SANS structural characterization of fullerenol-derived star polymers in solutions

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Abstract. We have studied the chain conformations of fullerenol-derived star polymers in two organic solvents using small-angle neutron scattering (SANS). The SANS results indicate that the six poly(urethane-ether) arms, chemically bonded on the fullerenol of the C_{60} -based star polymer, have a Gaussian chain conformation in toluene. However, these arms exhibit a pronounced excluded-volume effect in dimethylformamide solutions. We use a scattering model, with the polydispersity of the polymer taken into account, and a fractal model to extract the radius of gyration R_g values and the persistence lengths of the C_{60} -star polymers in these two organic solutions.

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Combining the polyol-function and the ball-shaped C_{60} cage in fullerenols, a strategy favored in designing dendritic molecules of a three-dimensional symmetry, we have synthesized C_{60} -based urethane-connected polyether dendritic polymers, C_{60} -star PU [1]. The thermal behaviors measured previously by differential scanning calorimetry (DSC) demonstrated that each polymer arm chemically bonded to the C_{60} molecules tended to behave individually in a gel phase upon variation of temperature in a similar manner to that of the parent linear PU polymers. In this study, we use SANS to characterize further the behaviors of these polymer arms of C_{60} -star PU in two organic solvents.

1 Materials and experiments

The synthesis of the C₆₀(OH)₁₂-derived urethane-connected polyether star polymers, C₆₀-star PU, was reported in [1]. The average molecular weight of the star polymer determined by GPC was $M_n = 18000$, with $M_w = 26100$, corresponding to a fullerenol-based star polymer with six linear urethaneconnected polyether arms [poly(tetramethyleneoxide) glycol

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(PTMO)] on average. The polymers were dissolved in deuterated toluene or deuterated DMF to provide a high scattering contrast between the polymer chains and the solvents. SANS measurements were conducted on the 8-meter SANS instrument at the National Institute of Standards and Technology (NIST). Standard SANS data reduction procedure (see, for instance, NIST SANS Instruments Data Acquisition Manual, 1999) was used for the scattering cross-section per unit sample volume I(Q), where $Q = (4\pi/\lambda_N) \sin \Theta$ was defined by the scattering angle 2Θ and the wavelength λ_N (two λ_N values, 5 Å and 10 Å, were used to extend the Q range).

In Fig. 1, we show the SANS data for the 1 wt. % (squares), 0.32 wt. % (circles), 0.16 wt. % (diamonds), and 0.04 wt. % (triangles) C_{60} -star PU in toluene measured at 25 °C. These four sets of data essentially resemble each other in shape, indicating a small concentration effect on



Fig. 1. SANS data for the C_{60} -star polymer solutions in toluene are fitted (*dashed curves*) with the model in (2)

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the C₆₀-star PU conformation in the *Q* range measured. The scattering profiles manifest a power-law scattering characteristic $I \sim Q^{-1/\nu}$ in a wide *Q* range. The characteristic scattering power of -2 fitted (straight line), namely $\nu = 1/2$, corresponds well to the behavior of unperturbed Gaussian chains [2]. Using the scaling law, we obtained an end-to-end distance $R_{ee} = [(3f-2)/f^2](N_w)^{1/2}l_o \approx 50$ Å for the C₆₀-star PU of *f* arms, with $l_o = 6.5$ Å estimated for the monomer length of the PU arm and $N_w = 295$ for the weight-averaged total number of segments for a C₆₀-star polymer [3].

