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Thermoreversible Polymerization. Formation of Fullerene-Diene Oligomers and Copolymers

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Diels−Alder reaction of C_{60} with bis-anthracene **3** provides linear copolymer **4**. This material is stable at room temperature but undergoes reversion to the monomeric species upon heating. This thermal depolymerization process was observed at temperatures above 60 °C, with an activation energy of 17.1 kcal/mol. This process can be cycled multiply without degradation of the reactive functionalities. In addition to its thermal properties, this polymer retains the rich redox chemistry of the fulleroids. Electrochemical and EPR studies demonstrate copolymer **4** undergoes multiple reductions without decomposition to monomeric species.

Thermoreversible polymerization processes have the potential to provide materials of varied and unique utility. Thermally reversible polymers possess the physical properties of thermosets, including rigidity and abrasion resistance.[1] Unlike thermosets, these polymers can be molded and extruded at elevated temperatures. As such, thermoreversible polymers are obvious candidates for recyclable materials, allowing efficient reprocessing and reuse. Additionally, these materials provide the opportunity for thermal annealing processes,[2] allowing the creation of stress-free rigid polymers.

Despite the obvious pragmatic applications of thermoreversible polymers, there have been very few reported examples exploring their formation. This arises from the unusual reactivity profile required for the utility of the thermoreversion process. An essential prerequisite for the formation of thermally reversible polymers is sufficiently differentiated polymerization and depolymerization temperatures. These temperatures must also be low enough to allow thermal cycling without degradation of the monomer units.[3] In recent investigations, we,[4] as well as others,[5] have explored the thermoreversibility of the Diels−Alder cycloaddition between fullerenes[6] and electron-rich dienes.[7] The unusual thermal stability profile of these adducts is ideal for the creation of thermally reversible polymers. We report here the formation, thermal properties, and electrochemical behavior of a fully thermoreversible fullerene-bis-diene copolymer.[8]

Results and Discussion

The choice of diene monomer for application in our polymerization strategy was dictated by the necessity of avoiding unwanted homocoupling reactions, ruling out dienes such as cyclopentadiene.[9] Studies have shown that C_{60} reacts readily with anthracene,[10] a molecule unreactive as a dienophile. To provide the bis-diene required for polymerization, anthracenemethanol (**1**) was reacted with dodecanedioyl dichloride (**2**) using catalytic 4-(dimethylamino)pyridine (DMAP) to provide the bis-anthracene monomer **3** (Scheme 1).

One-step polymerization of a 1:1 molar ratio of bis-anthracene ester **3** and C_{60} in toluene at room temperature provided polymer **4**.[11] The polymerization process

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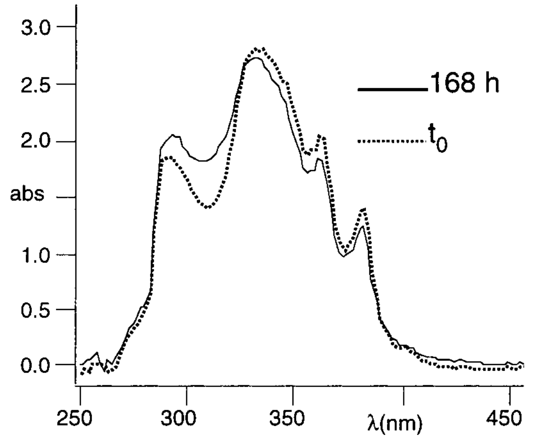


Figure 1. UV–vis spectra of C_{60} and monomer **3** before and after polymerization.

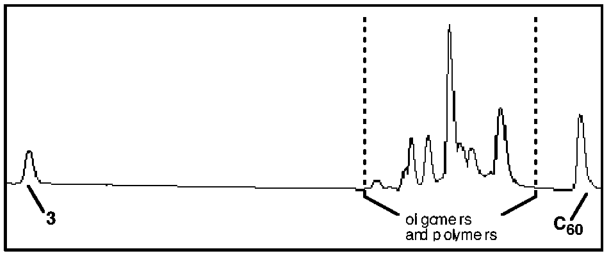
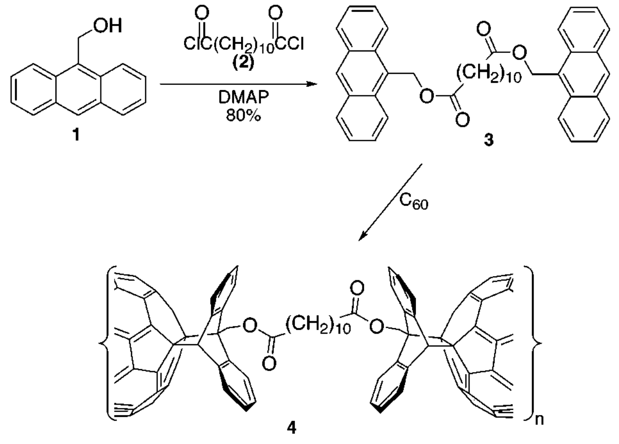


Figure 2. HPLC of C_{60}-monomer **3** solution after 168 h.

