6000 *Macromolecules* **1995,** *28,* 6000–6006

Synthesis and SANS Structural Characterization of Polymer-Substituted Fullerenes (Flagellenes)

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Received February 28, 1995; Revised Manuscript Received May 30, 1995[⊗]

ABSTRACT: Small-angle neutron scattering (SANS) has been shown to be an appropriate technique for the structural characterization of fullerenes in solvents with strong SANS contrast (e.g., CS_2) [Affholter, K. A.; Henderson, S. J.; Wignall, G. D.; Bunick, G. J.; Haufler, R. E.; Compton, R. N. *J. Chem. Phys.* **1993**, *99*, 9224]. Since deuterated solvents (e.g., toluene-d_8) have a high scattering length density (SLD) which is close to that of C_{60} and C_{70} fullerenes, there is virtually no SANS contrast with the solvent, and these particles are practically "invisible" in such media. On the other hand, the negative scattering length of hydrogen means that the SLD of ^1H-containing materials is much lower, so they have a strong contrast with toluene-d_8. Thus, SANS makes it possible to study the sizes and shapes of polymer-substituted fullerenes (flagellenes) [Samulski, E. T.; DeSimone, J. M.; Hung, M. O., Jr.; Menceloglu, Y. Z.; Jarnagin, R. C.; York, G. A.; Labat, K. B.; Wang, H. *Chem. Mater.* **1992**, *4*, 1153]. Mono- and dipolystyrene-substituted C_{60} were synthesized via termination of living anionic polymerization of styrene in an optimization of our previous work [Samulski et al.]. These materials were characterized by gel permeation chromatography (GPC) and small-angle neutron scattering (SANS). The extrapolated cross section at zero angle of scatter [$d\Sigma/d\Omega(0)$] is a function of the number of pendant chains, so SANS can be used to assess the number of "arms" which are covalently attached to the fullerene "core". Close agreement (±4%) between the measured and calculated values of $d\Sigma/d\Omega(0)$ and with independent estimates of the radius of gyration (R_g) and second virial coefficient (A_2) for a linear polystyrene calibration sample serves as a cross check on the validity of this methodology.

Introduction

Following the large effort to make low molar mass derivatives of fullerenes, in the last 2 years there has been increased interest in polymeric derivatives of C_{60} materials, e.g., polymer-substituted fullerenes,[2–5] C_{60} copolymers,[6] dendrimers,[7] and a host of other materials.[8,9] One motivation for preparing these derivatives is to modify C_{60} so that its unique properties may be retained in more tractable compounds, i.e., compounds which may be dissolved and processed into unstable forms for properties evaluation and potential applications. The synthesis of a new class of fullerene adducts—"flagellenes", a C_{60} "core" with one or more pendant linear polymer chains—was reported in 1992.[2] The following year small-angle neutron scattering (SANS) was applied for the first time to characterize fullerenes.[1] In this paper we report the application of the SANS technique to the structural characterization of flagellenes. The flagellenes considered herein are polymer adducts of C_{60} wherein linear polystyrene (PS) has been covalently attached to C_{60}, produced by reacting a living PS carbanion with C_{60} to give a mixture of materials with the formula $C_{60}(PS)_f$, with $1 < f < 5$. In conjunction with varying the scattering contrast (with respect to the solvent), we demonstrated that the SANS technique is appropriate for the structural characterization of the individual flagellene macromolecules.

Experimental Section

Reagents. Toluene (Fisher, certified grade) was distilled under argon from sodium metal. Tetrahydrofuran (Fisher; certified grade) was distilled under argon from the purple sodium benzophenone ketyl. Styrene (Fisher; certified grade) was vacuum distilled from dibutylmagnesium (FMC Lithium Division) following three freeze–thaw cycles. The initiator, *sec*-butyllithium (FMC Lithium Division) was used as received, and the molar concentration was determined by the Gilman double titration method.[10] Co_{60} (Texas Fullerenes; 98%) was used as received.

Synthesis of (Polystyrene)$_{3-4}$–C_{60}. The synthesis of these materials has been reported previously.[2] The sample (referred to as PS:C_{60} 10:1 in ref 2) is a mixture of the flagellene and proton-terminated polystyrene homopolymer. In order to isolate the pure $(PS)_{3-4}$–C_{60} sample without PS–H contamination, fractionation techniques would be required with associated low yields.

Synthesis of (Polystyrene)$_{1-2}$–C_{60}. Functionalization Method 1 (Cooled, Heterogeneous C_{60} Solution). A dark purple solution of 0.1 g of C_{60} in 50 mL of toluene and 50 mL of tetrahydrofuran was prepared in a round-bottomed flask equipped with a magnetic stirbar and a rubber septum under a 6–8 psig argon atmosphere. The anionic polymerization was conducted in a one-neck, 500-mL, round-bottomed flask equipped with a magnetic stirbar and a rubber septum under a 6–8 psig argon atmosphere. The flask was charged with 11.0 mL (10.0 g) of styrene in 100 mL of toluene and then cooled to 0 °C. The polymerization was initiated by the addition of 7.52 mL of a 1.33 M solution of *sec*-butyllithium (target $\langle M_n \rangle = 1000$). The resulting orange–red solution was allowed to stir for 1.5 h, after which the solution was cooled to −78 °C. Once the solution was at −78 °C, 100 mL of tetrahydrofuran was added via syringe. An aliquot of the polystyryl carbanion was taken into deoxygenated isopropyl alcohol, resulting in a proton-terminated sample (PS–H). A stoichiometric imbalance of 0.6:1 PS:C_{60} was used in order to

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1995.

