STRUCTURAL CHARACTERIZATION OF A POLYMER SUBSTITUTED FULLERENE (FLAGELLENE) BY SMALL ANGLE NEUTRON SCATTERING

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ABSTRACT

Small-angle neutron scattering (SANS) can structurally characterize fullerenes[1] in solvents with strong SANS contrast (e.g. CS_2). 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} moieties. Hence, 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 H^1-containing materials is much lower, so they have strong contrast with toluene-d_8. Thus, SANS makes it possible to study the size and shapes of modified buckyballs such as the polymer-substituted fullerenes, or flagellenes[2]. These consist of C_{60} cores to which 1-4 polystyrene chains (with a molecular weight, MW $\simeq$ 2000) are attached. 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 "sphere". Close agreement (± 4%) between the measured and calculated values of $d\Sigma/d\Omega(0)$ along with independent estimates of the radius of gyration (R_g) and second virial coefficient (A_2) for a calibration linear polystyrene sample serves as a cross check on the validity of this methodology.

INTRODUCTION

The synthesis of a new class of fullerene adducts, described as "flagellenes," has recently been reported[2]. These molecules are comprised of several flexible polymer chains covalently attached to a fullerene "sphere" and have topologies similar to flagellata, or unicellular protozoa with snake-like appendages[2]. Similarly, the technique of small-angle neutron scattering (SANS) has recently been applied to characterize fullerenes[1], and here we report the application of this technique for the structural characterization of a flagellene with the formula $C_{60}(PS)_f$, where $1 < f < 5$.

The present $C_{60}(PS)_f$ adducts consist of mixtures of flagellenes with different degrees of substitution (f) on the C_{60} core, though other 3-dimensional nanostructural architectures can also be envisioned. For example, reactions using polymer dicarbanions would be expected to yield networks having fullerene "crosslinkages", and the substitution of carbon nanotubes in place of fullerenes may yield novel, compatibilized reinforcements for polymer matrices. For each of these synthetic possibilities, the SANS technique is appropriate for the structural characterization of the individual molecules and solid state morphology of the resulting materials.

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EXPERIMENTAL

Approximately 20 mg of fraction number 1 (believed initially[2] to contain mainly adducts with f = 3 and f = 4 arms, each with M_n = 1925 and $M_w/M_n \sim 1.08$) and 40 mg of polystyrene (MW 1925, $M_w/M_n \sim 1.08$) were dissolved in approximately 2 ml of toluene-d_8 (99+% purity), and contained in quartz cells. After each SANS experiment the samples were diluted by removing a fraction of the flagellene and the polystyrene from the quartz cells and replacing that amount with toluene-d_8. All additions of toluene-d_8 and transfer of material were performed with disposable glass pasteur pipets to avoid contamination of the sample with toluene-soluble organic material, which occurs when using plastic syringes.

The experiments were performed on the W. C. Koehler 30m SANS facility at the Oak Ridge National Laboratory[3]. The neutron wavelength was 4.75Å ($\Delta\lambda/\lambda \sim 5\%$) and the beam was transported to a distance of 3.5m from the sample by means of moveable neutron guides. The beam was collimated by cadmium slits at the sample (1.6 cm dia.) and source (3.2 x 3.6 cm^2) and the sample-detector distance was 3.1m. The detector was a 64 x 64 cm^2 proportional counter with element size ~ 1 cm^2.

The transmission of the sample was measured in a separate experiment as described previously[1,4]. 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 T=0.68 respectively for a 5 mm path length. Run times were 1-4 hrs and 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. The corrected data were radially (azimuthally) averaged 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 pre-calibrated secondary standards, based on the measurement of beam flux, vanadium incoherent cross section, the scattering from water and other reference materials[5].

RESULTS AND DISCUSSION

In general, the differential scattering cross section of an homogenous particle or molecule [$d\Sigma/d\Omega(Q)$] per unit solid angle per unit sample volume (in units of cm^{-1}), is [1]

$$\frac{d\Sigma(Q)}{d\Omega} = \frac{d\Sigma(0)}{d\Omega} P(Q) \qquad (1)$$

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[6], whereas for a star molecule with f-arms, P(Q) is given by[7]

$$P(Q) = \frac{2}{u^2}\left(u - f\left(1-\exp(-u/f)\right) + \frac{f(f-1)}{2}\left(1-\exp(u/f)^2\right)\right) \qquad (2)$$

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 (r.m.s.) distance of all scattering elements from the center of gravity].

For particles suspended in a solvent medium, the (Q = 0) cross section is given[1] by

$$\frac{d\Sigma(0)}{d\Omega} = N_p(\rho_p - \rho_s)^2 V_p^2 \qquad (3)$$

where ρ_p and ρ_s are the scattering length densities (SLDs) of the particle and solvent respectively, N_p is the number of particles per unit volume and V_p is the particle volume. Equation (3) is based on the assumption that the particles scatter independently and hence is valid only in the dilute solution limit, typically where $N_pV_p < 0.05$.