Following the scattering form factor given by Benoit for a star-like molecule of a Gaussian chain conformation, we fit the scattering profiles using the form factor [3,4]

$$I(Q) = P(Q)$$

= $\frac{2}{x} \left(\frac{e^{-x} + x - 1}{f} + \frac{1}{f^2} (1 - e^{-x})^2 \sum_{i>j} e^{-\lambda_{ij}^2 Q^2} \right)$ (1)

where $x = nb^2Q^2/6$ with *n* for the chain segments of each arm and *b* for the persistence length of the polymer chains [5]. In (1), λ_{ij} is the distance between the nearest elements of the arm-branches *i* and *j* [3]. We approximate the summation term in (1) by $[f(f-1)/2] \exp(-\lambda^2 Q^2)$, with λ relating to a mean size for the cross-linking regions of the C₆₀-star PU (fullerenol with the hard segments of the PU arms in this case).

Considering the polydispersity effect, we derive an averaged form factor for the star polymers

$$\langle P(Q) \rangle = \frac{1}{(fX_{w})^{2}} \left\{ \left[\frac{f(f-1)e^{-\lambda^{2}Q^{2}}}{[(k+1)+2X_{w}]^{k}} - \frac{2\left[f(f-1)e^{-\lambda^{2}Q^{2}} - f\right]}{[(k+1)+X_{w}]^{k}} \right] \frac{(k+1)^{k+1}}{k} + 2fX_{w} + \left[f(f-1)e^{-\lambda^{2}Q^{2}} - 2f\right]\left(1 + \frac{1}{k}\right) \right\}$$
(2)

where $X_w = n_w b^2 Q^2/6$ with n_w for the weight-averaged number of segments in each polymer arm. In (2), we have used the Schulz distribution for the polymer polydispersity $p = M_w/M_n = 1 + U$ where U = 1/k [5]. With $\lambda = 0$, (2) reduces to the result given by Kriste [5]. The *z*-averaged [5] radius of gyration R_g for the star polymer deduced from (2) for small Q, where $\langle P(Q) \rangle \approx 1 - \langle R_g^2 \rangle_z Q^2/3$, is

$$\langle R_{g}^{2} \rangle_{z} = [(k+2)/(k+1)][(3f-2)/f] R_{go}^{2} + [3(f-1)/f] \lambda^{2}$$
(3)

Here, $R_{go} = (n_w b^2/6)^{1/2}$ is the radius of gyration for a single arm [5]. In the above calculation, we have neglected the small scattering contributions from the fullerenol branch zone of the star polymer, because the scattering-length-density of C₆₀-cages is very close to that for the deuterated solvents used.

In Fig. 1 we show that the four sets of SANS data for the toluene solutions of C_{60} -star PU can be fitted (dashed curves)

reasonable well using (2), with the fixed values of p = 1.45and f = 6 determined from the GPC result and the three dominant fitting parameters λ , b, and a contrast factor I_0 . The incoherent scattering was not a sensitive fitting parameter in the fitting process due to its small contribution in the dilute polymer solutions. We obtained a common λ value of 30 ± 2 Å for all the concentrations. Whereas the persistence lengths fitted are 15.7 ± 0.4 Å, 13.6 ± 0.3 Å, 14.2 ± 0.3 Å, and $11.8 \pm$ 0.1 Å for the C₆₀-star in the 0.04%, 0.16%, 0.32%, and 1% solutions, respectively. The corresponding R_g values, 87, 80, 82, and 73 Å, implies that the excluded-volume effect reduces as the concentration increases (discussed below). It is difficult to extract accurate $R_{\rm g}$ values from the Guinier approximation [5] due to the large polydispersity and the lack of sufficient low-Q data ($Q < 1/R_g \approx 0.015 \text{ Å}^{-1}$). Nevertheless, the Guinier R_g value $68 \pm 8 \text{ Å}$ extrapolated for the 1% data is roughly consistent with the result from our scattering model.