0024-9297/95/2228-6000$09.00/0

Table 1. Samples Characterized by SANS[a]

	sample	comment
1.	$(PS)_{3-4}-C_{60}$	*contains* PS homopolymer
2.	$(PS)_{1-2}-C_{60}$	prepared by functionalization method 2; contains *no* PS homopolymer
3.	PS−H	linear polystyrene calibration sample

[a] While functionalization method 1 yielded $(PS)_{1-2}-C_{60}$ with the highest percentage of $(PS)_1-C_{60}$, there was an insufficient amount of sample remaining for SANS analysis.

ensure that the C_{60} was always in excess and to increase the probability of monoaddition.[11] The C_{60} solution, at −78 °C, was the characteristic dark purple color but heterogeneous, due to the insolubility of C_{60} in tetrahydrofuran and the decreased temperature. When 1.6 mL of a polystyryl carbanion solution (0.08 g of PS^-) was added to the C_{60} solution, the solution became a reddish-black color. The solution was allowed to stir for 30 min, followed by addition of ca. 1.0 mL of a 1 vol % HCl/methanol solution, after which the solution remained dark red and heterogeneous. The $PS-C_{60}$ polymer was then isolated via removal of the solvent by rotary evaporation, followed by redissolution in 8 mL of tetrahydrofuran. $PS-C_{60}$ formed a dark amber solution in tetrahydrofuran which was filtered through a 0.45-μm PTFE filter to remove the insoluble C_{60}. The tetrahydrofuran was then evaporated, and $PS-C_{60}$ was recovered as a dark brown solid which was further dried under vacuum for 12 h.

Functionalization Method 2 (Ambient Temperature, Homogeneous C_{60} Solution). The same procedure was followed for generation of the polystyryl carbanion as described above, except the targeted molar mass was 2000. The polystyryl carbanion/toluene solution was cooled to −78 °C followed by addition of 20 mL of tetrahydrofuran. (This lower tetrahydrofuran volume was found to be adequate for breaking up the association of ion pairs and increasing the amount of solvent-separated ion pairs.) Thus, the volume of the polystyryl carbanion added to the C_{60} solution was 1.95 mL (0.17 g of PS^-). The C_{60} solution was prepared by dissolving 0.1 g of C_{60} in 100 mL of toluene and 10 mL of tetrahydrofuran at ambient temperature in order to assure the homogeneity of the solution. The C_{60} solution remained at room temperature during addition of the polystyryl carbanion solution. The product was then recovered as detailed previously.

Gel Permeation Chromatography. A Waters 150-CV gel permeation chromatograph with Ultrastyragel columns of 100-, 500-, 10^3-, and 10^4-Å porosites in tetrahydrofuran was used with polystyrene standards (Showa Denko) for the determination of molar mass and molar mass distribution. The GPC system was equipped with a refractive index (RI) detector and a Waters 484 ultraviolet−visible detector.

Small-Angle Neutron Scattering (SANS). The samples characterized using SANS are listed in Table 1. Three samples were prepared: approximately 20 mg of $(PS)_{3-4}-C_{60}$, 45 mg of $(PS)_{1-2}-C_{60}$ (functionalization method 2), and 40 mg of polystyrene homopolymer were dissolved in approximately 2 mL of toluene-d_8 (99+% purity), respectively. After 1 min of sonication, each sample was centrifuged for 2 min, carefully decanted, and transferred to quartz cells with 5-mm path length. After each SANS experiment each sample was diluted. The first dilution was made by removing about 25% by volume of the solutions from the quartz cells and replacing that amount with toluene-d_8. Samples were weighed to determine the exact amount of toluene-d_8 that was added. This procedure was repeated for the second dilution by removing approximately one-third of each of the samples and the third dilution by removing approximately half of each of the samples. All additions of toluene-d_8 and transfer of material were done with disposable glass Pasteur pipettes to avoid contamination.

The experiments were performed on the W. C. Koehler 30-m SANS facility at Oak Ridge National Laboratory.[12] The neutron wavelength was 4.75 Å ($\Delta\lambda/\lambda = 5\%$), and the beam was transported to a distance of 3.5 m from the sample by means of moveable neutron guides. The (round) sample and (rectangular) source Cd slits were 1.6 cm and 3.2 ~ 3.6 cm^2, respectively, and the sample−detector distance was 3.1 m. The samples were contained in quartz cells, and the area detector was a 64 × 64 cm^2 proportional counter with an element size of 1 cm^2.

The transmission of the sample was measured in a separate experiment[13] by collimating the beam with slits (irises) = 1 cm in diameter, separated by a distance = 7.5 m. A strongly scattering sample, porous carbon, was placed at the sample position to spread the beam over the detector. Without the carbon in position, the beam would either be blocked by the beam stop or be concentrated in a few detector cells, with the possibility of saturating or damaging the detector. The total count summed over the whole detector ($>10^5$) was recorded in a time period of approximately 2 min, and the sample being measured was placed over the source slit, thus attenuating the beam. The count was repeated over the same time interval, and the transmission is given by the ratio of the two counts after minor corrections ($<0.1\%$) for the beam-blocked background due to cosmic rays, etc. In this geometry no scattering from the sample at Q-values $> 10^{-3}$ Å^{-1} can enter the second iris and be rescattered by the porous carbon and hence be counted by the detector. All measurements were performed at room temperature ($T = 23$ °C), and typical values of the empty quartz cell and sample transmissions were $T = 0.95$ and 0.68 for a 5-mm path length. Typical run times were in the range 1−4 h.