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

$$\frac{d\Sigma}{d\Omega}(0) = N_p\left[\Sigma_i\, v_i(\rho_i - \rho_s)\right]^2 \qquad (4)$$

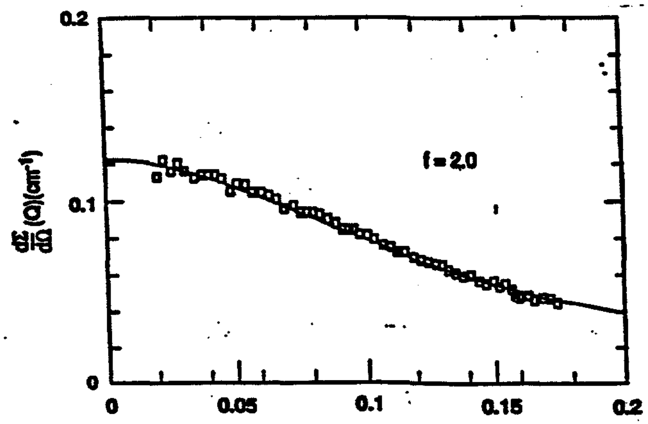
where the summation runs over the SLDs (ρ) and volumes (v) of the two components (fullerene and pendant chains in the case of flagellenes). Equation (4) reduces to equation (3) in the case of a 1-component homogenous particle or a system of two components, one of which has a SLD equal to that of the solvent[6].

According to equation (4), the Q = 0 extrapolated cross section is proportional to N_p or alternatively to the concentration, $c = N_p M_w/A_0$, where A_0 is Avogadro's number. In the case where there are significant particle-solvent interactions, equation (4) is modified[8] to

$$\frac{d\Sigma}{d\Omega}(0) = \frac{cA_0}{M_w(1 + 2A_2M_wc)}\left[\Sigma_i\, v_i(\rho_i - \rho_s)\right]^2 \qquad (5)$$

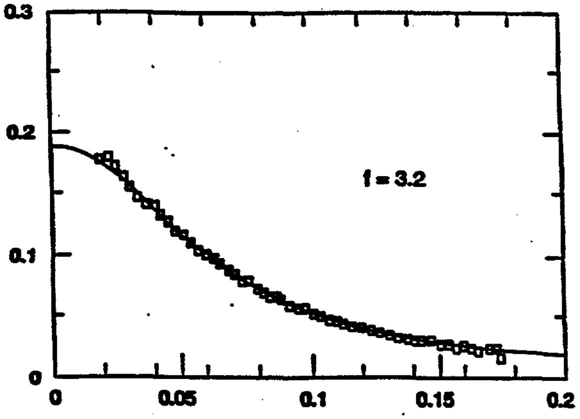
where A_2 is the second virial coefficient, which indicates whether a polymer chain swells or contracts in the presence of a solvent. In general, the second virial coefficient is a decreasing function of the (weight averaged) molecular weight, M_w. $A_2(M_w)$ can be empirically described by $A_2 \sim M_w^{-\delta}$, with $\delta = 0.3$ in various systems[9].

Figs. (1) and (2) show typical SANS data sets for the polystyrene calibration sample, and the flagellene fraction 1.



$\frac{d\Sigma}{d\Omega}$(Q) vs Q for 24.1 mg/ml of Polystyrene ($M_w = 2080$; $M_w/M_n = 1.08$) in Toluene – d_8

Figure 1



$\frac{d\Sigma}{d\Omega}$(Q) versus Q for 13.3 mg/ml of Flagellene in Toluene–d_8

Figure 2

Equation (2) reduces to the well known Debye formula[11] for a linear chain (f = 2) and the polystyrene data, fig. (1), 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[10]) incoherent cross section of the protons [$\sigma_{inc}(\lambda) \approx 90 \times 10^{-24}$ cm^2 at $\lambda = 4.75$Å, or $\sigma_{inc} \approx 90$ barns] in the pendant polystyrene chains. This was estimated in two different ways: firstly, by calculating the total H^1 incoherent cross section per unit solid angle (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}. Secondly, the background was scaled from the measured scattering of a solid protonated polystyrene (PSH) sample[5] (~ 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[11] because of the higher proton density in the solid sample. However, a correction[5] 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}.

