Reversible Covalent Attachment of C_{60} to a Polymer Support

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Buckminsterfullerene and its derivatives have been shown to possess an array of interesting magnetic,[1] electronic,[2] and chemical properties.[3] While these properties can be utilized directly, one way to enhance greatly the versatility of the fullerene system is through incorporation into,[4] or attachment onto,[5] a polymeric material. We report here the first readily reversible addition of C_{60} to a polymer resin.

Fullerenes readily undergo Diels–Alder cycloaddition with a variety of reactive dienes, including anthracene and cyclopentadiene.[3] These adducts are generally thermally unstable, undergoing cycloreversion to their component molecules upon heating.[6,7] In recent communications we synthesized and characterized[8] the C_{60}–cyclopentadiene adduct and determined the kinetic parameters for its thermal retro-Diels–Alder reaction.[9] This addition product was readily formed through room temperature addition of cyclopentadiene to C_{60}, and it reverted rapidly at temperatures over 95 °C to the starting materials.

To determine the applicability of Diels–Alder cycloadditions to the formation of polymer-bound fullerenes, we investigated the synthesis of cyclopentadiene-functionalized polymers (**1**) (Scheme 1). Reaction of Merrifield's peptide resin[10] (**2**) in toluene with excess sodium cyclopentadienylide at -20 °C provides a pale to dark brown solid.[11] Filtration, followed by rinsing with toluene and decalin, provides functionalized polymer **1**.[12] To provide a control system for fullerene absorption studies, resin **2** was reacted with sodium ethoxide under identical conditions to provide the ether-containing polymer **3**.

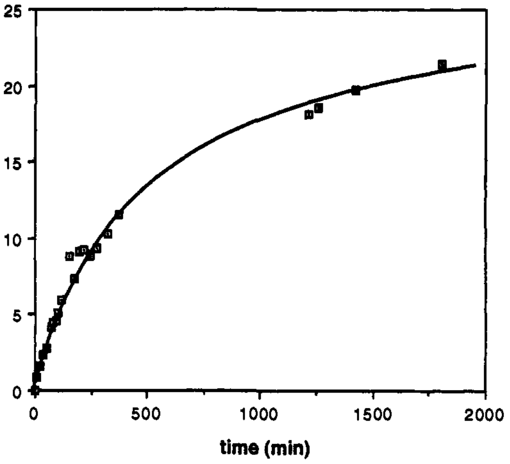
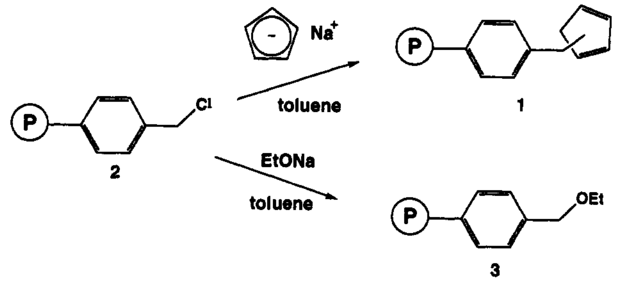
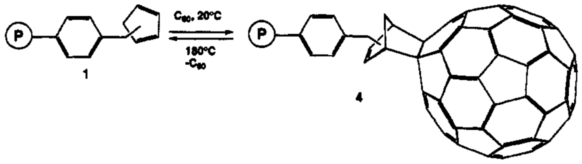


Figure 1. Plot of consumption of C_{60} vs time. Reaction was run at 20 °C in decalin, with gentle shaking. The initial concentration of C_{60} was 97 μM; the final concentration was 67 μM. Uptake of C_{60} was followed by HPLC, with detection at 280 nm.

Scheme 1



Scheme 2



Cyclopentadiene-functionalized polymer **1** reacts rapidly with C_{60} at room temperature (Figure 1) to give the fullerene-containing polymer **4** (Scheme 2). The capacity of resin **1**, as determined by prolonged reaction with C_{60} in decalin solution, was 23.5 ± 0.2 mg of C_{60}/g of resin (Figure 1).[13] Merrifield's resin (**2**) and ether-functionalized resin **3**, in contrast, absorb little or no C_{60} (<0.05 mg of C_{60}/g of resin).[14] Further evidence for the addition of C_{60} to polymer **1** occurring via Diels–Alder reaction is provided by two additional experiments. First, resin **1** did not react with polycyclic aromatics (including pyrene and naphthalene), which are unreactive as dienes in Diels–Alder cycloadditions. Second, pretreatment of resin **1** with either maleic anhydride or tetracyanoethylene (both potent dienophiles[15]) totally deactivates the resin toward addition of C_{60} (<0.05 mg of C_{60}/g of resin).

The addition of C_{60} to form polymer **2** is reversible: heating of resin **2** in decalin to 180 °C for 8 h in the presence of maleic anhydride releases 48% of the bound C_{60}.[16,17] In the absence of

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(11) In a typical run, sodium cyclopentadienylide (400 μL of a 2 M solution in tetrahydrofuran, 0.8 mmol, 8 equiv) was added dropwise to a -20 °C suspension of Merrifield's resin (100.0 mg, chloromethylated styrene-divinylbenzene copolymer, Sigma, 2% cross-linked, 1.04 mequiv of Cl/g) in toluene (10 mL). The suspension was stirred for 2 h at -20 °C, filtered, and washed with toluene (10 mL) and decalin (20 mL) to give a moist, pale to dark brown solid. This solid could be dried, then reconstituted, however, some loss of efficiency occurred.

(12) The resin as used was contaminated by inorganic salts. Elemental analysis for a water-washed sample of resin **1** (which retained activity): was C, 88.08; H, 7.42; Cl, 4.42. Elemental analysis for Merrifield's resin **2**: C, 83.21; H, 7.01; Cl, 9.20. This corresponds to 52% substitution of available sites.

(13) This corresponds to a 3.3% efficiency based on Cl equivalents of starting resin **2**, or 6.6% based on the 52% yield of Cl displacement.

(14) The lack of fullerene uptake by resins **2** and **3** excludes the possibility of simple physical adsorption.

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(16) The polymer resin was suspended in decalin, a 10-fold excess of maleic anhydride (based on C_{60} content) was added, and the mixture was heated to 180 °C for 8 h.

(17) The remaining fullerene is most likely cross-linked into the polymer at two or more points.

(18) This readdition could be avoided by continuous extraction using a modified Soxhlet apparatus. The product derived using this process was generally contaminated with $C_{60}C_5H_6$,[8] produced apparently through degradation of the resin at elevated temperatures.

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maleic anhydride, C_{60} was released from resin **2** upon heating, with readdition to the polymer occurring upon cooling.[18] This heating–cooling sequence could be repeated, demonstrating true reversibility of the addition–reversion process.[19]

In conclusion, we have developed a method for the covalent attachment of fullerenes to a polymer support through an apparant Diels–Alder cycloaddition. This addition has been shown to be readily reversible, allowing recovery of C_{60} upon heating of the resin. Further optimization and characterization of these polymers is being pursued. Additionally, their application to the nonchromatographic purification of fullerenes is currently under study and will be reported in due course.

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(19) The efficiency of this process diminished with repetition, due to polymer degradation.