The data were corrected on an element-by-element basis for the detector efficiency, instrumental (beam-blocked) background, and the scattering from the quartz cell filled with toluene-d_8, prior to radial (azimuthal) averaging to give a range of momentum transfer $0.05 < Q < 0.18$ Å^{-1}, where $Q = 4\pi \sin \theta/\lambda$, $\lambda = 4.75$ Å is the wavelength, and 2θ is the angle of scatter. The net intensities were converted to an absolute (±4%) differential cross section per unit sample volume [$d\Sigma/d\Omega(Q)$ in units of cm^{-1}] by comparison with precalibrated secondary standards, based on the measurement of beam flux, vanadium incoherent cross section, the scattering from water, and other reference materials.[14] The efficiency calibration was based on the scattering from light water and lead to angle independent scattering for vanadium, H−polymer blanks, and water samples of different thicknesses.

Results and Discussion

Synthesis and Molecular Characterization. As inferred from spectroscopic attributes, the electronic properties of C_{60} are minimally perturbed in derivatives wherein the degree of substitution on the C_{60} molecule is limited. Thus, it is of interest to produce a monopolymer-substituted C_{60} (monoflagellene) which should have increased solubility and film-forming capabilities relative to C_{60} itself. Due to the low yields of monoflagellenes inherent in fractionation techniques, our goal was to produce monoflagellenes directly via termination of a living anionic polymerization. As shown in our previous work, the six pyracyclenoid sites of C_{60} are quite reactive toward nucleophilic attack, resulting in multiarm flagellenes. Our current work has yielded a methodology in which mono- and diflagellenes are produced in high yield without fractionation or polystyrene homopolymer contamination.

The optimized synthesis of the flagellenes is outlined in Scheme 1. This synthesis contains two significant variations from the previous methodology: (1) the addition of >20 vol % tetrahydrofuran to the polystyryl carbanion solution and (2) the addition of tetrahydrofuran to the C_{60} solution and the cooling of the solution to −78 °C prior to termination. The first step was the living polymerization of styrene in toluene to yield the living polystyryl carbanion with controlled molar mass and narrow molecular weight distribution. Due to the aggregation of polystyryl carbanions in hydrocarbon solvents,[15] tetrahydrofuran was added to break up this aggregation in order to lessen the likelihood of multiple substitution on C_{60} due to the high local concentration

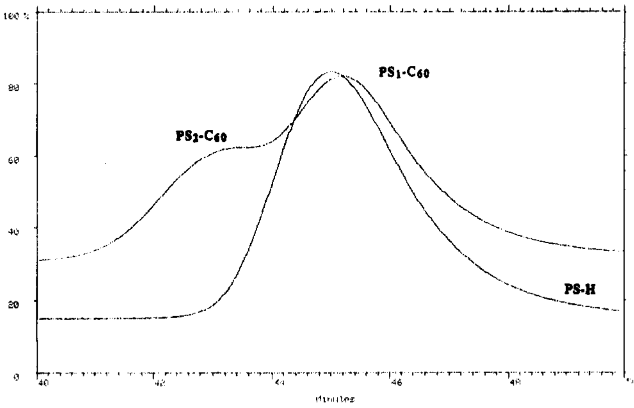
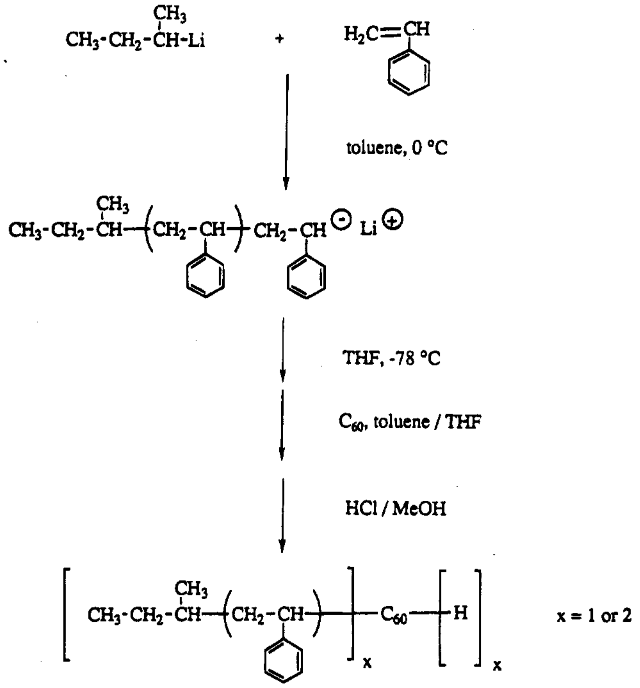


Figure 1. GPC overlay plot of RI traces of PS$-$C$_{60}$ prepared by functionalization method 1 and the PS$-$H aliquot.

