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Fullerene-Bound Dendrimers: Soluble, Isolated Carbon Clusters

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The reactivity and chemical derivatization of fullerenes has been actively investigated, and a range of functionalized fullerenes have been prepared.[1] However, limited attention[2–5] has been given to the functionalization of fullerenes with macromolecules. A potential advantage of the application of polymer chemistry to the functionalization of fullerenes is the encapsulation of fullerene clusters having conducting capabilities by a polymeric insulating layer, which also alters the physical properties and provides novel materials for the investigation of the properties of individual isolated carbon clusters. The reaction of living polystyrene with C_{60} has been reported,[2] in which a broad distribution of products was obtained, with the number of attached polymer chains ranging from 1 to 10. The covalent attachment of fullerenes to amine-containing linear polymers has also been reported;[3] however, some cross-linking was observed from reaction of more than one polymer chain with a given fullerene molecule. The coupling of compact dendritic macromolecules with prefunctionalized fullerenes is now described. This synthetic strategy, involving two species containing a precise number of functional groups, gives greater control over the formation of polymer–fullerene hybrid structures.

Phenol-functionalized fullerenes have been prepared[4] by reaction of C_{60} with bis(*p*-methoxyphenyl)diazomethane followed by hydrolysis of the methyl ethers with BBr_3. This synthesis has been tailored to yield a 6–6 bridged methano fullerene derivative carrying only two phenolic sites as the major product. Polyether dendrimers prepared by the convergent synthesis route[6–8] are ideally suited for attachment to phenol-functionalized buckyballs since they carry a single electrophilic site at their focal point, and their attachment to phenolic moieties has been studied extensively.

The formation of fullerene-bound dendrimers was accomplished by reaction of each of the two phenolic groups located at the surface of the functionalized fullerene with the single benzylic bromide group at the focal point[6] of a fourth-generation dendrimer [G-4]-Br **1**, in the presence of K_2CO_3 (Scheme I). Size-exclusion chromatography (SEC) is ideally suited for monitoring the coupling reaction in view of the significant differences between molecules obtained by incremental additions involving one or more units of [G-4]-Br (MW 3355) and diphenolic fullerene **2** (MW 919). Therefore, reaction of 2.7 equiv of **1** with **2** gave the hybrid structure **3**, having two dendrimers coupled with one fullerene together with a significant amount (ca. 30%) of higher molecular weight impurities (Figure 1a).

