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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 $C_{60}(OH)_{12}$-derived urethane-connected polyether star polymers, C_{60}-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 urethane-connected polyether arms [poly(tetramethyleneoxide) glycol (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

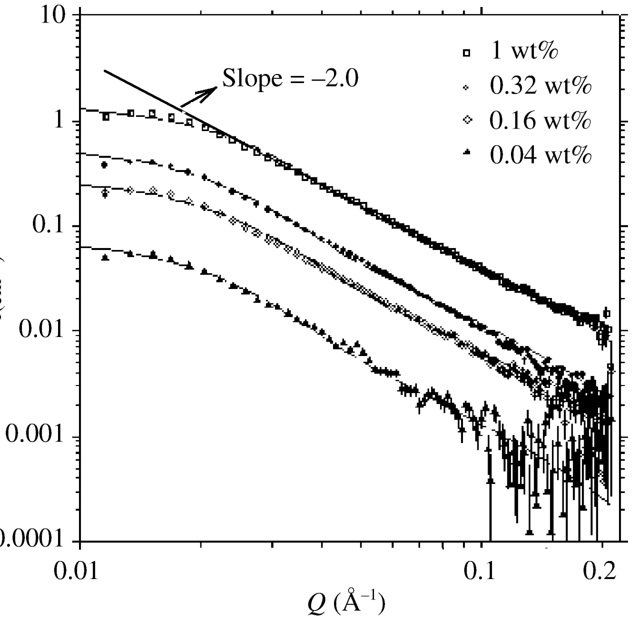

Fig. 1. SANS data for the C_{60}-star polymer solutions in toluene are fitted (*dashed curves*) with the model in (2)

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the C_{60}-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 $R_{\mathrm{ee}} = [(3f-2)/f^2](N_{\mathrm{w}})^{1/2} l_{\mathrm{o}} \approx 50$ Å for the C_{60}-star PU of f arms, with $l_{\mathrm{o}} = 6.5$ Å estimated for the monomer length of the PU arm and $N_{\mathrm{w}} = 295$ for the weight-averaged total number of segments for a C_{60}-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]

$$
\begin{aligned}
I(Q) &= P(Q) \\
&= \frac{2}{x}\left(\frac{\mathrm{e}^{-x}+x-1}{f} + \frac{1}{f^2}\left(1-\mathrm{e}^{-x}\right)^2 \sum_{i>j} \mathrm{e}^{-\lambda_{ij}^2 Q^2}\right) \qquad (1)
\end{aligned}
$$

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 $[f(f-1)/2]\exp(-\lambda^2Q^2)$, with λ relating to a mean size for the cross-linking regions of the C_{60}-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

$$
\begin{aligned}
\langle P(Q)\rangle = \frac{1}{(fX_{\mathrm{w}})^2} \Bigg\{ & \Bigg[\frac{f(f-1)\,\mathrm{e}^{-\lambda^2Q^2}}{[(k+1)+2X_{\mathrm{w}}]^k} \\
& - \frac{2\left[f(f-1)\,\mathrm{e}^{-\lambda^2Q^2} - f\right]}{[(k+1)+X_{\mathrm{w}}]^k} \Bigg] \frac{(k+1)^{k+1}}{k} + 2fX_{\mathrm{w}} \\
& + \left[f(f-1)\,\mathrm{e}^{-\lambda^2Q^2} - 2f\right]\left(1+\frac{1}{k}\right) \Bigg\} \qquad (2)
\end{aligned}
$$

where $X_{\mathrm{w}} = n_{\mathrm{w}}b^2Q^2/6$ 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 $p = M_{\mathrm{w}}/M_{\mathrm{n}} = 1 + U$ 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 $\langle P(Q)\rangle \approx 1 - \langle R_{\mathrm{g}}^2\rangle_z Q^2/3$, is

$$
\langle R_{\mathrm{g}}^2\rangle_z = [(k+2)/(k+1)]\,[(3f-2)/f]\,R_{\mathrm{go}}^2 + [3(f-1)/f]\,\lambda^2 \qquad (3)
$$

Here, $R_{\mathrm{go}} = (n_{\mathrm{w}}b^2/6)^{1/2}$ 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 C_{60}-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 $p = 1.45$ and $f = 6$ determined from the GPC result and the three dominant fitting parameters λ, b, and a contrast factor I_{o}. 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 ± 0.1 Å for the C_{60}-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_{g} values from the Guinier approximation [5] due to the large polydispersity and the lack of sufficient low-Q data ($Q < 1/R_{\mathrm{g}} \approx 0.015$ Å^{-1}). Nevertheless, the Guinier R_{g} value 68 ± 8 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_{o} for the branch zone. In this tentative approach, $r_{\mathrm{o}} = 17.5$ 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 $\mathrm{R_g}$ 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_{g} value approaches the 50 Å estimated pre-

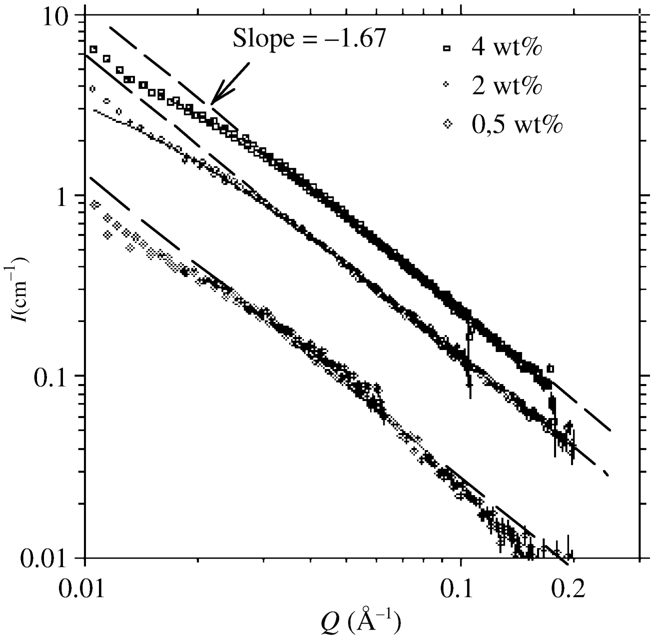

Fig. 2. SANS data for the C_{60}-star polymers solutions in DMF are fitted with the *dash lines* of a slope of -1.67. The 2% data are also fitted with the fractal model (*solid curve*)

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 C_{60}-star polymers. Since (3) does not take into account the excluded volume effect, we adopt a fractal-model with the scattering intensity

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

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 $C_{60}(OH)_{12}$-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 C_{60}-star polymers in DMF due to the cross-linking effect.

2 Conclusions

Using SANS, we have characterized the chain conformations of the C_{60}-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 C_{60}-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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