Scheme 1. Optimized Synthesis of PS$-$C$_{60}$



of the polystyryl carbanion. The resulting solvent-separated ion pairs and free ions are more likely to attack a single pyracyclenoid site of C$_{60}$ (in a 1:1 or lower (i.e., 0.6:1) stoichiometry), since the free and solvent-separated ion pairs are more evenly distributed in the solution. This difference can be observed by comparing the gel permeation chromatograms from this study (Figures 1–4) with those of the 0.8:1 PS:C$_{60}$ from our earlier work.[2] The materials made with the addition of >20 vol % THF have predominantly one and two polystyrene arms and have no polystyrene homopolymer. In contrast, the materials made via addition of only 2 vol % THF (ref 2) have predominantly three and four polystyrene arms and a significant amount of polystyrene homopolymer.

The temperature was lowered to -78 °C following propagation for two reasons. First, if the temperature was not lowered prior to addition of a large amount of THF (>20 vol %), then chain transfer to tetrahydrofuran may occur. Second, it appears that cooling the C$_{60}$ solution (functionalization method 1) affects the rate of nucleophilic attack enough such that the predominant product was the monosubstituted flagellene over the disubstituted flagellene, even though the C$_{60}$ solution was heterogeneous. As shown by the overlay of the chromatograms from the refractive index detector of the polystyrene aliquot ($\langle M_n \rangle = 940$, MWD = 1.16) and the PS$-C_{60}$ (Figure 1), the main product is the monosubstituted fullerene ($M_{\rm Peak} = 1100$) with a significant amount of the disubstituted fullerene ($M_{\rm Peak} = 2100$). This is confirmed by comparison of the PS$-$C$_{60}$ chromatograms (Figure 2) from the refractive index detector and the ultraviolet detector ($\lambda = 600$ nm) showing the presence of C$_{60}$ throughout the sample and the absence of polystyrene homopolymer, since only C$_{60}$ absorbs at 600 nm while polystyrene does not.

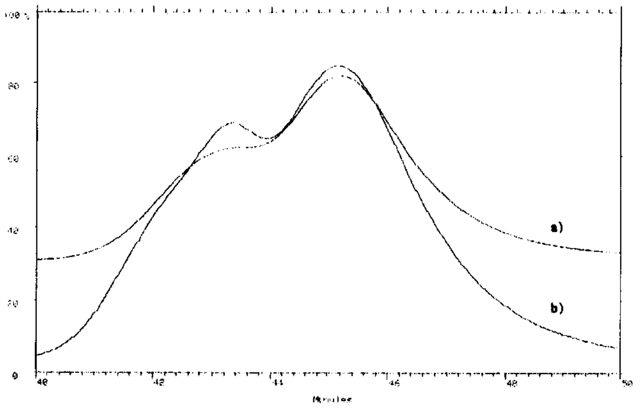


Figure 2. GPC overlay plot of PS$-$C$_{60}$ prepared by functionalization method 1: (a) RI detector; (b) UV detector ($\lambda = 600$ nm).

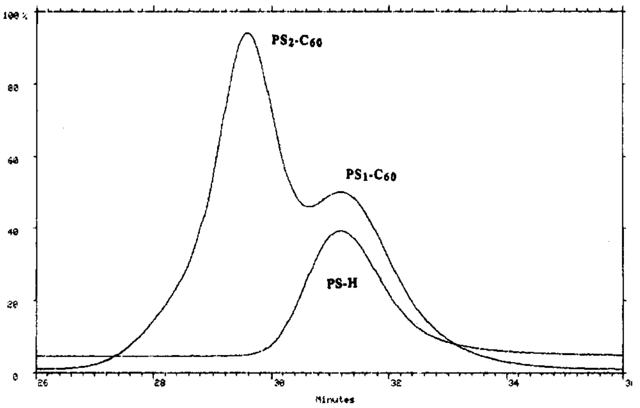


Figure 3. GPC overlay plot of RI traces of PS$-$C$_{60}$ prepared by functionalization method 2 and the PS$-$H aliquot.

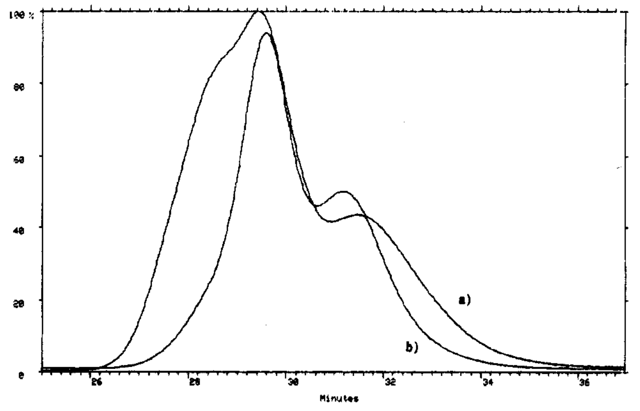


Figure 4. GPC overlay of PS$-$C$_{60}$ prepared by functionalization method 2: (a) UV detector ($\lambda = 600$ nm); (b) RI detector.

