Free Radical Copolymerization of Styrene and C_{60}

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ABSTRACT: C_{60} reacts with free radicals produced by AIBN thermal decomposition and/or propagating polystyrene radicals to form adducts or polymers with significantly modified optical properties. C_{60} competes with styrene for AIBN radicals acting as a free radical retarder that can be incorporated into the final polymer. In general, the weight percent of C_{60} in the polymer is increased at the expense of the polymer yield and molecular weight. The average number of C_{60} moieties per polymer is close to unity for the reaction conditions studied, but an analysis of size exclusion chromatographic traces suggests that multiple C_{60} moieties can be incorporated into the polymer.

Introduction

Chemical modification of fullerenes has been actively pursued with the objective of improving the processibility of these materials, since they are sparingly soluble in many common solvents. One such approach has involved attaching fullerenes to functionalized polymers[1−4] or using the fullerenes as a trap for an anionic polymerization.[5] Several groups have independently observed that fullerenes can copolymerize with common monomers (styrene[6,7] and methyl methacrylate[8]) by standard free radical methods. The attachment of a free radical species to a fullerene significantly modifies its photophysical properties, which implies that the conjugation and/or the symmetry is strongly perturbed. With the conditions described herein, increasing the mole fraction of C_{60} always occurs at the expense of the polymer molecular weight and yield. This is evidently a consequence of the strong competition of C_{60} for the AIBN radicals and a slow propagation reaction of a C_{60} radical with styrene.

The objective of this paper is to present some systematic studies of the reaction of AIBN, styrene, and C_{60} that provides more detailed insight to these simple copolymerizations and that are of general interest in the field of fullerene chemistry.

Methods

(a) Purification of Materials. Styrene (99%, Aldrich Chemical) was distilled under reduced pressure and passed through a DTR-7 column from Scientific Polymer Products, Inc. AIBN (azobisisobutyronitrile, 99%, Kodak Chemicals) was recrystallized two times from methanol. Spectral grade benzene (Fisher Chemical) was refluxed over sodium and freshly distilled before use. A similar treatment was used for certified THF (Fisher), except that activated charcoal was included in the refluxing solution. The following solvents were used without further purification: (1) spectrophotometric grade methanol from Mallickrodt, (2) HPLC grade heptane from Fisher, and (3) spectrophotometric grade 1,4-dioxane from Aldrich; 99.9% C_{60} from SES Research, Inc. was used as received.

(b) Reaction Conditions. Reaction of C_{60} and AIBN. In 10 mL of benzene were dissolved 0.0056 mmol of C_{60} and the number of moles of AIBN indicated by the ratios in Table 1. The solution was transferred into an ampule, deoxygenated by Ar bubbling for 15 min, and sealed. The reaction was carried out at 120 °C for either 1 or 12 h. Similar reactions were observed at 65 °C.

Table 1. Reaction of AIBN with C_{60} at 120 °C[a]

sample	[AIBN]/[C_{60}]	reaction time (h)
AIBN1	14.2	1
AIBN2	4.8	1
AIBN3	1.3	12

[a] See Methods for reaction conditions.

Polymerization. To 44 mL of benzene was added 3.5 g of styrene, along with variable amounts of C_{60} (see Table 2). The mixture was vortexed for 30 min to produce a homogeneous solution. Various amounts of AIBN were added, and the solution was transferred to a glass ampule, degassed by four cycles by freeze−pump−thaw under 30 mTorr, and sealed. The polymerization was carried out at 65 °C for 37 h.

(c) Purification of Product. The products of the reaction are adducts of C_{60} with AIBN radicals, oligomers of polystyrene (PS) or PS-C_{60}, and higher molecular weight polymers in addition to unreacted styrene (all C_{60} is consumed under the conditions of our polymerization studies). In determining yield and molecular weight distribution, the following method was used: The polymerization mixture was divided into two portions. One was freeze-dried, which removes benzene, unreacted styrene, and decomposition products of AIBN that are not bound to nonvolatile products. To assure that all styrene was removed, the sample was redissolved in 1,4-dioxane, freeze-dried a second time, and weighed. This sample contains C_{60} adducts, oligomers, and higher molecular weight polymers. Since all C_{60} reacts, the total weight percent of C_{60} is known for this sample. The second portion is precipitated from benzene into heptane and methanol (two times each). This procedure removes oligomers as well as unreacted styrene. All precipitate was carefully collected by centrifugation, and the final precipitate was dissolved in 1,4-dioxane and freeze-dried. This sample will always have a slightly lower yield and a higher M_n (see Table 2).