Plotting $c^{-1}d\Sigma/d\Omega(0)$ versus concentration (c) for the polystyrene calibration sample and extrapolating to c = 0 gives $c^{-1}d\Sigma/d\Omega(0) = 0.055$ cm^2gm^{-1}, compared to 0.057 cm^2gm^{-1}, calculated via equation (3) and the GPC molecular weight. The slope is negative and leads to $A_2 \sim 18 \times 10^{-4}$ $cm^3gm^{-2}mol$. There is a dearth of measurements of the second virial coefficient for polystyrene in toluene at such small molecular weights, and most studies have been undertaken on molecules with higher mass. For example, Rahlwes[12] used light scattering (LS) to measure $A_2 = 2.2 \times 10^{-4}$ cm^3 gm^{-2} mol at $M_w = 2.95 \times 10^6$ and scaling to $M_w \sim 2 \times 10^3$ ($A_2 \sim M_w^{-\delta}$; $\delta \sim 0.3$) leads to an estimate of $A_2 = 19.6 \times 10^4$ cm^3 gm^{-2} mol. The only direct measurements that we are aware of are those of Huber et al.[13] (who measured 3 points by SANS) and Zhang et al.[14], who measured 5 points via LS in the range $1.2 < 10^{-3}M_w < 4.0$. However, osmometry measurements[13] give grossly different estimates. As the SANS and LS measurements are in agreement with data scaled from higher mass, we have therefore taken these 8 points and fit them with an empirical scaling relationship $A_2 \sim 24.2M_w^{-0.34} \times 10^{-3}$ cm^3 gm^{-2} mol. This leads to $A_2 \approx 18 \times 10^{-4}$ cm^3 gm^{-2} mol for $M_w \approx 2080$, in good agreement with the SANS result.

The average radius of gyration of the 3 highest concentration samples [via fitting a Debye coil as in Fig. (1)] is $R_g = 12.5$Å, and Zimm fits in the Q-range $0.019 < Q < 0.085$Å^{-1} lead to 12.8Å. 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[15] has estimated numerical corrections for this effect as a function of QR_{max} and QR_{gmin} and after these were applied, the Debye-fit and Zimm (12.2 ± 0.5)Å values are in agreement within the experimental error. These may be compared with $R_g = 10.1$Å extrapolated from the 3 SANS data points of Huber et al[13]. 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[11] as $R_{gw} = (0.27 \pm 0.005)M_w^{0.5}$, where R_{gw} and M_w refer to weight-averaged quantities. After a slight polydispersity correction (~ 4%), this leads to 12.7 ± 0.2Å, 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[13] than the melt dimensions, and accordingly we have assumed that the chains are unperturbed.

Plotting $c^{-1}d\Sigma/d\Omega(0)$ versus concentration (c) for the flagellene fraction 1 and extrapolating to c = 0, gives the average number of pendant chains f = 3.2, via equation 2. The slope is again slightly negative, and leads to an estimate of $A_2 = (8.5 \pm 5) \times 10^{-4}$ cm^3 gm^{-2} mol, compared to a value of 12×10^{-4} cm^3 gm^{-2} mol, extrapolated from the SANS and LS data[13,14] for linear PS chains. We believe that the difference is within the experimental and systematic errors.

The latter arise because of the expression 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 [equation (2)]. Although the contribution of this component is subtracted from the Q = 0 cross section [via equation (4)], this limitation may be the cause of the slight differences in the shapes of the measured and fitted scattering at finite Q [e.g. fig. (2)]. We are currently unaware of any better formulae that have been developed for such unique systems though the data were also extrapolated to (Q = 0) via the well know Zimm approximation as a cross check. This led to very similar results (± 2%) for $d\Sigma/d\Omega(0)$ and R_g.

The Zimm and Debye-fit radii of gyration (averaged over the 3 highest concentrations) for the flagellene fraction 1 are 23.1/23.4Å, after the former have been corrected[15] for the finite range of QR_g. For linear chains with a length equivalent to 3.2 arms one would expect an $R_g \sim 23.4$Å, assuming that the chains are unperturbed. As the fullerene core contributes 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 been calculated by Benoit[16] on the assumption of a Gaussian distribution of chain elements, $R_{g0} = [(3f-2)/f^2]^{0.5}R_{gl}$ where R_{gl} is the radius of a linear chain with the same number of segments. For f = 3.2 this leads to $R_{g0} = 20.2$Å respectively. Boothroyd and Ball[17] 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 independent of the total number of segments. The calculated R_g is given by

$$R_g \approx R_{g0} + 1.075\, r_o\, [(3f-2)/6f]^{0.5} \tag{6}$$

The concept of pendant chains originating from an impenetrable sphere seems particularly appropriate for flagellenes as long as the radius of the core $r_0 \sim 4$Å is smaller than the individual chain R_g. For f = 3.2 and $r_0 \sim 4$Å, equation (6) predicts a difference of 2.7Å between the measured $R_g = 23.25$Å (Zimm/Debye 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.

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 methodology can be successfully applied on such small length scale, involving as few as 60-70 atoms[1], gives reasonable expectation that the SANS technique will continue to be useful when applied to higher fullerenes and their derivatives.

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