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Thermally Controlled Formation of Fullerene−Diene Oligomers and Copolymers

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Formation of thermally reversible polymers is an important goal in materials science. Thermoreversible polymers are obvious candidates for recyclable materials, allowing facile reprocessing and reuse. Additionally, these materials combine the physical properties of thermosets, while still allowing processing to be performed at elevated temperatures. These polymers also present the opportunity of annealing, allowing the creation of stress-free rigid polymers. Two important requirements for the formation of thermally reversible polymers are sufficiently differentiated polymerization and depolymerization temperatures and low enough depolymerization temperatures to allow thermal cycling without degradation of the monomer units.[1]

To provide a system that possesses the thermal stability profile required for the creation of thermoreversible polymers, we have investigated the Diels−Alder cycloaddition of fullerenes with bis-dienes.[2] Fullerenes react as electron-deficient dieneophiles with a number of electron-rich dienes, including aromatic and nonaromatic systems.[3] These additions are generally thermally reversible,[4] with a reversion to the starting materials occurring at relatively low temperatures.[5] To demonstrate the application of the fullerene Diels−Alder methodology to the creation of thermoreversible polymers, we have examined the reaction of bis-dienes with C_{60}. We report here the creation of covalently assembled, fully thermal reversible fullerene−diene copolymers[6] capable of repeated cycling without degradation.

Thermoreversible polymer **2** uses bisanthracene ether **1** as the dienophile component,[7] both to provide a low reversion temperature and to prevent diene−diene dimerization reactions. Monomer **1** was synthesized in good yield by the Williamson reaction of 9-anthracenemethanol (**2**) with 1,10-diiodododecane (Scheme 1).[8]

One-step polymerization of a 1:1 molar ratio of bisanthracene ether **1** and C_{60} in toluene at room temperature provided the sparingly soluble polymer **2**.[9,10] The polymerization occurs in a one-to-one stoichiometry consistent with previous observations that the first and second additions of anthracene to C_{60} are much faster than the third additions.[3c,d] The polymerization process was followed using UV−vis spectroscopy[11] and was complete after 168 h (Figure 2) to provide a homogeneous solution. Evaporation followed by sonication with THF provided a soluble and insoluble fraction. Gel permeation chromatography using polystyrene as a standard in THF provided information on molecular weight distribution of the THF-soluble component of the polymerization.[12] The soluble fraction consisted of oligomers and polymers with an estimated molecular weight range of 3000−25 000 (Figure 1),[13] along with some remaining monomeric material. Molecular weight distribution for the insoluble fraction could not be determined; however the thermal behavior of this material indicates that it is a higher molecular weight fraction of polymer **2** (*vide infra*).

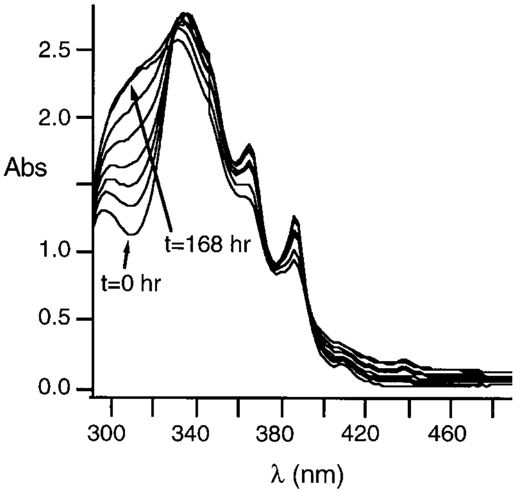


Figure 1. UV spectra for the reaction of bisanthracene ether **1** with C_{60} in toluene at room temperature. The absorbance at 312 nm increases vs time and the absorbances at 334, 348, 336, and 386 nm decrease vs time.

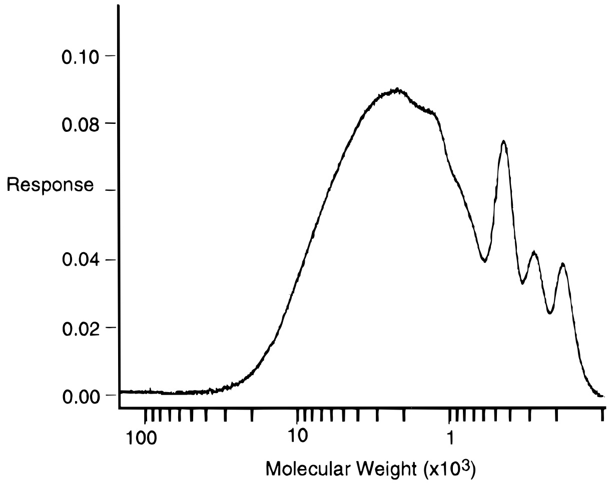
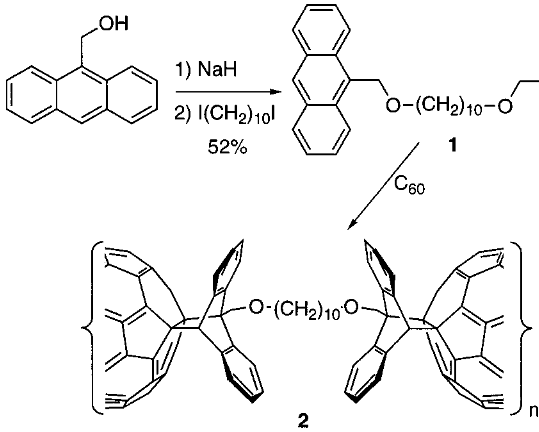


Figure 2. Gel permeation chromatogram for the reaction of bisanthracene ether **1** with C_{60}, using polystyrene as a standard and THF as a solvent.

