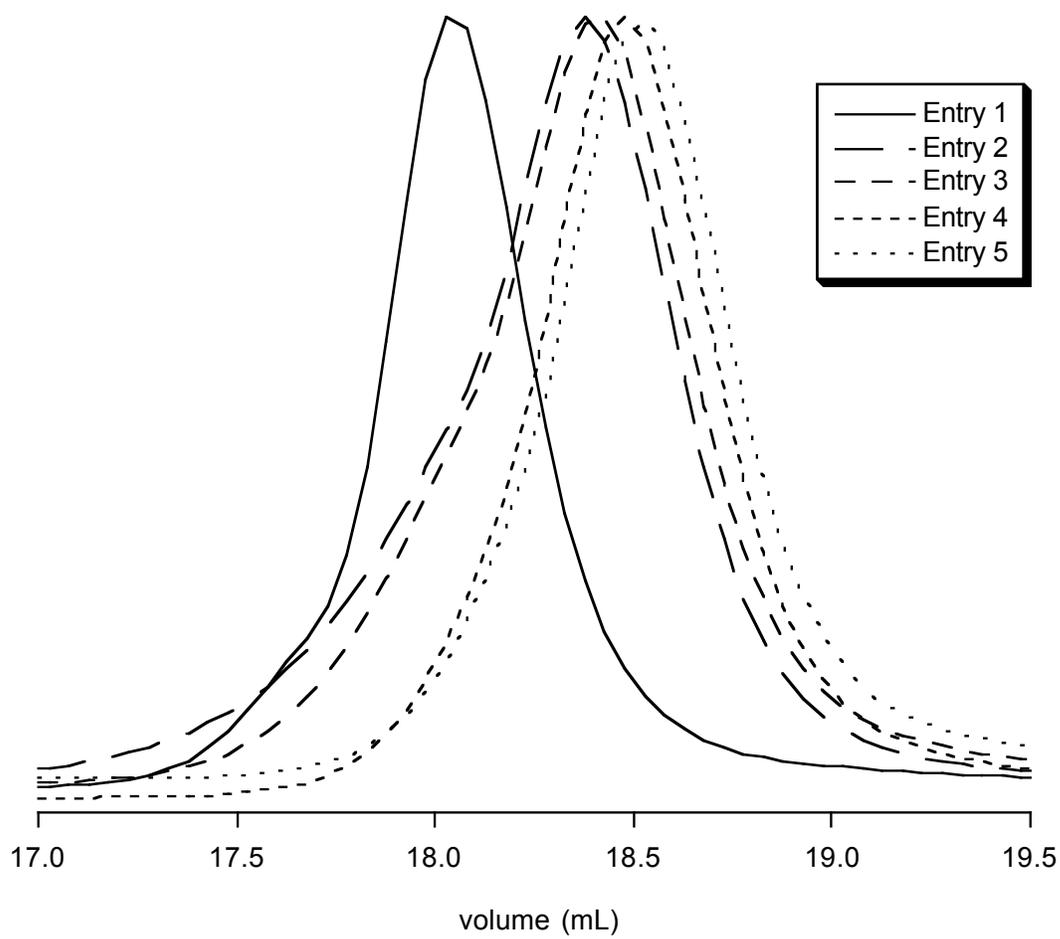
**Figure S1.**  $^1\text{H}$  NMR spectrum (300 MHz, chloroform-*d*) of polycarbonate **1** (Table 1, entry 1).



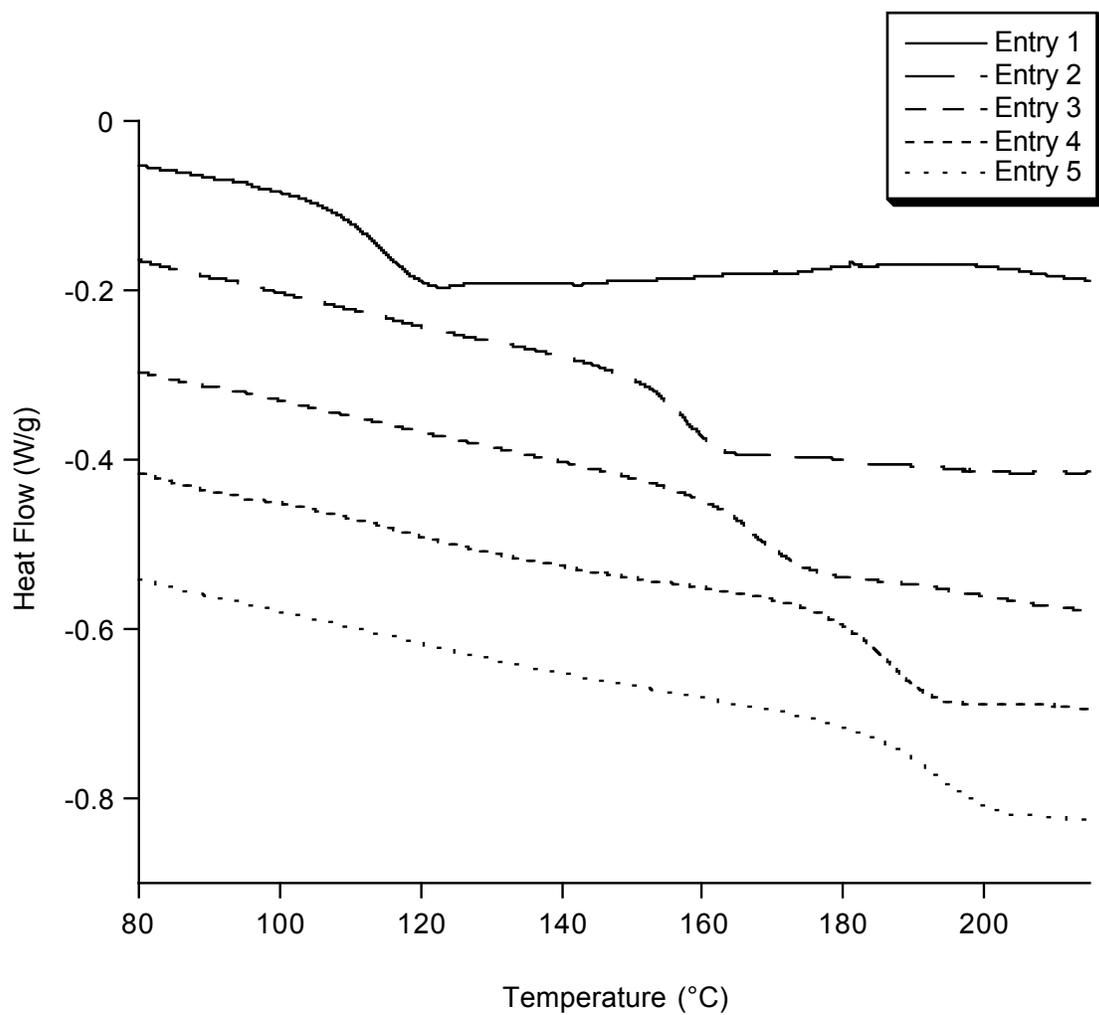
**Figure S2.**  $^1\text{H}$  NMR spectrum (300 MHz, chloroform-*d*) of cross-linked nanoparticle **3** (Table 1, entry 5).



**Figure S3.**  $^1\text{H}$  NMR spectrum (400 MHz, chloroform-*d*) of hydrolyzed **3** (Table 1, entry 2).



**Figure S4.** Gel permeation chromatograms of **1** and **3** (Table 1, entries 1-5).



**Figure S5.** Differential scanning calorimetry traces of **1** and **3** (Table 1, entries 1-5).