Neutron Scattering Studies of Structure and Self-Assembly of Star-Shaped Polymers with Fullerene Centres in Solutions

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Summary: Protonated star-shaped polystyrenes with single and double fullerene C_{60} core and the hybrid stars with pairs of polar and non-polar arms (tertbuthylmetacrylate, polystyrene) have been studied in deuterated toluene (20 °C) by small-angle neutron scattering at low and moderate polymer concentrations ($c_1 \sim 1$ g/dl, $c_2 \sim 3$–6 g/dl) to evaluate the peculiarities of fullerene centre action on polymers self-assembly in solutions. As we found, the cores composed of two fullerenes, linked via $Si(CH_3)_2$-bridge, induce stars' anisotropic interactions and association into chain-like structures (correlation radius ~400–600 nm). Meanwhile, the single-core stars of polystyrene and hybrids organize globular clusters (size $\sim 10^3$ nm) those geometry do not change significantly by polymer content variation.

Keywords: neutron scattering; star polymers; structure

Introduction

A growing attention is currently attracted to the fundamental problem of fine regulation of self-assembly of polymers in solutions, especially regarding to the first synthesized fullerenes' polymeric derivatives of a complicated architecture (star-shaped macromolecules).[1,2] During the last decade there was created a variety of molecular objects with fullerene C_{60} branching centre by means of variation of chemical composition, functionality and structure of centre, i.e. by using polar and non-polar arms, single or double fullerene core with short or long link between fullerenes.[3–5] The progress in molecular design of fullerene-containing macromolecules serves to the aim of creation of various nano-materials for non-linear laser optics (photonics),[1,2] gas(liquid)-separating and effective proton-conducting highly selective membranes,[6] electroluminescent devices[7] etc. Obviously, a directed synthesis of multifunctional macromolecules cannot be realized without monitoring the polymerization and the examination of obtained polymers by fine structural methods such as X-ray and small-angle neutron scattering. The latter allows recognize a lot of subtle structural features of complicated star-shaped polymers and study their specific interactions and self-assembly being a main process governing the creation of highly ordered nano-materials. The aim of our study is a comparative analysis of behaviors of star-shaped polymers in solutions as dependent on their chemical nature and type (functionality) of centers.

Experimental Part

Star-shaped polymers with fullerene core have been synthesized by ''living'' chain method.[8] In this way there were prepared single-core stars $C_{60}(PS)_f$ ($f = 6$, the mass of polystyrene arm $M_{PS} = 5 \cdot 10^3$) and 12-arm

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stars $(PS)_fC_{60}$-[Si-$(CH_3)_2$]-$C_{60}(PS)_f$ ($f = 6$, the mass of an arm $M_{PS} = 4 \cdot 10^3$) with a double core where fullerenes are linked by [Si-$(CH_3)_2$]-bridge (Figure 1). It is apparent that a small (point-like) double core as itself cannot create any substantial shape anisotropy of stars and induce their ordering. Meanwhile, a short bridge between fullerenes provides their π-electron systems overlapping. This interaction of fullerenes' π-electron systems in cores can induce dipole moments and causes stars' assembly via dipole forces. Another opportunity to initiate stars' self-organization is a grafting of polar arms to fullerene cores. There were synthesized the 12-arm stars $(PS)_fC_{60}(PTMBA)_f$ ($f = 6$, the mass of PS-arm $M_{PS} = 4 \cdot 10^3$, the mass of PTBMA-arm $M_{PTMBA} = 6 \cdot 10^3$) with 6 pairs of polar and non-polar chains (tertbuthylmetacrylate, PS) grafted to single fullerene[5] (Figure 1).

For neutron scattering experiments there were prepared the solutions of protonated stars in deuterated toluene to have a good contrast in scattering. In the first series of experiments the content of polymer $c_1 = 1$ g/dl was chosen lower by an order in magnitude than the threshold of polymers' overlapping according to Debye criterion, $c^* = 1/[\eta] \sim 10$ g/dl where $[\eta]$ is the intrinsic viscosity. The latter was measured in benzene at 25 °C where $[\eta] = 0.098$; 0.10 and 0.11 g/dl for 6-arm PS-stars, 12-arm double center and hybrids.

