A Simple and Versatile Method for the Synthesis of C_{60} Copolymers

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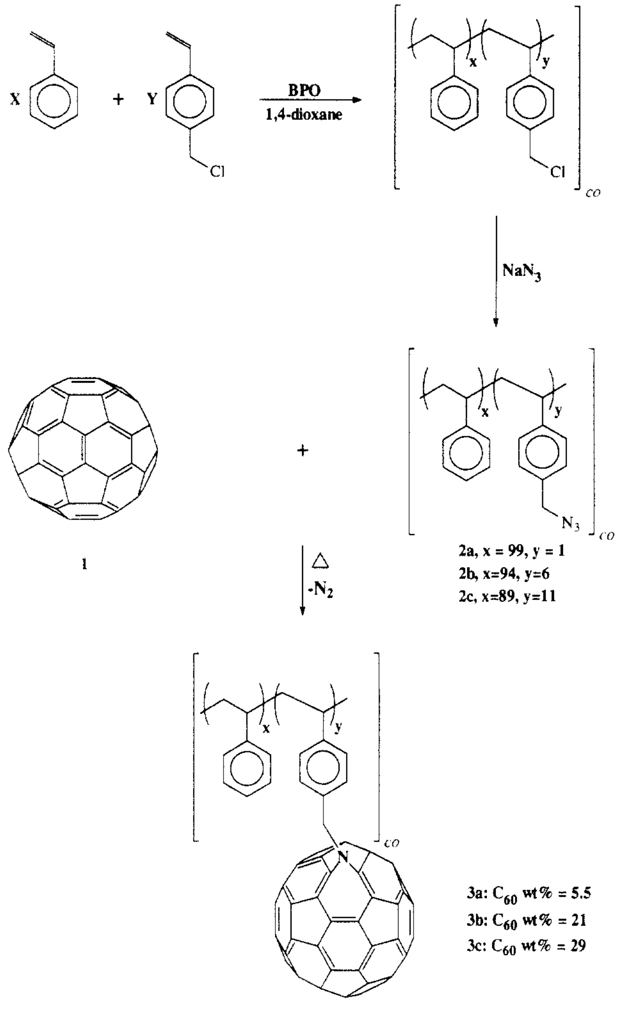
The physical properties of buckminsterfullerene (C_{60}, 1) have been extensively investigated, and a variety of interesting conducting,[1] magnetic,[2] photochemical,[3] and electrical properties[4] have been observed. Unfortunately the ability to fabricate devices based on C_{60} has been limited due to its poor processability. To overcome this difficulty, a number of groups[5,6] have prepared polymeric derivatives of C_{60}; however, multiaddition to the fullerene nucleus resulting in cross-linked intractable materials readily occurs. The use of prefunctionalized fulleroids[7] and monofunctional polymers[8] leads to soluble processable polymers but either increases the complexity of the synthesis or limits the choice of polymers that can be attached to the C_{60} nucleus. We report the preparation of C_{60}–styrene copolymers by the cycloaddition reaction[9] of azido-substituted polystyrenes with C_{60}. The ease of preparation of azide-containing polymers, the lack of cross-linking, and the retention of the fullerene's electronic properties make this procedure a simple and versatile method for the synthesis of fullerene-containing polymers.

We have recently shown[10] that the reaction of azides with C_{60} proceeds primarily through monoaddition, with little or no triaddition and higher addition products being observed. This crucial observation circumvents the usual problem of multiaddition leading to cross-linking and allows the development of a novel procedure for the synthesis of C_{60} copolymers. Simple linear polymers containing azide functional groups can therefore be used and would be expected to react with C_{60} to give soluble processable polymers. To investigate the versatility of this method, the preparation of C_{60}–styrene copolymers was explored. The required azidomethyl-substituted polystyrenes, **2a–c**, were prepared as shown in Scheme 1, with the percentage of azidomethyl units being controlled by the initial feed ratio. Reaction of **2** with 1 mol equiv of C_{60} in refluxing chlorobenzene was followed by infrared spectroscopy; after 16 h the strong band at 2095 cm^{-1} for the azide group had completely disappeared, and no insoluble cross-linked material was observed. After removal of the solvent the crude reaction mixture was redissolved in dichloromethane and filtered to remove any unreacted C_{60}. Precipitation into hexane afforded multigram quantities of the C_{60}–styrene copolymers, **3a–c**, as brown powders (Scheme 1).[11]

Confirmation of the covalent attachment of C_{60} to the polystyrene backbone was by a variety of techniques. In the ^{13}C NMR spectrum a broad set of resonances was observed between 133 and 148 ppm, with the characteristic resonance at 143 ppm for C_{60} being absent. No resonances were observed in the aliphatic region corresponding to a ring-closed aziridinofullerene which is consistent with previous work.[9,10] Also the resonance for the benzylic CH_2 in the ^{1}H NMR spectrum was observed to shift from 4.30 to 4.55 ppm on reaction of **2** with C_{60}. These results are consistent with the expected azafulleroid structure as shown in Scheme 1, as were the UV–vis spectrum and electrochemical properties of **3**. The C_{60}–styrene copolymers, **3a–c**, proved to be extremely soluble in a variety of organic solvents such as $CHCl_3$, THF, etc. This solubility behavior is similar to polystyrene itself and totally unlike C_{60}, which demonstrates the dramatic effect polymer attachment has on the processability of fullerene derivatives.