Comparison of these two portions using GPC with dual detection provides an estimate of the weight percent of C_{60} as a function of molecular weight. The GPC of the freeze-dried sample was run with differential refractive index and UV detection (at 350 nm, where there is no detectible signal from pure polystyrene). The ratio of the integrated UV signal to the ΔRI signal was assumed to be proportional to the weight percent of C_{60}, which is known for this sample (see earlier discussion), i.e.,

$$\kappa(\text{UV area})/(\Delta\text{RI area}) = \text{wt \% } C_{60} \qquad (1)$$

The same proportionality constant (κ) is used for the precipitated sample, or for evaluating the wt % of C_{60} as a function of molecular weight. The reproducibility of the ratio in eq 1 has been found to be very good (±3%). However, there could be a systematic error in eq 1 because it is assumed that all molecular weight components of polystyrene contribute equally to the ΔRI signal, which is not likely to be true for AIBN

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Table 2. Reactions of Styrene,[a] AIBN, and C_{60} at 65 °C

(a) Styrene Alone

AIBN (mmol)	yield (%)[b]	M_n (kg/mol)[c]	M_w/M_n[c]
0.347	39.1 (43.5)	10.8 (7.8)	1.7 (2.1)
0.270	35.5 (40.4)	12.9 (10.6)	1.7 (2.0)
0.210	34.0 (37.6)	13.8 (11.8)	1.7 (2.0)
0.140	28.8 (32.7)	17.3 (13.7)	1.8 (2.1)
0.079	24.3 (26.3)	25.1 (20.5)	1.7 (2.0)

(b) Styrene Plus Constant C_{60}[d]

AIBN (mmol)	yield (%)[b]	M_n (kg/mol)[c]	M_w/M_n[c]	wt % C_{60}[e]
0.347	25.7 (29.1)	12.9 (8.8)	1.8 (1.7)	2.2 (2.9)
0.270	14.4 (16.7)	13.8 (9.2)	1.8 (2.5)	3.7 (5.0)
0.210	3.8 (6.2)	8.5 (5.7)	1.5 (2.3)	11.4 (13.4)
0.140	0.58 (2.4)	2.4 (1.2)	1.6 (1.7)	41.1 (35.8)
0.079	0.83 (1.5)	1.2 (0.74)	2.5 (2.8)	56.9 (54.2)

(c) Styrene Plus C_{60} (Constant AIBN[f])

C_{60} (mmol)	yield (%)[b]	M_n (kg/mol)[c]	M_w/M_n[c]	wt % C_{60}[e]
0	40.5 (47.1)	8.3 (5.9)	1.8 (2.4)	0
0.014	36.9 (41.3)	6.0 (4.1)	1.8 (2.1)	0.5 (0.7)
0.028	32.6 (36.3)	12.5 (9.1)	1.7 (2.3)	1.2 (1.6)
0.040	25.7 (29.1)	12.9 (8.8)	1.8 (1.7)	2.2 (2.9)
0.055	11.8 (14.5)	10.8 (5.8)	1.7 (2.7)	6.1 (7.8)

[a] In all cases, 33.7 mmol of styrene used. See Methods for details. [b] Yields for the precipitated product and, in parentheses, the product purified by freeze-drying. [c] Based on GPC elution curves and polystyrene standards. See Methods for details. [d] 0.040−0.041 mmol of C_{60}. [e] Based on eq 1 in the text. [f] 0.347 mmol of AIBN.

adducts with C_{60} or very low molecular weight oligomers. These GPC runs also demonstrated that there is no unreacted C_{60}, which elutes later than the solvent front.