In general, in such dilute solutions ($c_1 = 1$ g/dl) one can expect to detect only small thermodynamic fluctuations of concentration and weak molecular association effects. In order to study possible strong macromolecular associations, we have enhanced the concentration of polymers up to the values of $c_2 \sim (0.3–0.6)c^*$ being different for different stars: $c_2 = 6.2$ g/dl, $c_2 = 3.8$ g/dl, $c_2 = 3.4$ g/dl for 6-arm PS-stars, double core stars and hybrids. We tried to fulfill the condition $c_2 \cdot f \approx$ const taking into account the variation of stars' functionality, $f = 6$; 12. It allows keep a statistical probability of star's association at the same level. Indeed, each arm in star may serve as a link associating this star with a neighboring one when a probability to meet it is proportional to polymer concentration c_2. Finally this leads to the equation $c_2 \cdot f \approx$ const the validity of which has enabled us to observe the main specific features of stars' self-organization not disturbed by trivial concentration effects.

The scattering measurements have been carried out at low momentum transfers $q = 0.001–0.06\ nm^{-1}$ (neutron wavelength $\lambda = 0.476$ nm, diffractometer V12A, HMI, Berlin) and at intermediate $q = 0.1–5\ nm^{-1}$ ($\lambda = 0.345$ nm, diffractometer "Yellow submarine", Budapest Neutron Centre) to cover the spatial range $\sim 1/q \sim 10^0–10^3$ nm from chain segmental length to molecular (supramolecular) sizes. The raw data were normalized to the scattering intensities detected at the same conditions for a standard sample (1 mm-layer of H_2O with known scattering cross section). As a result there were found the absolute cross sections of solutions $\sigma(q) = (1/V)d\sigma/d\Omega$ per cm^3 of sample volume (V) and unit solid angle (Ω).

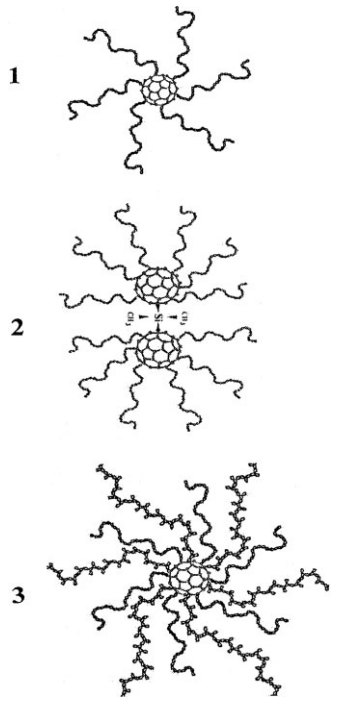

Figure 1.
Star-shaped polymers: single-core 6-arm stars (1), double-core 12-arm stars and hybrids (3) including polar and non-polar arms.

The behaviors of cross sections normalized to concentrations are shown in Figure 2, 3 for the scattering data at $q = 0.1–5\ nm^{-1}$ and $q = 0.001–0.06\ nm^{-1}$.

The following data treatment was based on the Fourier-transform of cross sections σ(q) (software packages ATSAS (GNOM)[9]) to find the molecular spatial correlation functions of polymers (Figure 4, 5)

$$\gamma(R) = (\Delta K \cdot V_1)^2 \cdot \langle \Delta n(0) \cdot \Delta n(R) \rangle = (1/2\pi)^3 \int \sigma(q)[\sin(qR)/(qR)] 4\pi q^2 dq. \quad (1)$$

Here V_1 is the volume of a chain unit, ΔK is the contrast factor between polymer and solvent; $\Delta n(0)$, $\Delta n(R)$ are the deviations of chain units concentrations from an average magnitude in the points at the distance R. Since the solutions are isotropic, the modified functions $G(R)/c = \gamma(R)R^2/c$ normalized to concentrations are used. The functions $G(R)$ characterize chain units' distributions in spherical layers (radius R) around a given unit. In eq. (1) the cross sections

$$\sigma(q) = \Delta K^2 \cdot N_p \cdot V_P^2 F(q)^2 \cdot S(q) \quad (2)$$

are dependent on the number N_P of macromolecules (each dry volume V_P, contrast factor ΔK) in the unit volume of the sample (cm^3). The structure and assembly of macromolecules in solutions are described by their form-factor $F(q)$ and structure factor $S(q)$. Except of these relatively large structures, the spectra of correlations for all polymers have shown a local chain units' correlation (segmental scale) (Figure 4). A peak at small distance $R_S \sim 0.5\ nm$ is explained by a short-range correlation within a segment of chain. For a segmental length of poly(styrene), $L \approx 2\ nm$, we have computed the gyration radius of a segment $r_G = L/\sqrt{12} \approx 0.6\ nm$. Really, the position of peak ($R_S \sim 0.5\ nm$) corresponds to gyration radius of statistical segment.

