Communications to the Editor

Free-Radical Copolymerization of Fullerenes with Styrene

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Various methods to chemically modify the fullerenes have been reported in the last few years since the production of large-scale amounts of fullerene soot that contains primarily C_{60}, a lesser amount of C_{70}, and traces of higher fullerenes. Fortunately, these components can be separated from each other by standard chromatographic methods, permitting convenient experimentation on relatively pure components (see Table 1, footnote *b*). We have found that C_{60} and C_{70} copolymerize with styrene in a standard free-radical polymerization, either in the bulk or codissolved in an aromatic solvent. The resulting polymers are soluble in common solvents that dissolve polystyrene and possess a dark brown color. The absorption spectrum of the copolymer is strongly modified from that of the parent fullerene, and the fluorescence is blue-shifted and much stronger.

One of the major efforts has been to incorporate fullerenes into polymer chains in order to improve their solubility and/or processibility. Such polymers might be of the "pearl necklace" or "pendent chain" type which differ as to the point of attachment to the polymer chain.[1] Loy and Assink presumably produced the former by a copolymerization with *p*-xylylene, but the product was insoluble due to cross-linking and was not air stable.[2] Geckeler and Hirsch[3] and Patil et al.[4] attached C_{60} to soluble amino polymers by the well-known amine addition to C_{60} double bonds. A pendent chain fullerene–styrene copolymer was reported by Hawker in which a copolymer of styrene and *p*-(azidomethyl)styrene was reacted with C_{60} in which $-CH_2N$: is inserted between two carbons of C_{60}.[5] Hawker et al. used a similar chemical step to attach a functionalized dendrimer to C_{60}.[6] Weis et al.[7] have recently reported a method to end-cap polystyrene with a C_{60} moiety by using an amino-terminated polystyrene. A structure that is starlike, referred to as "flagellenes", has been reported by Samulski et al.[8] In this method polystyrene anions are reacted with C_{60}, followed by a capping reaction with methyl iodide. Multiple polystyrene arms (1–10) may be attached to the C_{60} core. This material was apparently quite stable, and cast films phase-separate into C_{60}-rich domains. This is in contrast to the modified linear chains of Hawker in which T_g was elevated by the incorporation of C_{60} but a single T_g was observed, implying a single-phase system.[5]

The present paper describes a very simple method for direct incorporation of C_{60} or C_{70} into polystyrene by direct free-radical copolymerization under routine conditions. While a great deal remains to be done to characterize fullerenes as comonomers in free-radical polymerization, this method is so direct and simple that it may be of interest to a wide range of researchers working in the area of fullerene chemistry. We note a report by Gong et al. in which a polymerization of styrene and α-methylstyrene was carried out in the presence of C_{60} using benzoyl peroxide as an initiator.[9] These authors explicitly state that the C_{60} retains its normal absorption spectrum and is dispersed within the resulting solid polymer matrix. No other characterization is presented to demonstrate if chemical attachment of the C_{60} to the polymer occurred.

It is well-known that C_{60} reacts with free radicals to produce various adducts.[1] Thus, in carrying out a standard free-radical polymerization, we propose the following:

$$\text{AIBN} + \text{styrene} \rightarrow \text{PS}^{\bullet} \quad (1)$$

$$\text{PS}^{\bullet} + C_{60} \rightarrow \text{PS}-C_{60}^{\bullet} \quad (2)$$

The $PS-C_{60}^{\bullet}$ could propagate by reacting with another styrene monomer

$$\text{PS}-C_{60}^{\bullet} + \text{S} \rightarrow \text{PS}-C_{60}-\text{PS}^{\bullet} \quad (3)$$

or react with another $PS^{\bullet}$ to terminate the reaction,

$$\text{PS}-C_{60}^{\bullet} + \text{PS}'^{\bullet} \rightarrow \text{PS}-C_{60}-\text{PS}' \quad (4)$$