Scheme 1



Variable temperature UV−vis spectroscopy was used to examine the thermal reversibility of polymer **2**. Polymer **2** began to dissociate at 50 °C, with complete depolymerization occurring at temperatures above 70 °C. As shown in Figure 3, heating of polymer **2** at 75°C for 20 min resulted in complete reversion to the monomer **1** and C_{60}. The ratio of monomer to C_{60} was

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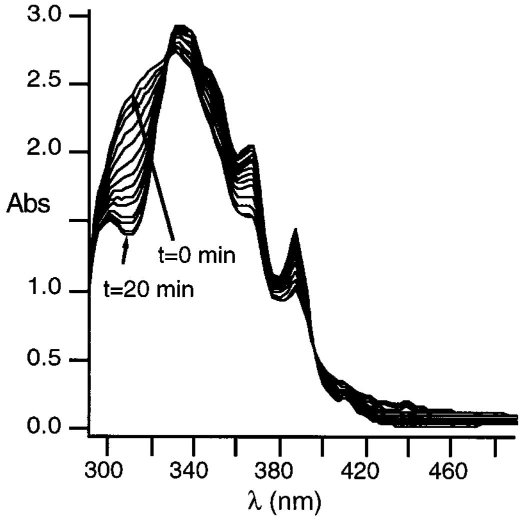

Figure 3. UV spectra for the cycloreversion of polymer **2** in toluene at 75 °C. The changes observed are completely complementary to those observed during polymerization: the absorbance at 312 nm decreases vs time, and the absorbances at 334, 348, 336, and 386 nm increase vs time.

approximately one-to-one, consistant with the chain structure shown in Scheme 1. Upon cooling, repolymerization was observed, providing polymer **2** identically by UV−vis and showing similar molecular weight distributions by gel permeation chromatography (GPC) to the original polymer **2**. This polymerization−depolymerization cycle was repeated multiple times under aerobic conditions with no evidence of monomer decomposition, demonstrating the true reversibility of the polymerization process, as well as the environmental stability of the polymer and monomers. The THF-insoluble fraction formed in the polymerization process likewise underwent complete reversion to monomeric species: upon heating to 75 °C, this material reverted cleanly and rapidly to a one-to-one ratio of monomer **1** and C_{60}, establishing that this material represents either a higher molecular weight fraction or cross-linked portion of polymer **2**.

In summary, we have used the Diels−Alder cycloaddition of C_{60} with bis-anthracene **1** to create a fullerene-based copolymer. This addition is fully reversible upon heating to 75 °C, providing a fully thermoreversible polymer capable of multiple polymerization−depolymerization cycles. These materials demonstrate the utility of fullerenes for the creation of recyclable and thermally processable polymers. Further structural characterization of this polymer to determine the regiochemistry of the Diels−Alder additions is currently underway and will be reported in due course.

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Supporting Information Available: IR spectra of monomer **1**, C_{60}, and polymer **2** (2 pages). See any current masthead page for ordering and Internet access information.

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(8) 9-Anthracenemethanol (625.9 mg, 3.0 mmol) was added to a suspension of sodium hydride (81.9 mg, 3.4 mmol) in DMF (25 mL) at 0 °C, providing a dark red−purple solution. To this solution was added 1,10-diiododecane (500 mg, 1.4 mmol), and the mixture was allowed to stir at room temperature for 4 h. The reaction mixture was quenched with water (5 × 100 mL), and the resulting suspension was extracted with ethyl acetate (2 × 100 mL). Chromatography (SiO_2, hexane/ethyl acetate) provided 393.9 mg (52%) of bis-anthracene **1** as a yellow solid. The product was characterized by NMR IR and elemental analysis. Anal. Calcd $C_{40}H_{42}O_2$: C, 86.59; H, 7.64. Found: C, 86.45; H, 7.65.

(9) A solution of bisanthracene ether **1** (15.48 mg, 28 μmol) and C_{60} (20 mg, 28 μmol) in toluene (15 mL) was stirred at room temperature for 5 days. Addition of THF (5 mL) resulted in the formation of a precipitate (7.1 mg, 20% by weight of the total product).

(10) The Diels–Alder polymerization reaction occurred at much lower temperatures than those used for the cycloaddition of anthracene to C_{60} (ref 7).

(11) The polymerization process could also be followed by IR spectroscopy: concurrent with formation of polymer **2** were the disappearances of C_{60} absorbtions at 527, 577, 1183, and 1429 cm^{-1} and appearance of bands at 1672 and 1726 cm^{-1}.

(12) Gel permeation chromatography was carried out on a *HP* 1050 GPC connected to a Wyatt Interferometric Refractometer detector, using polystyrene as a standard and THF as a solvent. Five columns connected in a series in order of decreasing pore size as follows: Permagel column (10^6 Å, 10 μm, 7.8 × 300 mm, Pacific Column Co.), μstyragel column (10^5 Å, 5 μm, Waters Associates), Ultrastyragel column (10^4 Å, 5 μm, Column Resolution Inc.), Ultrastyragel column (10^3 Å, 5 μm, Column Resolution Inc.), and Permagel column (500 Å, 5 μm, 7.8 × 300 mm, Pacific Column Co.).

(13) The actual molecular weights should be higher due to the lower hydrodynamic radius of **2** arising from the lower solubility of this polymer in THF relative to polystyrene.

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