In Figure 4 the spectra of correlations display the peculiarities in molecular and supramolecular structure of single- and double-core stars as compared to hybrids. Each spectrum has a main peak which

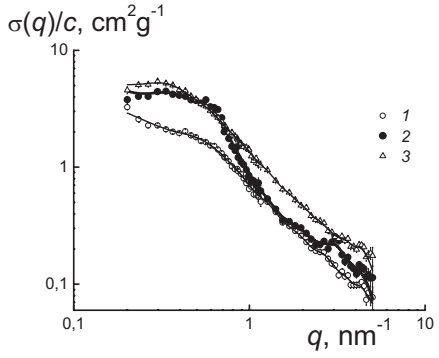

Figure 2.
Cross sections σ(q)/c vs. $q = 0.1–5\ nm^{-1}$ for star-shaped polymers in D-toluene (concentration $c = c_2$): 1 – single-core 6-arm PS; 2 – double-core 12-arm PS; 3 – hybrids. Lines are scattering functions corresponding to correlation functions (1).

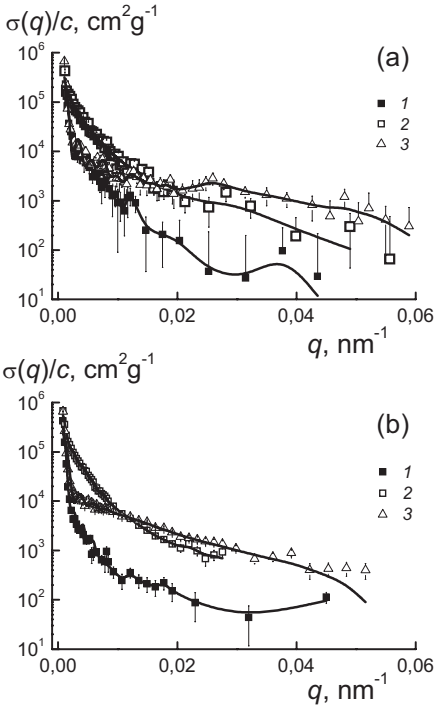

Figure 3.
Cross sections σ(q)/c vs. $q = 0.001–0.06\ nm^{-1}$ for polymers in D-toluene at concentrations c_1 and c_2 (a,b): 1 – single-core 6-arm PS; 2 – double-core 12-arm PS; 3 – hybrids. Lines are scattering functions corresponding to correlation functions (1).

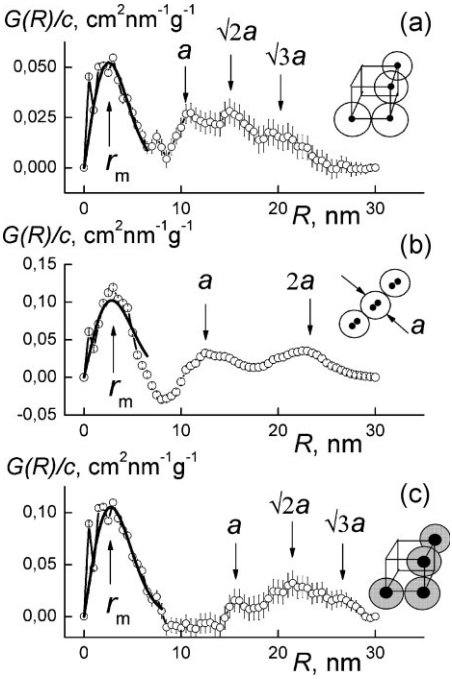

Figure 4.
Spectra of correlations *G(R)/c* in star-shaped polymers' solutions (concentration $c = c_2$): (a) – single-core 6-arm PS; (b) – double-core 12-arm PS; (c) – hybrids. Maxima positions r_m correspond to stars' gyration radii (data approximation by function (3)). The secondary maxima indicate the distances between neighboring particles in clusters like in simple cubic lattice (a,c) (period *a*) or in chain structures.