We try to relate the λ term in (3) to that given by the displaced random walks model of Boothroyd et al. [6] for star polymers having a sphere-like exclusion zone of a radius r_0 for the branch zone. In this tentative approach, $r_0 = 17.5 \text{ Å}$ deduced from [6] is close to $\lambda/2 = 15$ Å, which is roughly consistent with the radius of a fullerenol (≈ 6.5 Å) plus the size of diisocyanate hard segment (10 Å) of the PU arm anchored on the fullerenol with a bond angle of 110° [1]. With the persistence lengths obtained, we can also approximate the radius of gyration R_g for ideal conditions where polydispersity and branch zone are small, namely, $k \gg 1$ and $\lambda \approx 0$ in (3). The ideal R_g thus deduced for the four solutions, 0.04 wt. % to 1 wt. %, are 73 Å, 64 Å, 66 Å, and 55 Å, respectively. This result implies that, as the concentration increases to the chain-overlapping concentration ($\sim 1\%$) for the semidilute region, the $R_{\rm g}$ value approaches the 50 Å estimated pre-



Fig. 2. SANS data for the C₆₀-star polymers solutions in DMF are fitted with the *dash lines* of a slope of -1.67. The 2% data are also fitted with the fractal model (*solid curve*)

viously for the ideal Gaussian chains of no excluded-volume interaction effect [2, 7].

For the C60-star polymers in DMF, the SANS data measured for the 0.5 wt. % (diamonds), 2% (triangles), 4% (squares) sample solutions at 25 °C can overlap each other very well after normalized to concentration. The power-law scattering characteristic of a scattering power -1.67 fitted (dashed lines in Fig. 2) in a larger-*Q* region, corresponds to a ν value of 3/5, which is a typical value for the excluded-volume interactions of polymer chains [7]. This result indicates that DMF is a good solvent for C₆₀-star polymers. Since (3) does not take into account the excluded volume effect, we adopt a fractal-model with the scattering intensity

$$I(Q) \propto \frac{1}{Q^{D}} \frac{D\Gamma(D-1)}{\left(1 + (Q\xi)^{-2}\right)^{(D-1)/2}} \sin\left[(D-1)\tan^{-1}(Q\xi)\right]$$
(4)

to describe the star polymers of a morphology constructed by their monomers in a self-similar geometrical arrangement in the DMF solutions. Here, *D* is the fractal dimension and ξ the correlation length defining loosely the fractal region of the star polymers [8]. Requiring (4) to conform to the Guinier approximation $I(Q) \propto \exp(-R_g^2 Q^2/3)$ for small *Q*, we can deduce an averaged radius of gyration $R_g^* = [D(D + 1)/2]^{1/2}\xi$ for the star polymers [8].

Typically, the fractal model can describe the 2% data well (the solid curve in Fig. 2) with $\xi = 97 \pm 16$ Å and D = 1.67. The *z*-averaged radius of gyration obtained from $R_g^* = [D(D+1)/2]^{1/2}\xi$ is 145 ± 24 Å, which is consistent with the value 170 ± 20 Å obtained from the Guinier approximation using the best small-*Q* data we have.

We have also synthesized a $C_{60}(OH)_{12}$ -crosslinked PU film using the same PU prepolymers and fullerenols as those used in synthesizing C_{60} -star polymers. Interestingly, the linear dimension, ≈ 123 Å, characterized for the soft PU segments in the elastomer film using SANS [9] is relatively closer to the radius of gyration of C_{60} -star polymers in DMF (145 Å) than that in toluene (~ 80 Å). It seems that, after being cast out from solvent, the C₆₀(OH)₁₂-crosslinked PU elastomer film synthesized in a good solvent environment (THF/DMF mixture) can preserve a similar excluded-volume chain conformation as that measured for the C₆₀-star polymers in DMF due to the cross-linking effect.

2 Conclusions

Using SANS, we have characterized the chain conformations of the C₆₀-star PU in two organic solvents. The modified scattering model derived for the star polymers can describe the SANS data satisfactorily. From the scattering results, the PU chains of the C₆₀-star polymers behave as if free in toluene solutions ($\nu = 1/2$), but subject a pronounced excluded-volume interaction ($\nu = 3/5$) in DMF solutions.

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