If reaction (4) dominates, then there should be only one C_{60} or C_{70} per chain. The reactions (2) and (3) suggest that multiple reactions could occur, leading to a structure like the flagellenes. Our SEC traces do not show separate components as was observed for the flagellenes, but the molecular weight distribution of the polystyrene segments will be much broader from a free-radical polymerization than from the anionic polymerization used by Samulski et al.[7] Thus, different numbers of polystyrene arms (i.e., $(PS)_nC_{60}$ or $(PS)_nC_{70}$) may not be distinguishable by SEC. The following observations were made:

(1) The fullerene is attached to the polymer and is present in the full range of molecular weight of the C_{60}–PS or C_{70}–PS, based on the excellent correspondence of traces from the UV detection at 332 nm (specific to fullerenes) and ΔRI (polystyrene)). For the bulk polymerization the maximum of the UV peak is always to the higher MW side of the ΔRI peak, while for the solution-phase polymerization the peak maxima are very close.

(2) The weight percent of C_{60} or C_{70} in the polymer (estimated by UV spectroscopy) for bulk polymerization is much lower than polymerization carried out in solution (see Table 1). The number of fullerenes per chain (as determined by UV spectroscopy, discussed later) is on the order of unity (the range of values is from 0.6 to 1.1 using the M_n values in Table 1 and ranges from 1.1 to 2.5 using the M_w values). However, a careful examination of the GPC traces implies that the number of fullerenes/chain is proportional to the molecular weight, which would imply that propagation of $PS-C_{60}^{\bullet}$ is possible. The reactivity ratios and general

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Table 1. Polymerization Conditions[a] and Physical Properties of Polymers

fullerene (mg)[b]/ AIBN (mg)/styrene (g)	solvent (mL)	yield (wt %)	fullerene (wt %)[c]	M_w[d] ($\times 10^{-3}$)	M_w/M_n[d]	M_w[e] ($\times 10^{-3}$)	D_h[f] (nm)
C_{60} (11.1)/55.0/3.80	none	83	0.21	256	3.3	326	37.2
C_{60} (39.7)/69.1/3.83	benzene (44)	16	4.0	14.4	1.4		
C_{70} (9.3)/56.7/3.83	none	85	0.25	208	3.0	226	31.0
C_{70} (31.0)/42.7/2.96	benzene (34)	10	5.1	15.5	1.3		

[a] Solution always deoxygenated by either Ar bubbling or freeze–pump–thaw cycles, followed by sealing. Polymerization at 60–65 °C for 12–24 h. All polymers were purified by precipitation from benzene into heptane (2×) and then into methanol (1×). The yields reflect the loss of unreacted monomer and oligomer. [b] Fullerenes obtained from SES Research, Houston, TX. $C_{60} \geq 99.5\%$, $C_{70} \geq 97.0\%$ purity. [c] Estimated by UV spectroscopy (see text). [d] Obtained from GPC chromatography with a calibration curve obtained with linear polystyrene standards. [e] Obtained by static light scattering in THF. [f] Obtained from quasi-elastic light scattering (QELS) in THF. For a polystyrene standard with a molecular weight of 390K, D_h = 32.7 nm was obtained.

dependence of the molecular weight on reaction conditions are currently being investigated in more detail in our laboratory.

(3) The yield of polymer produced in a solution polymerization after workup is relatively low (ca. 20%) which suggests that the free radical becomes trapped on the fullerene (eq 2) and does not propagate but can terminate (eq 4). The polydispersity of the final purified polymer is low (1.3–1.4) which is consistent with the combination mode of termination but may also be the result of the polymer workup before the GPC characterization. The large polydispersity of the bulk-polymerized samples is probably the result of the high degree of conversion and the exhaustion of the available fullerene before all styrene has reacted.

The properties of the polymers produced under different reaction conditions are collected in Table 1. The C_{60} and C_{70} content is estimated by the UV absorption a 350 nm, although it is clear that the photophysical properties are modified by copolymerization (see the next section). The high molecular weight samples are suitable for light scattering characterization. The M_w was obtained by comparing the static light scattering of polystyrene molecular weight standards to the fullerene-containing polymer (all in THF). The M_w obtained by light scattering agreed reasonably well with that obtained from GPC, and the hydrodynamic diameter obtained by QELS was slightly larger than a similar linear polystyrene standard (Table 1). This latter effect is expected for a z-average quantity like D_h. Since the GPC and light scattering molecular weights are in reasonable agreement, we conclude that the bulk polymerization yields primarily a linear polymer. The fluorescence spectra for the bulk- and solution-polymerized samples are different, so this conclusion may not be valid for the latter polymer.