(d) GPC and LC Characterization. For liquid chromatography, a Resolve column from Waters (5 μm spherical silica particles) was used with 1:1 v/v THF/heptane as the mobile phase at 0.5 mL/min. The GPC used a bank of Waters μstyragel columns with nominal pore sizes from 5×10^2 to 5×10^5 Å with THF as the eluting solvent at a flow rate of 1.5 mL/min. Calibration curves were constructed using PS standards (from Pressure Chemical, 390*K*, 200*K*, 35*K*, 20.4*K*, 2.0*K*, and from Scientific Polymer Products, 0.517*K*, with M_w/M_n between 1.06 and 1.1). M_n and M_w values were constructed from the ΔRI signal. The UV absorption spectrum of components was also collected using a HP Model 1050 diode array detector. This instrumentation is very powerful for these studies because the unreacted C_{60} absorption spectrum is distinct from C_{60} adducts. We cannot distinguish multiple adducts with C_{60}, and, in general, we do not know if our C_{60} polymers contain a significant fraction of star polymers. The GPC data were used to estimate the weight percent of C_{60} in the various polymer samples, as discussed above.

(e) Dilatometry. Dilatometry was carried out with a homebuilt glass apparatus, similar to that illustrated in standard textbooks.[9] A small magnetic stir bar was placed in the solution to help speed temperature equilibration in the 60 °C temperature bath. The change in height was measured with a traveling telescope and ranged from ~0.8 to 4.0 cm, depending on the reaction time. The reproducibility of this procedure was not particularly good (duplicate solutions could be offset by as much as ±10 min), but this accuracy was sufficient to demonstrate the inhibiting effect of C_{60} on the styrene polymerization.

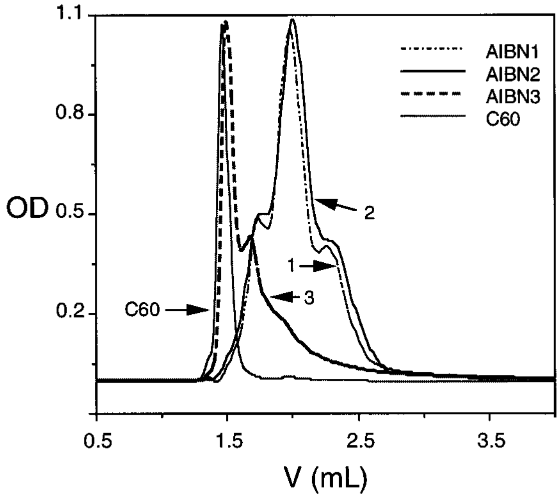

Figure 1. Chromatography traces of AIBN-C_{60} adducts (C_{60} at 1.5 mL is shown for comparison; see Table 1 for identification of other species).

Results

(a) Reaction of C_{60} with AIBN. Initial studies involved mixtures of C_{60}, styrene, and AIBN at elevated temperatures (typically 120 °C) in benzene (other similar solvents are suitable, but C_{60} is sparingly soluble in many common organic solvents). The color change from a deep purple to a dark brown occurs within a few minutes and does not require the presence of styrene. A series of reactions in benzene was carried out in which the AIBN to C_{60} ratio was varied (AIBN*x* in Table 1). At the lowest AIBN concentration, unreacted C_{60} could be easily observed in liquid chromatography, along with distinct new peaks (Figure 1), with an absorption spectrum characteristic of the adduct (i.e., long tail to the red, loss of the 328.5 nm peak, see ref 6). There are three distinct peaks in the elution curve of AIBN1 and AIBN2. For AIBN3, the elution curve is shifted toward the direction of unreacted C_{60}. We separated the three components of AIBN2 with TLC and reinjected them (Figure 2). The spectrum of the earliest eluting component is slightly different from the other two, but all are very distinct from the spectra C_{60} (spectra not shown). It is well known that C_{60} can react with multiple radicals (i.e., $^{\bullet}C_{60}(\text{benzyl})_n$ for $n = 3$ and 5 is particularly stable[10]). Mass spectroscopy of these various components is not very helpful, because C_{60} adducts have a strong tendency to lose the adduct and yield a strong 720 Da peak. However, it is certainly reasonable to assume that the various chromatography components represent different numbers of AIBN arms and possibly the dimerization of C_{60} radicals, i.e.,