In the case of functionalization method 2, it appears that the homogeneity of the C$_{60}$ solution is less important than (1) the temperature of the solution during termination and (2) the degree of aggregation of the polystyryl carbanions (as a function of tetrahydrofuran concentration). As shown in Figure 3, the GPC refractive index detector overlay of the polystyrene aliquot ($\langle M_n \rangle = 2180$, MWD = 1.07) and the PS$-C_{60}$ shows that the main product is the disubstituted fullerene ($M_{Peak} = 4500$), with the monosubstituted fullerene ($M_{Peak} = 2400$) as the minor product. The overlay of the GPC refractive index and ultraviolet ($\lambda = 600$ nm) detectors (Figure 4) shows the presence of C_{60} throughout the sample. The ultraviolet detector chromatogram also shows the presence of a higher molecular weight shoulder at a $M_{Peak} = 7000$, which presumably corresponds to a trisubstituted fullerene. Thus, this comparison of the refractive index and ultraviolet detector ($\lambda = 600$ nm) shows that, although the C_{60} solution was homogeneous in functionalization method 2, the degree of substitution was less controlled than under the conditions of functionalization method 1.

Sans Structural Characterization. In general, the differential scattering cross section of a homogeneous particle or molecule [$d\Sigma/d\Omega(Q)$ per unit solid angle per unit sample volume (in units of cm^{-1}) is given by an equation of the form

$$d\Sigma(Q)/d\Omega = d\Sigma(0)/d\Omega\, P(Q) \tag{1}$$

where $P(Q)$ is the form factor describing the shape of the scattering entity [$P(0) = 1$]. For solid or hollow spheres, $P(Q)$ is represented by Bessel functions,[16] whereas for a star molecule with f-arms, $P(Q)$ is given by[17]

$$P(Q) = (2/u^2)(u - f(1 - \exp(-u/f)) + (f(f-1)/2)(1 - \exp(u/f)^2)) \tag{2}$$

where $u = (Q^2 R_g{}^2 f^2)/(3f - 2)$ and R_g is the radius of gyration [i.e., the root-mean-square (rms) distance of all scattering elements from the center of gravity]. For a homogeneous system suspended in a solvent medium, the ($Q = 0$) cross section is given by

$$d\Sigma/d\Omega(0) = N_p(\varrho_p - \varrho_s)^2 V_p{}^2 \tag{3}$$

where ϱ_p and ϱ_s are the scattering length densities of the particle and solvent, respectively, N_p is the number of particles per unit volume, and V_p is the particle volume.

Where the particle consists of two components (e.g., fullerene core and attached pendant chains), eq 3 is modified to

$$d\Sigma/d\Omega(0) = N_p[\Sigma_i v_i(\varrho_i - \varrho_s)]^2 \tag{4}$$

where the summation runs over the SLDs (ϱ) and volumes (v) of the two components (fullerene and pendant chains in the case of flagellenes). Equation 4 reduces to eq 3 in the case of a one-component homogeneous particle or a system of two components, one of which has a SLD equal to that of the solvent.[16]

According to eq 4, the $Q = 0$ extrapolated cross section is proportional to N_p (or alternatively to the concentration, $c = NpM_w/A_0$, where A_0 is Avogadro's number). In the case where there are significant particle$-$solvent interactions, eq 4 is modified[18] as follows:

$$d\Sigma/d\Omega(0) = (cA_0/M_w(1 + 2A_2M_wc))[\Sigma_i v_i(\varrho_i - \varrho_s)]^2 \tag{5}$$

where A_2 is the second virial coefficient, which indicates whether a polymer chain swells or contracts in the presence of a solvent. In general, the second virial coefficient is a decreasing function of the (weight-averaged) molecular weight, M_w. When the range in M_w is narrow, i.e., 1$-$2 decades, $A_2(M_w)$ can be empirically described by $A_2 - M_w{}^{-\delta}$, with $\delta = 0.3$ in various systems.[11]

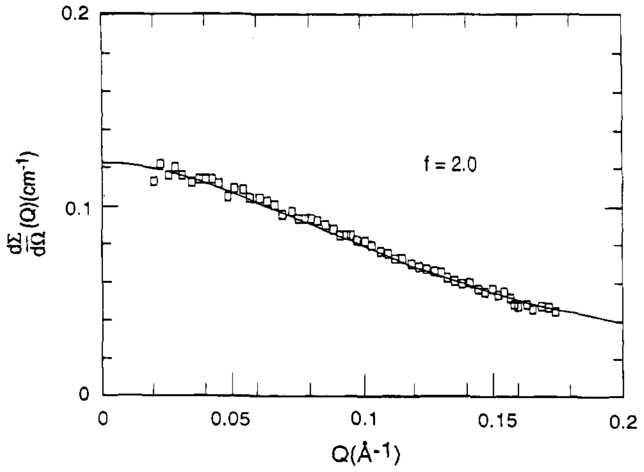


Figure 5. $d\Sigma/d\Omega(Q)$ vs Q for 24.1 mg/mL of polystyrene (Table 1, entry 3: PS$-$H, $M_n = 2180$, MWD = 1.08) in toluene-d_8.

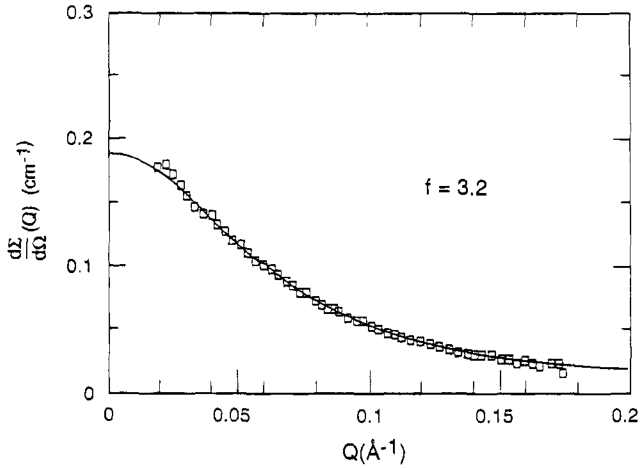


Figure 6. $d\Sigma/d\Omega(Q)$ vs Q for 13.3 mg/mL of $(PS)_{3-4}-C_{60}$ (Table 1, entry 1) in toluene-d_8.