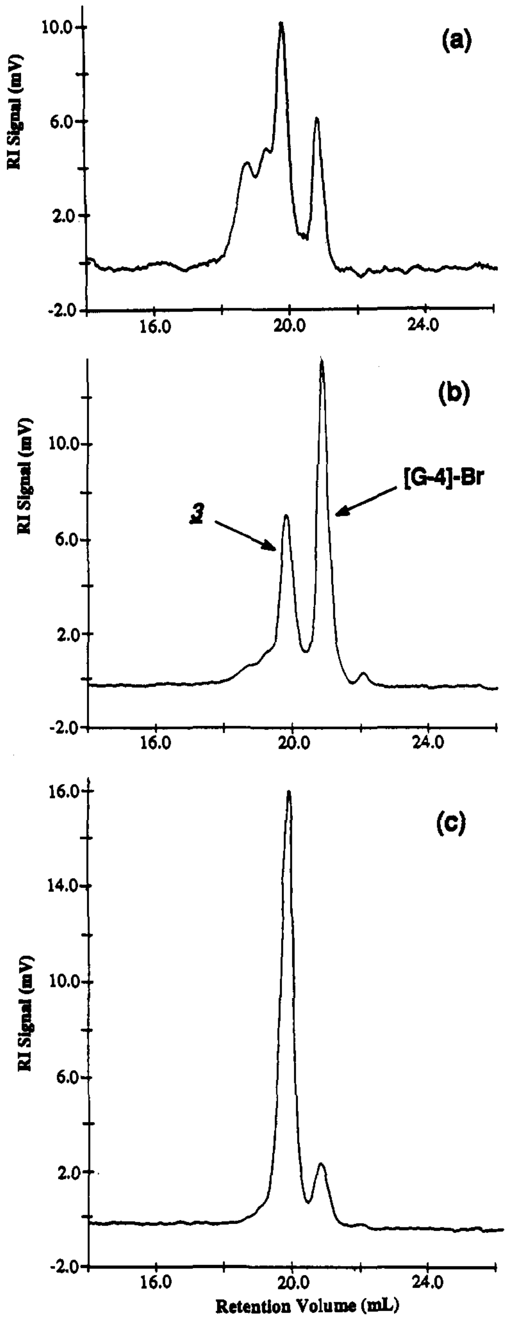

Figure 1. SEC chromatograms of (a) crude reaction mixture of [G-4]-Br (0.37 g, 0.11 mmol, 2.7 equiv) and diphenolic fullerene (0.040 g, 0.04 mmol) in THF (100 mL); (b) crude reaction mixture of [G-4]-Br (0.146 g, 0.0435 mmol, 4.0 equiv) and diphenolic fullerene (0.0099 g, 0.011 mmol) in THF (50 mL), demonstrating the decrease of high molecular weight impurities through dilution and the use of higher ratios of [G-4]-Br **1** to fullerene **2**; and (c) product from reaction in b above, after flash chromatography.

To fully characterize the products and determine the structures of the high molecular weight impurities, isolation of each of the products was necessary. Purification by flash chromatography or precipitation gave only partial separation of the products; as a result, preparative SEC[9] was used to obtain samples of each of the products.

A ^1H NMR spectrum of the desired product, in which two dendrimers are attached to the surface of the fullerene, is shown in Figure 2. The ABq for the 1,4-substituted aromatic rings of

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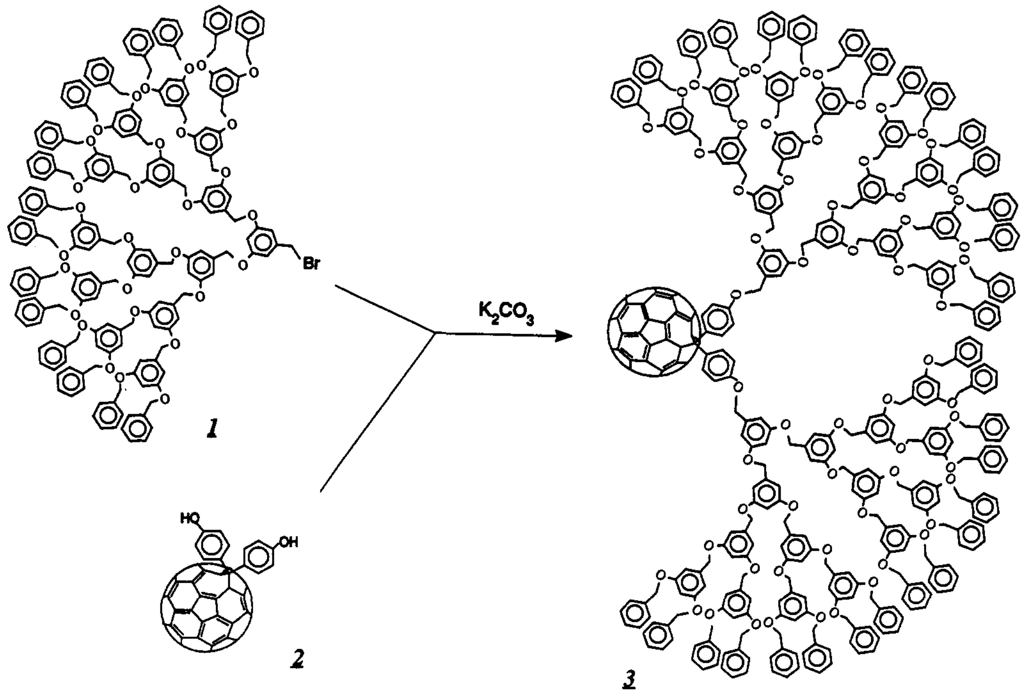
Scheme I