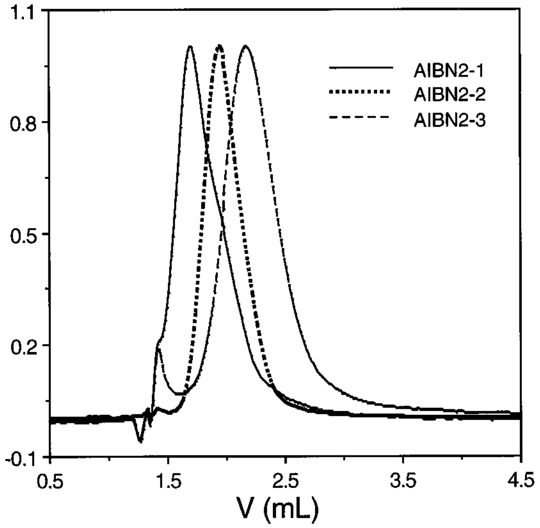

Figure 2. Traces from reinjection of three major peaks of AIBN2.

$$I_2 \rightarrow I^{\bullet} + N_2 \tag{2}$$

$$I^{\bullet} + C_{60} \rightarrow I\text{-}C_{60}^{\bullet} \tag{3}$$

$$I^{\bullet} + I\text{-}C_{60}^{\bullet} \rightarrow I\text{-}C_{60}\text{-}I \tag{4}$$

$$2\ I\text{-}C_{60}^{\bullet} \rightarrow I\text{-}C_{60}\text{-}C_{60}\text{-}I \tag{5}$$

where $I^{\bullet} = (CN)(CH_3)_2C^{\bullet}$. Since the spectra are so similar for all chromatographic components, it seems likely that destruction of the high symmetry of C_{60} is the main effect of adduct attachment. Work is continuing to characterize the reaction of C_{60} with free radicals such as produced by the decomposition of AIBN.

(b) Copolymerization of C_{60} with Styrene. It seems clear that the C_{60} competes efficiently with styrene for $I^{\bullet}$ radicals and that if the $[C_{60}]/[AIBN]$ ratio is large, then the yield of polystyrene is low (note that the total weight of C_{60} is very small compared to that of styrene, such that if the polymerization of styrene is repressed, the mass of recovered material is low). For AIBN and styrene alone, the M_n and yield correlate very well with $[AIBN]^{-1/2}$ and $[AIBN]^{1/2}$, respectively, as expected (see Figure 3). When the same styrene/AIBN ratios are examined in the presence of C_{60}, the yield and molecular weight of recovered material drops precipitously (see Table 2a and b). In Figure 4, the ratio of yields with and without C_{60} are compared for the same styrene and AIBN concentrations as a function of the ratio $[C_{60}]/[AIBN]$. It is interesting that the data fall on a universal curve with respect to $[C_{60}]/[AIBN]$. For the data in Table 2c, the yield drops as the amount of C_{60} is increased, but the M_n of the product is only modestly affected. For this data set, the maximum amount of C_{60} is still much smaller than the amount of AIBN (cf. 0.055 with 0.347 mmol), while for the results in Table 2b, the amounts of C_{60} and AIBN became comparable (cf. 0.040 mmol with the lowest amount of AIBN, 0.079 mmol). Thus, if one assumes that the C_{60} reacts much more rapidly with the AIBN radicals, the M_n values are approximately in the expected range for 0.347−0.292 mmol of AIBN (i.e., subtracting the 0.055 mmol of C_{60} from the amount of AIBN; this is a rough estimate because, as shown earlier, multiple reactions of C_{60} with AIBN radicals are possible). The fraction of C_{60} increases in the final precipitated product as the amount of C_{60} in the reaction mixture increases, primarily by preventing styrene polymerization. Thus, for high contents of C_{60}, there is very low polymer yield (<1%) and a very low M_n (<3*K*).