Scheme 1



The solubility of the copolymers, **3a–c**, and the complete reaction of the azide groups provide further evidence for the lack of multiaddition during the cycloaddition of azides to C_{60}. Addition information was also obtained from size-exclusion chromatography (SEC) and thermal gravimetric analysis (TGA). Figure 1 shows an overlay of the SEC traces for the starting azide **2c** and the C_{60} copolymer **3c**. As can be seen, no shift in the peak maximum occurs on reaction with C_{60}. However a small amount of higher molecular weight material is observed as a shoulder at lower elution times which leads to an increase in M_w and polydispersity from 27 000 and 2.04 for **2c** to 38 500 and 3.12 for **3c**.[12] The weight percent of C_{60} incorporated into the copolymers could be determined by TGA since the polystyrene backbone decomposes at 350–400 °C to leave C_{60} which undergoes only minor weight loss up to 600 °C. Comparison with starting materials and physical mixtures confirmed the TGA results. Interestingly the weight percent of C_{60} was found to be ca. 80% of the theoretical value.[13] The above results are all consistent, with monoaddition being the dominant process, and demonstrate the viability of this procedure for the preparation of copolymers with high loadings of C_{60}.

Interestingly, as the weight percent of C_{60} increases from 5.5% to 21% to 29% for the copolymers, **3a–c**, only a single glass transition temperature is observed in each

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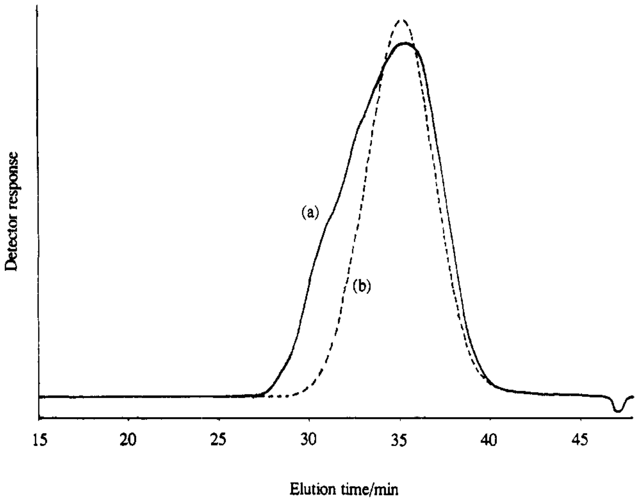

Figure 1. Size-exclusion chromatographs for the C_{60} copolymer **3c** (29 wt % C_{60}) and the starting azidomethyl copolymer **2c** (solvent, THF; flow rate, 1.0 mL/min).

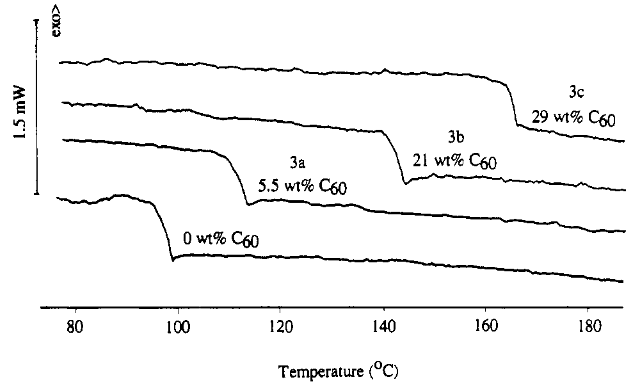

Figure 2. Differential scanning calorimetry traces for the copolymers **3a–c** and the starting azidomethyl copolymer **2b** (scan rate, 10 °C/min).

case, indicating that phase separation is not occurring in these systems even at 29 wt % of C_{60} (Figure 2). Also the values for the glass transition temperatures were found to increase from 112 to 142 to 166 °C on going from **3a** to **3c**, respectively. Since the molecular weights of all three samples are similar, this dramatic increase in the glass transition temperature from ca. 97 °C for the starting materials, **2a–c**, can only be due to the increasing amount of C_{60} in the copolymer.

In conclusion, we have shown that soluble polymer-modified fullerenes can be prepared by the reaction of linear polystyrenes containing azide functional groups with C_{60}. The resultant copolymers retain both the electronic properties of the fullerene moiety and the solubility and processability properties of the polystyrene. The simple and versatile nature of this procedure allows for a wide variety of copolymers to be prepared. We are currently investigating the limits of the azide route to the preparation of linear copolymers of C_{60} as well as water-soluble polymeric fullerenes.

References and Notes

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(11) All new compounds gave satisfactory IR, ^1H and ^{13}C NMR, UV-vis spectra, and elemental analyses (C, H, and N were within 0.4% of theoretical values).

(12) Polystyrene equivalent molecular weights.

(13) Theoretical value calculated assuming quantitative reaction and monoaddition.