Figures 5 and 6 show typical SANS data sets for the polystyrene calibration sample and the $(PS)_{3-4}-C_{60}$, respectively. Equation 2 reduces to the well-known formula for a (linear chain) random coil for $f = 2$ and the polystyrene data; i.e., data in Figure 5 were fit with only $d\Sigma/d\Omega(0)$ and R_g as variables. Although the flat background (0.05 cm^{-1}) due to the toluene-d_8 solvent is removed by subtracting the scattering of a "blank" solvent run, there remains a small (flat) incoherent background due to the (wavelength-dependent[19]) incoherent cross section of the protons [$\sigma_{inc}(\lambda) = 90 \times 10^{-24}$ cm^2 at $\lambda = 4.75$ Å, or $\sigma_{inc} = 90$ barns] in the pendant polystyrene chains. This was estimated in two different ways: first, the total ^1H incoherent cross section per unit solid angle was calculated (e.g., $N_H\sigma_{inc}/4\pi$), where N_H is the number of protons per unit volume. For the polystyrene sample with 10 mg/mL, this gave a background of 3.3×10^{-3} cm^{-1}. Second, the background was scaled from the measured incoherent scattering from a solid proton-terminated polystyrene (PS$-$H) sample[14] (0.6 cm^{-1}, at $\lambda = 4.75$ Å) via the proton density (N_H). It is well-known that there is an appreciable amount of multiple scattering in protonated polymer blanks[20] because of the higher proton density in the solid sample.

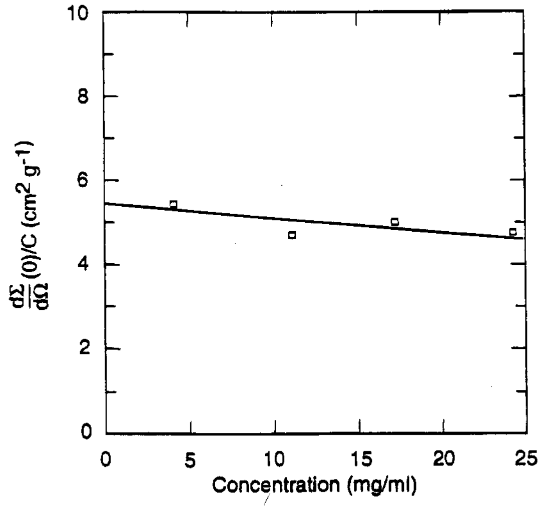


Figure 7. $d\Sigma/d\Omega(0)/C$ vs concentration (C) for polystyrene (Table 1, entry 3: PS–H, M_n = 2180, MWD = 1.08).

However, a first-order correction[14] for this effect led to an estimate (2.9×10^{-3} cm^{-1}) in good agreement with the previous approximation. Such corrections were calculated and subtracted from the data at all concentrations by the two different methods and were consistent to within $\pm 5 \times 10^{-4}$ cm^{-1}.

Figure 7 shows the dependence of c^{-1} $d\Sigma/d\Omega(0)$ on concentration for the polystyrene calibration sample, and the extrapolated value at ($Q = 0, c = 0$) $d\Sigma/d\Omega(0)$ = 0.055 cm^{-1}, compares to a value of 0.057 cm^{-1}, calculated via eq 3 and the GPC molecular weight. The (negative) slope leads to $A_2 = 18 \times 10^{-4}$ cm^3 g^{-2} mol. There is a dearth of measurements of the second virial coefficient for PS in toluene at such small molecular weights, and most studies have been undertaken on molecules with several orders of magnitude higher mass. For example, Rahlwes[21] used light scattering (LS) to measure $A_2 = 2.2 \times 10^{-4}$ cm^3 g^{-2} mol at $M_w = 2.95 \times 10^6$, and scaling to $M_w = 2 \times 10^3$ ($A_2 = M_w^{-\delta}$; $\delta = 0.3$) leads to an estimate of $A_2 = 19.6 \times 10^{-4}$ cm^3 g^{-2} mol. The only direct measurements that we are aware of are those of Huber et al.[22] (who measured three points by SANS) and Zhang et al.,[23] who measured five points via LS in the range $1.2 < 10^{-3}M_w < 4.0$. However, osmometry measurements[22] give grossly different estimates. As the SANS and LS measurements are in broad agreement with data scaled from higher M_w, we have therefore taken these eight points and fit them with an empirical scaling relationship $A_2 = 24.2M_w^{-0.34} \times 10^{-3}$ cm^3 g^{-2} mol. This leads to $A_2 = 18 \times 10^{-4}$ cm^3 g^{-2} mol for M_n = 2180, in good agreement with the SANS result (Figure 7).