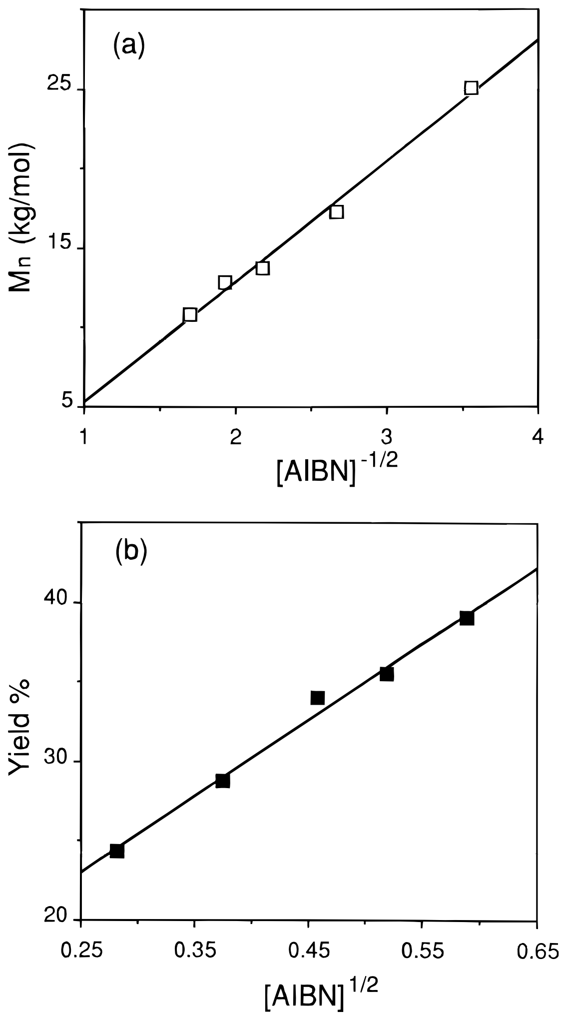

Figure 3. (a) M_n vs $[AIBN]^{-1/2}$ for polystyrene. (b) Yield of polystyrene versus $[AIBN]^{1/2}$.

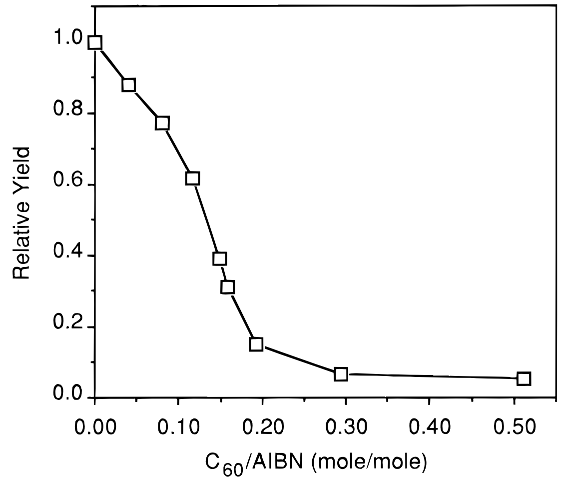

Figure 4. Plot of ratio of the yield of polymer in the presence of C_{60} to the yield of polystyrene with the same AIBN concentration versus $[C_{60}]/[AIBN]$.

Since the interception of $I^{\bullet}$ by C_{60} decreases the molecular weight of polymer, we assume that propagation is slow, i.e.,

