Supporting Information

Insertion Metathesis Depolymerization

Michael D. Schulz, Rachel R. Ford, and Kenneth B. Wagener

The George and Josephine Butler Polymer Research Laboratory, Department of Chemistry and Center for Macromolecular Science and Engineering, University of Florida, Gainesville, FL 32611, United States

wagener@chem.ufl.edu

Materials and Measurements

Acrylates and other chemicals were purchased from Aldrich and used as received. Polybutadiene samples were a gift from Firestone and used as received. Polymer 1: M_n = 100 kDa, 97% cis, PDI= 2.3. Polymer 2: M_n = 125 kDa, 40% cis, PDI= 1.2. Catalysts were donated by Materia, Inc. All ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts for ¹H and ¹³C NMR were referenced to residual signals from CDCl₃ (¹H 7.25 ppm and ¹³C 77.00 ppm). Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments Q1000 equipped with a liquid nitrogen cooling accessory and calibrated using sapphire and high purity indium metal. All samples were prepared in hermetically sealed pans (4–7 mg/sample) and were referenced to an empty pan. A scan rate of 10 °C per minute was used. Glass transition temperatures were taken as the midpoint of a step change in heat capacity. Thermal experiments were conducted as follows: samples were heated through 220 °C, followed by cooling at 10 °C per minute to –80 °C, and then heated through 22 °C 0 at 10 °C per minute. Data reported reflects this second heating scan.

General Depolymerization

A flame-dried Schlenk tube was charged with polymer (~0.03g segments, 1 eq. repeat unit) and catalyst (0.005 eq.) under argon. Acrylate (2.03 eq. relative to the repeat unit of the polymer) was then injected. The reaction was stirred at 50 °C. Subsequently, the reaction was exposed to air and the extent of depolymerization was determined by NMR.

The depolymerization products all displayed similar spectra. Characteristic spectra peaks for complete depolymerization are given below.

¹H NMR (300 MHz, CDCl₃): $\delta = 6.878$ (m, 2H, CO₂CH-CH-CH₂), 5.792 (d, 2H, CO₂CH-CH), 4.144 (q, 4H, CO₂CH₂CH₃), 2.336 (m, 4H, CH-CH₂CH₂-CH), 1.245 (t, 6H, CO₂CH₂CH₃). ¹³C NMR (75 MHz, CDCl₃): $\delta = 166.4$ (2C, C=O), 146.9 (2C, OCCH=CH), 122.4 (2C, OCCH=CH), 60.4 (2C, CH₂-CH=CH), 30.5 (2C, O-CH₂), 14.3 (2C, O-CH₂CH₃). FT-IR (ATR): 3024-2829 (m, ν_{CH}), 1717 (s, $\nu_{C=O}$), 1653 (m), 1462 (m), 1393 (w), 1367 (m), 1267 (m), 1199 (s), 1181 (s), 1154 (s), 1096 (m), 1038 (m), 979 (m), 860 (w), 713 (w).

Conversion of polybutadiene to polyamide

A flame-dried Schlenk tube under Ar was charged with 0.5g **P1** and 0.029g of **2**. Acryloyl chloride (1.8 mL) was then added and the reaction was stirred for 2 h at room temperature. The product was dissolved in hexane and poured into a beaker containing 1,6-diaminohexane in water, resulting in interfacial polymerization. The product was an intractable solid and characterized by IR spectroscopy and differential scanning calorimetry.

Polyamide: FT-IR (ATR): 3290 (m, v_{NH}), 2921 (m, v_{CH}), 1655 (m, v_{C-N}), 1617 (s, $v_{C=0}$), 1540 (s, $v_{C=C}$), 965.