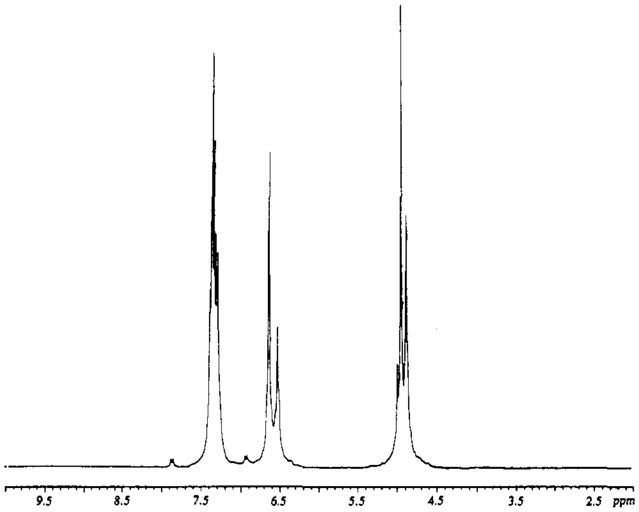


Figure 2. ^{1}H NMR spectrum of the purified hybrid dendrimer-fullerene macromolecule containing two dendrimers, 3.

the fullerene unit are observed at 7.85 and 6.91 ppm. The remainder of the resonances in the spectrum are due to the protons of the dendritic unit. As expected, the resonance for the focal point methylene group shifts from 4.36 (CH_2Br) to 4.97 (CH_2-OAr–fullerene) ppm on reaction with the fullerene. Comparison of integration values for the resonances from the protons of the fullerene aromatic rings with those from the protons of the dendrimer allowed the relative amounts of dendrimer and fullerene present in the structure to be determined. Evaluation of each of the fractions of products separated by preparative SEC showed that the relative amount of dendrimer in the sample increases and essentially doubles from those products containing one dendritic unit to products containing two dendritic units, per fullerene. However, the impurities isolated consisting of higher molecular weight products show a decreasing percentage of dendrimer relative to fullerene. In addition, the sharpness of the ^{1}H NMR resonances is lost with increasing molecular weight. Complementary characterization of the attachment of the dendrimers to the fullerenes was obtained by ^{13}C NMR spectroscopy. The relative ratios of dendrimer to fullerene were obtained from both infrared and UV–vis spectroscopy, confirming the above results.

This finding of increasing fullerene content with increasing molecular weight is consistent with the attack of a nucleophilic species onto the fullerene giving coupling between fullerene units. Possible nucleophiles include either the phenolic groups attached to the fullerene or carbonate from K_2CO_3. Coupling via these nucleophiles would lead to polyfullerenes containing fewer than two phenolic groups per fullerene, affording a lower dendrimer to fullerene ratio. The possibility of fullerene impurities containing more than two phenolic groups per fullerene being the cause of the higher molecular weight impurities can be ruled out, since this would give an increasing dendrimer to fullerene ratio with increasing molecular weight of the side products.

To overcome the side reactions, the synthesis was performed at twice the dilution and with a 4-fold excess of [G-4]-Br. Under these reaction conditions, only a small amount (5–10%) of the coupling products was observed by SEC (Figure 1b), and the desired product containing two dendrimers per fullerene was obtained in ca. 90% yield (SEC). This mixture was purified by flash chromatography eluting with 15% hexanes/CH_2Cl_2 to give a 79% isolated yield of the didendritic surface-functionalized fullerene, 3, as a light brown-colored glass.

In conclusion, we have demonstrated the functionalization of the surface of buckminsterfullerene with a controlled number of dendritic macromolecules. The dendritic macromolecules dramatically improve the solubility of the fullerenes and should provide a more compact insulating layer around the clusters than would linear polymers, while maintaining the globular shape of the structures. Further characterization and study of the properties of the products, as well as other routes toward the synthesis of dendritic–fullerene hybrid structures, are currently being investigated.

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(9) Preparative SEC was performed on three 5-μm Polymer Laboratories columns (300 × 7.7 mm) connected in series in order of increasing pore size (100 Å, 500 Å, 1000 Å), with THF as solvent and with ca. 5 mg/100 μL sample per injection.