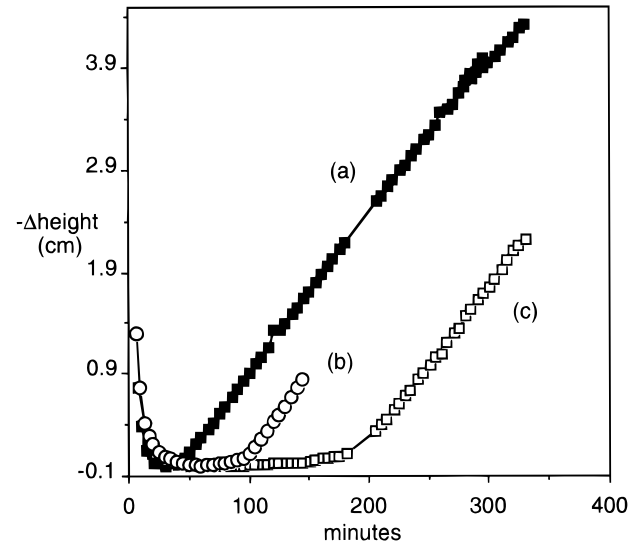

Figure 5. Change in height of the benzene solution (11.6 mL containing 123 mmol of styrene and 6.4 × 10^{-2} mmol of AIBN). Curves b and c include 1.6 × 10^{-3} and 3.1 × 10^{-3} mmol of C_{60}, respectively. The initial increase in height (negative-going values) is from heating from room temperature to 60 °C.

$$\text{I-C}_{60}^{\bullet} + \text{styrene} \rightarrow \text{slow reaction} \qquad (6)$$

$$\text{PS}''^{\bullet} + \text{C}_{60} \rightarrow \text{PS-C}_{60}^{\bullet} + \text{styrene} \rightarrow \text{slow reaction} \qquad (7)$$

but termination is facile,

$$\text{PS}'^{\bullet} + \text{PS-C}_{60}^{\bullet} \rightarrow \text{PS-C}_{60}\text{-PS}' \qquad (8)$$

$$\text{I}^{\bullet} + \text{PS-C}_{60}^{\bullet} \rightarrow \text{PS-C}_{60}\text{-I} \qquad (9)$$

It is also possible that the reacted C_{60} can suffer further attack,

$$\text{PS-C}_{60}\text{-PS}' + \text{PS}'''^{\bullet} \rightarrow (\text{PS})(\text{PS}')(\text{PS}'')\text{C}_{60}^{\bullet} \qquad (10)$$

producing a star polymer. While we have no evidence for the existence of these species, a similar reaction could increase the number of C_{60} moieties per polymer (see later).

Further evidence that C_{60} acts as an inhibitor for the styrene polymerization comes from simple dilatometry experiments. The change in reacting solution volume was monitored as a function of time for styrene in benzene and AIBN initiator (at 60 °C) with and without C_{60} being present. After an initial thermal expansion, the solution began to contract smoothly as polymerization proceeded. The slopes of the time-dependent ΔV curves were very similar with and without C_{60} but showed a longer induction period if C_{60} was present (Figure 5). However, the color change that accompanies the reaction of C_{60} with radicals was observed at the earliest times.[11] Therefore, we conclude that C_{60} reacts with $I^{\bullet}$ much faster than styrene, such that styrene polymerization occurs only after sufficient C_{60} is consumed to permit the reaction of $I^{\bullet}$ with styrene to compete. This is consistent with the idea that the propagation reactions (eqs 6 and 7) are sluggish.

The average number of C_{60} moieties per polymer can be estimated from the weight percent of C_{60} in the polymer and the M_n of the polymer (see Table 2 data). The values also fall on a universal curve when plotted as a function of $[C_{60}]/[AIBN]$ (see Figure 6). The largest values are approximately 1.3–1.4, which could arise from the C_{60} coupling termination reaction (like eq 5 above). However, since the assumptions underlying eq 1 are most likely to be invalid for very low molecular weights with a high content of C_{60}, this value cannot be stated with confidence to be greater than unity. However, the proportionality constant in eq 1 and the ratio of the ΔRI and 350 nm UV signal as a function of elution volume can be used to relate the C_{60} content as