Scheme 1



was followed with UV–vis spectroscopy[12] and reached a limiting value after 168 h (Figure 1), providing a homogeneous solution. HPLC analysis of the solution indicated the presence of C_{60} and bis-anthracene **1**, along with multiple peaks arising from polymers and oligomers (Figure 2). GPC confirmed this interpretation (Figure 3), indicating the formation of a polydisperse polymer, M_w = 4884, with a molecular weight ranging from 1500 to >30,000.[13]

The HPLC of C_{60} and monomer **3** after polymerization showed an 87% conversion of C_{60} to oligomers and polymers. At this time there was an approximately 2:1 ratio of unreacted monomer **3** to C_{60}. This excess of bis-anthracene **3** provides evidence for polymer **4** possessing a linear structure (as opposed to star or highly branched polymers that would consume **3** more rapidly than C_{60}), with C_{60} at the polymer termini. This is consistent with the lower reactivity of C_{60} with increasing functionalization. The relatively high solubility of the polymer rules out alternative highly cross-linked structures that might possess similar stoichiometries.

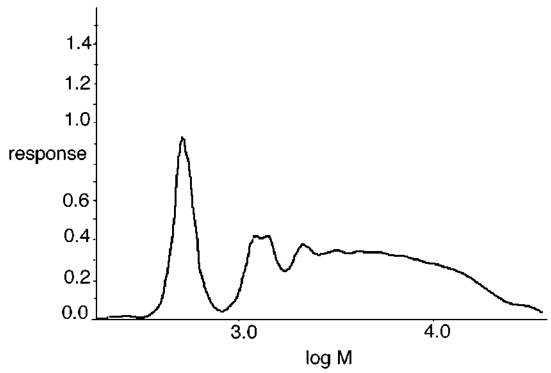


Figure 3. GPC of C_{60}-monomer **3** solution after 168 h.

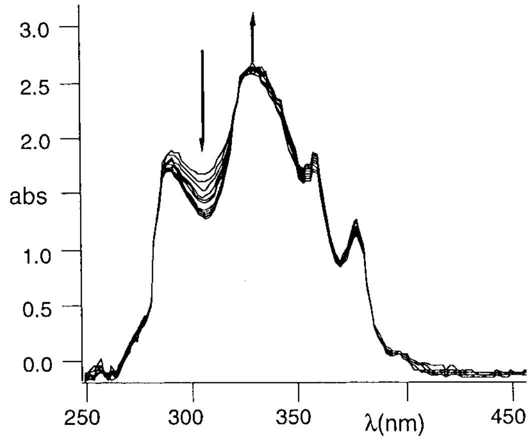


Figure 4. UV spectra for the cycloreversion of polymer **4** in toluene at 60 °C.

As was previously observed with most fullerene Diels–Alder adducts, polymer **4** readily underwent cycloreversion to provide monomer **3** and C_{60}. Upon heating to 60 °C, polymer **4** is almost completely dissociated to the monomeric species (Figure 4).[14] The polymerization–depolymerization process could be repeated multiply without decomposition (as monitored by HPLC), demonstrating the true thermoreversibility of polymer **4**.

To determine the kinetic parameters for the dissociation of **4**, the rates of decomposition were obtained in the temperature range of 60–82 °C (Figure 5). Fitting of the kinetic data in Figure 5 to the Arrhenius form of the rate expression, $k = Ae^{-E_a/RT}$ (Figure 6), provided an activation energy of 17.1 kcal/mol, consistent with the low activation barriers observed with fullerene retro-

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(11) The Diels–Alder polymerization reaction occurred at much lower temperatures than those used for the cycloaddition of anthracene to C_{60} (ref 7). It likely that these reactions did not occur during heating but upon cooling after reaction.

(12) The polymerization process could also be followed by IR spectroscopy: concurrent with formation of polymer **4** were the disappearances of C_{60} absorptions at 527, 577, 1183 and 1429 cm^{-1}, and appearance of bands at 1672 and 1726 cm^{-1}.

(13) The actual molecular weights should be higher due to the lower hydrodynamic radius of **4** relative to polystyrene. This is evidenced by the indicated molecular weight of 540 for unreacted C_{60} in the GPC chromatogram.

(14) The completion of depolymerization was verified by HPLC analysis in which all of the oligomeric and polymeric peaks disappeared.