The average radius of gyration of the three highest concentration samples (via fitting a Debye coil as in Figure 5) is R_g = 12.5 Å, and Zimm fits in the Q-range $0.019 < Q < 0.085$ Å^{-1} lead to 12.8 Å. It is well-known that the Zimm analysis is valid only in the limit $QR_g \ll 1$, and when this is exceeded, the procedure overestimates both R_g and $d\Sigma/d\Omega(0)$. Ullman[24,25] has estimated numerical corrections for this effect as a function of $QR_{g,\max}$ and $QR_{g,\min}$, and after these were applied, the Debye fit and Zimm 12.2 ± 0.5 Å values are in agreement within experimental error. These may be compared with R_g = 10.1 Å extrapolated from the three SANS data points of Huber et al.[22] We are unaware of any other measurements of the chain dimensions of polystyrene in toluene in this M_w range, though for such short chains containing only 20 segments, the swelling in a good solvent should be negligible. The unperturbed dimensions for polystyrene have been measured several times in the melt and in θ-solvents and may be summarized[20] as R_{gw} = (0.27 ± 0.005 Å)$M_w^{0.5}$, where R_{gw} and Mw refer to weight-averaged quantities. After a slight polydispersity correction (4%), this leads to 12.7 ± 0.2 Å, which is close to the (z-averaged) dimension measured in this work. It is hard to see how the radius in toluene could be smaller[22] than the melt dimensions, and accordingly we have assumed that the chains are unperturbed.

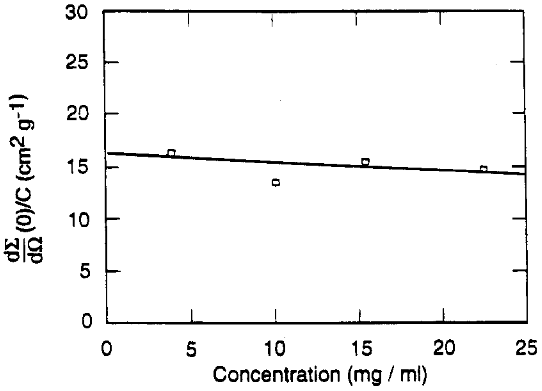


Figure 8. $d\Sigma/d\Omega(0)/C$ vs concentration (C) for $(PS)_{3-4}$–C_{60} (Table 1, entry 1).

Figure 8 shows a plot of c^{-1} $d\Sigma/d\Omega(0)$ versus concentration (c) for $(PS)_{3-4}$–C_{60}. After extrapolating to c = 0, the average number of pendant chains was calculated to give f = 3.2, via eq 2. The slope is again slightly negative and leads to an estimate of $A_2 = (8.5 \pm 5) \times 10^{-4}$ cm^3 g^{-2} mol, compared to a value of 12×10^{-4} cm^3 g^{-2} mol, extrapolated from the SANS and LS data,[22,23] and we believe that the difference is within experimental and systematic errors. The latter arise because of the limitations of the model used to fit the data, as a flagellene contains a fullerene, which is not accounted for in the model of a star-shaped polymer molecule. Although the contribution of this component is subtracted from the $Q = 0$ cross section (via eq 4), the deficiencies of the model result in slight differences in the shapes of the measured and calculated scattering at finite Q, e.g., Figure 6. Nevertheless, we believe that this is the best approximation currently available for fitting the data. To our knowledge, this is the first attempt to measure and fit the scattering from such unique molecules, and no better formulas have hitherto been developed for such systems. The possibility of modeling the scattering exactly via Monte Carlo techniques is under consideration.

Figure 9 shows the concentration dependence of $d\Sigma/d\Omega(0)$ for $(PS)_{1-2}$–C_{60}, and an average value of f = 2.2 PS chains per particle was calculated from the c = 0 intercept. The slope is virtually zero, leading to an estimate of $A_2 = (0 \pm 12) \times 10^{-4}$ cm^3 g^{-2} mol, compared to 14×10^{-4} cm^3 g^{-2} mol, estimated for free PS chains from the SANS and LS data.[22,23] The error is larger than that of $(PS)_{1-2}$–C_{60}, because the particle cross section for a given concentration is approximately 35% lower. Also, the fraction of the particle mass (14%) accounted for by the fullerene is higher than that for $(PS)_{3-4}$–C_{60}. Corrections are made for the scattering due to the fullerene core after extrapolating to Q = 0 and c = 0. These adjustments amount to only 2.2% for f = 3.2 and 3.1% for f = 2.2, as the scattering contrast for the fullerene in toluene-d_8 is much lower than that for the PS chains. The flagellenes are undoubtedly a

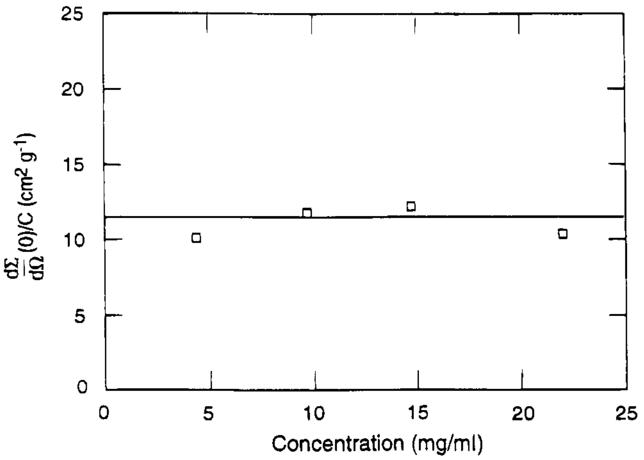


Figure 9. $d\Sigma/d\Omega(0)/C$ vs concentration (C) for $(PS)_{1-2}-C_{60}$ (Table 1, entry 2).