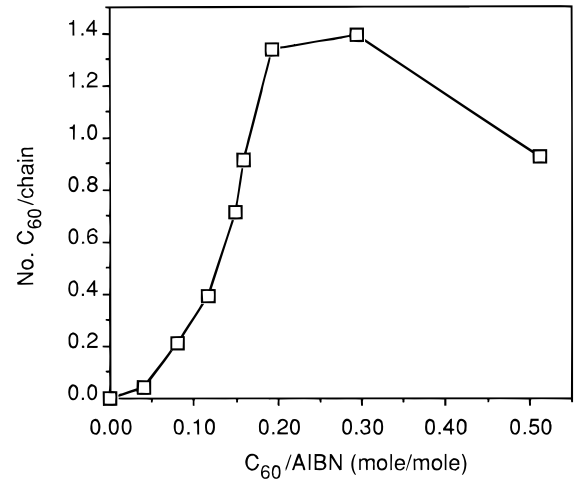

Figure 6. Estimated average number of C_{60} moieties per chain (see text) as a function of $[C_{60}]/[AIBN]$.

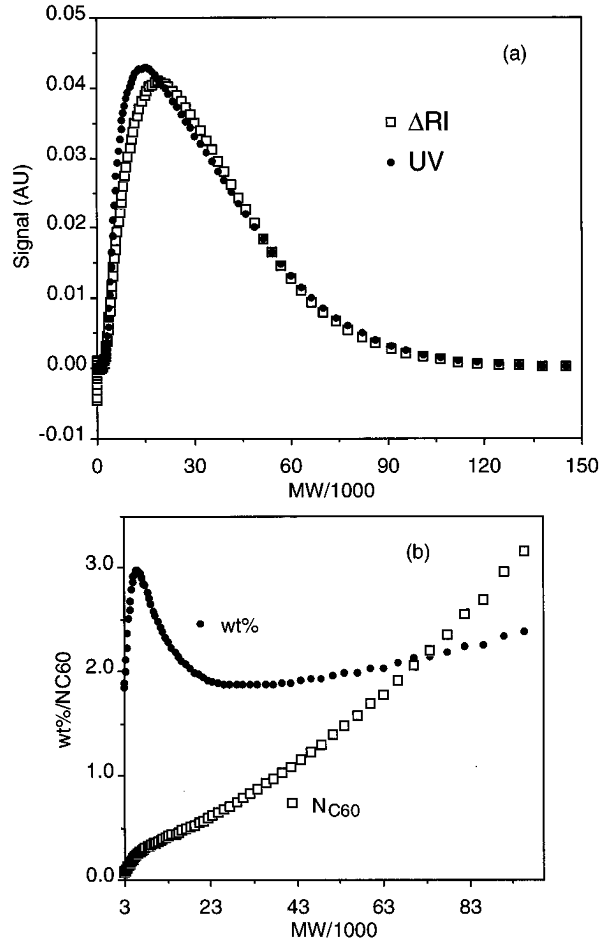

Figure 7. (a) Scaled ΔRI and UV absorbance (at 350 nm) as a function of molecular weight (from GPC elution volume and calibration curve). (b) Calculated weight percent and $N_{C_{60}}$ from the data in part a. These data are for the first entry in Table 2b. The numerical axis is the same for both of these quantities (i.e., 2 wt percent corresponds to $N_{C_{60}} = 2$).

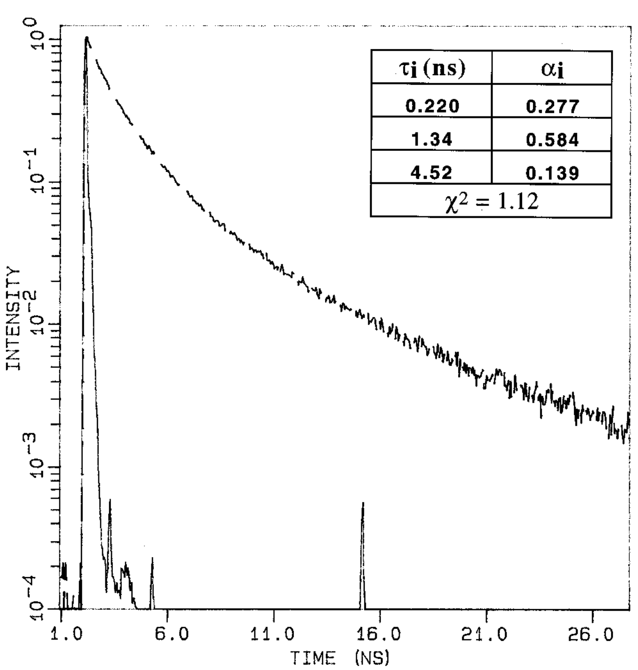

Figure 8. Fluorescence decay of PS-C_{60} excited at 577 nm and observed at 620 nm. Fitting parameters are indicated on the figure.