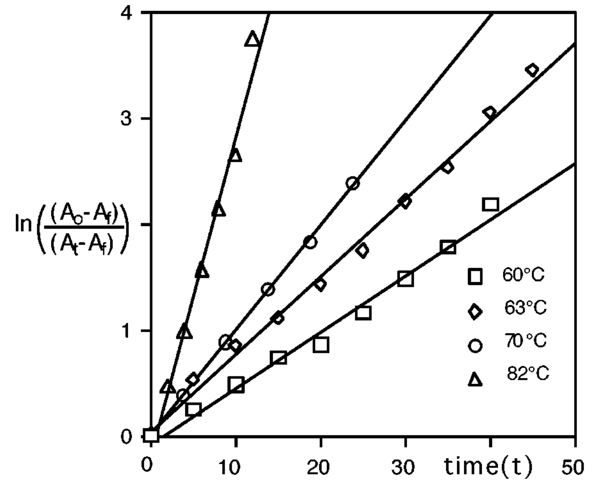

Figure 5. Plot for the first-order decomposition of **4** in toluene. Absorption was measured at 312 nm.

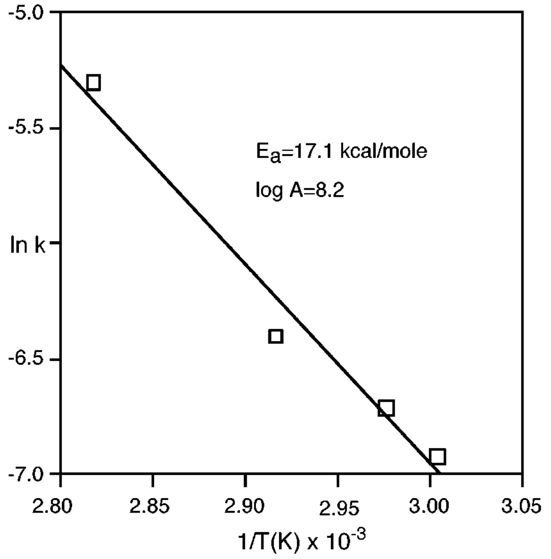

Figure 6. Plot of ln *k* vs 1/*T* for the decomposition of **4**.

Diels–Alder reactions.[3b] The logarithm of preexponential factor *A* is 8.2, a somewhat low value arising from the fact that most cycloreversion reactions of polymer **4** are internal to the polymer strand, producing smaller polymers rather than monomers.

Electrochemistry and Spectroelectrochemistry of Polymer 4. Fullerenes undergo a rich array of redox processes, allowing the facile formation of a variety of redox states.[15] An important issue for polymer **4** is the stability of the polymer strand to electrochemical reduction. Cyclic voltammetry (Figure 7) of this polymer provided a series of partially resolved quasireversible reduction and oxidation couples. These couples included those arising from residual C_{60} at −1.03 and −1.44 V versus ferrocene,[16] as well as resolved couples arising from the polymer at −1.10, −1.24, and −1.62 V. The couple at −1.10 V is consistent with the first reduction couple observed with monosubstituted C_{60}[17] and is tentatively assigned to the terminal fullerenes in the polymer strands. The couple at −1.24 V is likewise consistent with that observed for difunctionalized C_{60}[18] and is assigned to the monoreduction of internal fullerenes.

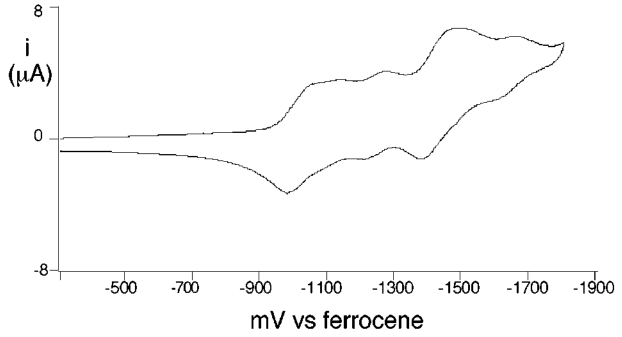

Figure 7. Cyclic voltammogram of polymer **4** in CH_2Cl_2 (0.1 M n-Bu_4NClO_4) at a platinum electrode. Sweep rate: 200 mV/s. Ferrocene internal standard.

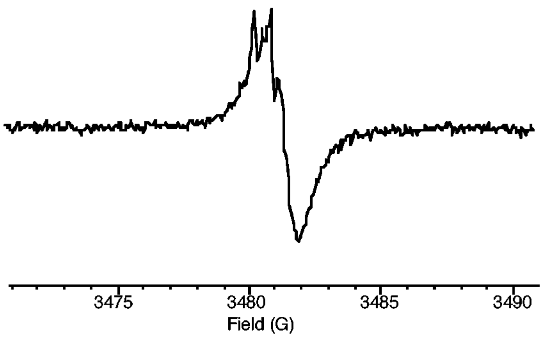

Figure 8. SEEPR spectrum of polymer **4** at −1300 mV (vs ferrocene) in CH_2Cl_2 (0.1 M *n*-Bu_4NClO_4).