mixture of regioisomers wherein the positions of attachment of the PS arms to the buckyball will vary. In this case $I(0)$ is independent of the point of attachment, so we can count the average number of arms uniquely. R_g will be a bit different for different placements, so we measure an average over all different points of attachment on the fullerene. Thus, we believe that the estimates of the average number of chains per particle are accurate to ±5%. There is of course no a priori reason why a PS chain with an attached fullerene should have the same thermodynamic properties as a free chain, and in view of the novelty of such systems, we are unaware of any attempt to model the differences. However, modeling the data as a star polymer is most appropriate in the limit of large f, where the fullerene forms an appreciable fraction of the particle. The divergence between the shape of the measured and model scattering may lead to somewhat larger errors in the concentration- and Q-dependence of the SANS data from the particle with the least number of pendant chains.

The Zimm and Debye fit radii of gyration (averaged over the three highest concentrations) for the flagellene samples are respectively 19.6/18.8 ($(PS)_{1-2}-C_{60}$) and 23.1/23.4 Å ($(PS)_{3-4}-C_{60}$), after the former have been corrected[24,25] for the finite range of QR_g. For linear chains with a length equivalent to 2.2 and 3.2 arms one would expect R_g = 19.4 and 23.4 Å, respectively, assuming that the chains are unperturbed. As the fullerene core contributes only insignificantly to the average R_g in view of the low contrast, the measured R_g is determined almost completely by the pendant chains.

The radius of gyration of an f-arm star R_{g0} has bene calculated by Benoit[26] on the assumption of a Gaussian distribution of chain elements, $R_{g0} = [3f - 2)/f^2]^{0.5}R_{g1}$ where R_{g1} is the radius of a linear chain with the same number of segments. For f = 2.2 and 3.2 this leads to R_{g0} = 19.0 and 20.2 Å, respectively. Boothroyd and Ball[27] have modeled the conformational properties of star molecules unperturbed by excluded–volume effects and shown that the nonideal behavior in the neighborhood of the branch point may be simulated via a spherical exclusion zone, whose radius (r_0) is a constant (c) independent of the total number of segments. The calculated R_g is given by

$$R_g \approx R_{g0} + 1.075r_0[(3f - 2)/6g]^{0.5} \qquad (6)$$

The concept of pendant chains originating from an impenetrable sphere seems particularly appropriate for flagellenes as long as the radius of the core (r_0 = 4 Å) is smaller than the individual chain R_g. For f = 3.2 and r_0 = 4 Å, eq 6 predicts a difference of 2.7 Å between the measured R_g = 23.25 Å (Zimm/Debye fit average) and the calculated R_{g0} = 20.2 Å, and thus the perturbation of the chain trajectory seems to be well accounted for by this model.

For $(PS)_{1-2}-C_{60}$, an average of f = 2.2 is very close to the linear chain value (f = 2), for which the model of Boothroyd and Ball[27] would predict $R_g = R_{g0}$, as there is no branch point. However, for a flagellene with an exclusion zone caused by the fullerene core (r_0 = 4 Å), with a pair of chains attached randomly over the surface, eq 6 predicts $R_g - R_{g0}$ = 2.5 Å, through such an increment over R_{g0} is not observed. On the other hand, if the chains are anchored close to each other on the surface of the C_{60}, the configuration should be very close to that of a linear chain (R_g = 19.4 Å) and the measured R_g = 19.2 Å (average of the Zimm-fitted values) and R_{g0} = 19.0 Å are all within experimental error. For larger values of f, there will be an excluded-volume-driven tendency for the chains to be distributed more evenly over the surface of the fullerene.[1] Further studies are needed to fully understand the perturbation of the trajectory by the fullerene and to explore the utility of the model[27] as a function of the number of pendant chains, molecular weight, etc.

Conclusions

An optimized synthesis of mono- and dipolystyrene-substituted C_{60} has been accomplished via the adjustment of temperature and chain-end aggregation in reactions involving the termination of the polystyryl carbanion with C_{60}. The materials were characterized using GPC and SANS. SANS appears to be a promising technique for characterizing fullerenes and their derivatives. By adjusting the contrast of the constituents with respect to the solvent, a particular component can be highlighted for structural characterization. The fact that SANS concepts can be successfully applied on such a small length scale, involving as few as 60–70 atoms,[1] gives reasonable expectation that the SANS technique will continue to be prove useful when applied to higher fullerenes and their derivatives.

Acknowledgment. The authors are grateful to A. T. Boothroyd, S. J. Henderson, and J. D. Londono for helpful discussions. The research was sponsored by the Division of Materials Science, U.S. Department of Energy (USDOE), and the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed for the USDOE under Contract No. DE-AC05-840R21400 with Martin Marietta Energy Systems Inc. This work is supported, in part, by Wright Patterson Materials Laboratory under Air Force Prime Contract F3361-90-C-5813. This work was also supported in part by the National Science Foundation through a Presidential Faculty Fellowship (J.M.D.: 1993–1997). We also thank FMC-Lithium Division for the generous supply of alkyllithiums.

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MA950260E