a function of molecular weight. If these two signals track each other perfectly, then the weight percent of C_{60} would be constant across the molecular weight distribution. In this case, the molecular weight range is sufficiently high that we may assume that the ΔRI signal is related only to the polystyrene. These data are presented in Figure 7a for a typical polymer (precipitated sample). As can be seen, the UV signal is proportionally stronger at lower molecular weights (this effect is more pronounced for the freeze-dried sample, which retains oligomeric polystyrene and low molecular weight C_{60} adducts). These data are plotted as the weight percent of C_{60} and the average number of C_{60} moieties/chain ($N_{C_{60}}$) in Figure 7b. In this latter plot, the lower limit of the molecular weight is taken to be 3000, because the assumption that ΔRI is independent of polystyrene molecular weight is not expected to be valid in the low molecular weight regime, as discussed above. For molecular weights above ~25*K*, the weight percent remains approximately constant, which means that $N_{C_{60}}$ increases approximately linearly.

In the earlier discussion, we have argued that C_{60} propagates slowly with styrene, but there must be some propagation or else $N_{C_{60}}$ would remain constant, presumably near unity. Other than propagation to produce a linear polymer (eqs 6 and 7), it is possible that reactions between C_{60} species could increase the C_{60} content (like eq 5). However, none of our characterization methods would provide unequivocal proof of this unusual propagation mechanism.

(c) Photophysics of PS-C_{60}. In the earlier reports, it was noted that the absorption spectrum of fullerenes is strongly modified upon copolymerization and the fluorescence is blue-shifted and much stronger than that for the parent fullerene.[6,7] The fluorescence spectrum depends on the wavelength of excitation, and the excitation spectrum depends on the wavelength of observation and does not correspond to the absorption spectrum. This is not the case for the parent fullerene.[12] These observations demonstrate that there must be different points of attachment of the adducts with slightly different energy levels.[13] The fluorescence decay of PS-C_{60} is highly nonexponential, with an average lifetime of 1.47 ns.[14] The complexity of the decay could be the result of the multiple species being excited at this wavelength (see Figure 8). Unfortunately, we are not in a position to evaluate the decay curves as a function of excitation wavelength.

One of the interesting photophysical observations is the absence of a transient absorption spectrum between 700 and 960 nm when excited at 355 nm (2.5 mJ/pulse) immediately after the laser pulse to ~3 ns (in 150 ps steps).[15] For the parent fullerenes, one observes both S-S and T-T absorption in this region.[16]

Much more detailed work is planned for the future of the photophysical characterization of various copolymerized fullerenes.

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(11) This was also observed by removing aliquots of the reaction mixture in a separate experiment. There is an immediate loss of the 328.5 nm peak and a growth of absorption at longer wavelengths, resulting in a darkening of the reacting mixture.
(12) Sun, Y.-P.; Wang, P.; Hamilton, N. B. *J. Am. Chem. Soc.* **1993**, *115*, 6378.
(13) The complexity of the energy level diagram for C_{60} is illustrated by the application of a simple particle-on-a-sphere model. See: Savina, M. R.; Lohr, L. L.; Francis, A. H. *Chem. Phys. Lett.* **1993**, *205*, 200. Presumably, the adducts will cause considerable mixing of these states as the symmetry is lowered.
(14) Based on a multiexponential fit of the decay, the average lifetime is given by $\sum\alpha_i\tau_i$, where $\sum\alpha_i = 1$.
(15) Dr. P. V. Kamat, Radiation Laboratory, University of Notre Dame, private communication.
(16) See, for example: Gevaert, M.; Kamat, P. V. *J. Phys. Chem.* **1992**, *96*, 9883.

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