The absorption spectrum of PS–C_{60} and PS–C_{70} is completely structureless compared to the parent fullerenes (Figure 1). We have found the same modification of the absorption spectrum for the adduct in a direct reaction of the fullerenes with AIBN or for the low molecular weight component separated from the polymer by precipitation. It is by comparing the UV absorption of the low molecular weight components to that of the polymer and conservation of mass that we estimate the weight percent of fullerene in the polymers (see Table 1). Based on the UV spectrum, it appears that all the fullerene is consumed in the reaction.

Fullerenes have very low fluorescence quantum yields.[10] We have found that the fluorescence of PS–C_{60} and PS–C_{70} is on the order of 10–20 times more intense than the parent compounds. Presumably, this effect is a result of the lower symmetry of the fullerene–polystyrene adduct such that the $S_1 \rightarrow S_0$ transition is strengthened and fluorescence can compete with intersystem crossing. Fluorescence detection of the SEC eluant demonstrates that the fluorescent species is incorporated uniformly into the polymer. The fluorescence spectrum is blue-shifted, and the blue shift is larger for the solution polymerized samples ($\lambda_{max} \approx 580$ nm) than for those polymerized in bulk ($\lambda_{max} \approx 630$ nm). The photophysics of these fullerene-tagged polymers will be the subject of further research in our laboratory.

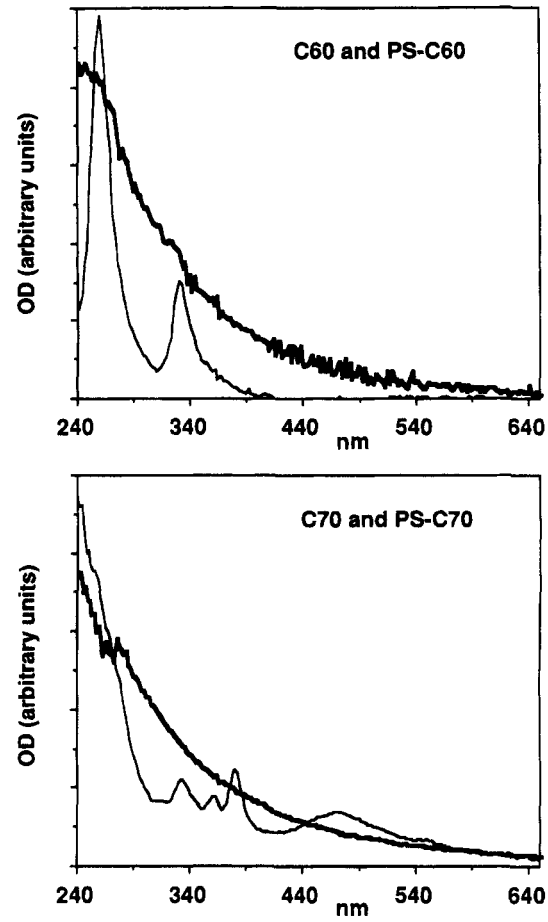

Figure 1. Comparison of C_{60} and C_{70} UV absorbance (thin line) with that of PS–C_{60} and PS–C_{70} (thick line), all in cyclohexane (all scaled arbitrarily for ease of comparison; the weak C_{60} band between 450 and 650 nm does not show up on this scale). For the polymer spectrum the reference solution was untagged polystyrene at the same weight percent in cyclohexane. The PS–fullerenes have a very strong absorbance between 200 and 230 nm (molar extinction coefficient $\approx 10^6$ M^{-1} cm^{-1}). This region is not shown because of the difficulty in accurately subtracting the contribution from the polystyrene and cyclohexane.

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