To provide further evidence for the redox stability of polymer **4**, we used simultaneous EPR and electrochemistry (SEEPR) to obtain EPR spectra of electrochemically reduced polymer **4**. (Figure 8). In contrast to C_{60},[19] the EPR of reduced polymer **4** shows a complex pattern. This is consistent with the multiple radical anion species expected on the basis of our CV studies.

In summary, we have demonstrated the efficient thermoreversibility of a fullerene-bis-anthracene alternating copolymer. This polymer retained many of the redox properties of the parent fullerene. Applications of the fullerene Diels–Alder methodology to polymer cross-linking, as well as in the creation of electroactive materials, are currently underway.

Experimental Section

Materials and General Methods. C_{60} was obtained from MER Corp. (Tucson, Az). Other chemicals were reagent grade, obtained from Aldrich Chemical Co, and were used without further purification. Solutions were prepared using reagent grade CH_2Cl_2 dried via distillation over CaH_2. Tetrabutylammonium perchlorate (TBAP, obtained from SACHEM, electrometric grade) was recrystallized twice from water and dried for several days under high vacuum.

Monomer 3. Dodecanedioyl dichloride (**2**) (0.116 g, 0.43 mmol) was added to a solution of 9-anthracenemethanol (**1**)

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[16] The couples arising from C_{60} are large, despite the relatively low proportion of free C_{60} in solution. This arises from the enhanced mobility and accessibility of the monomeric fullerene.

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(0.181 g, 0.87 mmol) and DMAP (0.106 g, 0.87 mmol) in dry CH_2Cl_2 (2.5 mL). The reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure, and the resulting solid residue was purified by silica gel column chromatography with (hexane/ethyl acetate) as eluent yielding 0.212 g (80%) of **3** as yellow solid. Anal. Calcd for $C_{42}H_{42}O_4$: C, 82.59; H, 6.93. Found: C, 82.51; H, 6.93.

C_{60}-Diester Polymer (4). A (1:1) ratio solution of C_{60} (0.02 g, 0.028 mmol) and diester (**3**) (0.017 g, 0.028 mmol) in 20 mL of dry toluene was allowed to stand at room temperature for 168 h. Solvent was then evaporated, and the resulting dark brown solid was dried in vacuo.

GPC and HPLC. All of the stoichiometric values were obtained by making use of calibration curves. HPLC was performed on a Rainin C18 HPLC column, with detection at 350 nM. A 0−100% CH_2Cl_2/MeOH gradient (20 min) was used to resolve the fullerene and polymer. Gel permeation chromatography was carried out on a HP 1050 GPC connected to a Wyatt Interferometric Refractometer detector, using polystyrene as standard and $CHCl_3$ as solvent. Five columns connected in series in order of decreasing pore size as following: Permagel column (10^6 Å, 10 μm, 7.8 × 300 mm, Pacific Column Co.), μstyragel column (10^5Å, 5 μm, Waters Associates), Ultrastyragel column (10^4 Å, 5 μm, Column Resolution Inc.), Ultrastyragel Column (10^3 Å, 5 μm, Column Resolution Inc.), Permagel column (500 Å, 5 μm, 7.8 × 300 mm, Pacific Column Co.).

Simultaneous Electrochemistry and EPR. SEEPR experiments were carried out in a quartz flat cell,[20] containing three ACE no. 7 threaded joints sealed via Teflon ferrules to hold the electrodes, and a septum-capped ground glass joint for degassing and sample injection. The platinum gauze working electrode was inserted into the flat part of the cell. The silver wire pseudoreference electrode was positioned directly above the working electrode in order to minimize the *iR* drop. The auxiliary electrode, a platinum wire spiral of large surface area, occupied the solvent reservoir above the flat section. The electrode leads were insulated via Teflon heat shrink tubing.

EPR spectra were recorded on an IBM ESP 300 X-band spectrometer equipped with a TE_{104} dual cavity. Solutions of polymer **4** ($\sim 10^{-3}$ M in CH_2Cl_2, 0.1 M TBAP) were degassed by bubbling argon through them for 5 min and then injected into the cell, which was previously flushed with argon. The cell was mounted within the spectrometer using custom manufactured cell holders, which allow for precise alignment of the cell within the cavity in order to maximize the Q-factor. Bulk electrolysis was carried out simultaneous to signal acquisition (25 kHz field modulation, modulation amplitude 0.0475 G).

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Supporting Information Available: IR and UV spectra of monomer **3**, C_{60}, and polymer **4**, and NMR spectrum of monomer **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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