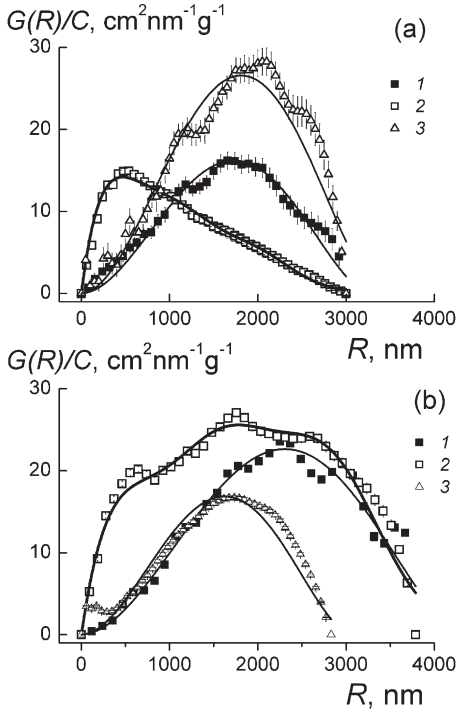

Figure 5.
Large-scale correlations of star-shaped polymers in solutions: 1 – single-core 6 arm stars, 2 – double-core 12 arm stars, 3 – hybrids. The correlation functions are normalized to concentrations c_1 and c_2 (a,b). Lines are fitting functions (4),(5).

maximum position, $R = r_m \approx R_{GST}$, corresponds approximately to star's gyration radius. The profile of peak is described by function

$$G_m(R)/c = \beta \cdot R \cdot \exp[-R^2/2(bR_{GST})^2]. \quad (3)$$

Here the magnitude of β - parameter is determined by stars' dry volume and contrast. The parameter $b \sim 1$ and depends weakly on star's functionality ($b \approx 0.95$ at $f = 6$; $b \approx 0.98$ at $f = 12$). As we established, the behavior of function (3) is very close to the behavior of Fourier-transform of Benoit scattering function[10] derived for stars with gaussian arms. Thus, in the first approximation the studied star-shaped macromolecules possess the gaussian arms.

As a result of data approximation with function (3) the gyration radii of stars were found: $R_{GST} = 2.69 \pm 0.03$ nm (single-core 6-arm stars); $R_{GST} = 2.90 \pm 0.02$ nm (double-core 12-arm stars); $R_{GST} = 2.81 \pm 0.03$ nm (hybrids). A comparison of gyration radii shows that the 12-arm stars are larger by 5–8% in size than 6-arm stars. This can be treated as an effect of steric repulsion of arms around the centre of high functionality. The functionality of single-core PS-stars ($f_{SPS} = 6$) was determined previously.[11] The number of arms $f_D \approx 12$ in double-core stars was estimated from the ratio $f_D/f_{SPS} = S_D/S_{SPS} \approx 1.95$ where S_D and S_{SPS} are the areas under the main correlation peaks for double- and single-core PS-stars. The relationship between the peaks' areas for hybrids and 6-arm PS-stars is at the same level that confirms hybrids' functionality $f_H \approx 12$.

While, all the stars possess close radii ($R_{GS} \sim 3$ nm) their interactions and the characters of short range order are substantially different in the cases of single- and double-core objects (Figure 4). Both types of single core stars are partially arranged into globular clusters being fragments of simple cubic lattice. Its period (a) is comparable to stars' diameter d_{ST} $\sim 10\,\text{nm} \sim a$ (Figure 4a,c).

Inside such structures the centers of neighboring particles are localized at characteristic distances (a, $\sqrt{2}a$, $\sqrt{3}a$ ...). On the other hand, the double-core stars are assembled into chain-like clusters where distances are multiple to period a (Figure 4b). These low-dimensional structures are substantially anisotropic due to anisotropic interactions between particles via dipole forces between paired fullerenes.

In fact, their delocalized π-electron systems may be polarized spontaneously, and then a dipole attraction between double-core stars give rise to large-scale ordering at $R \geq 10^3$ nm (Figure 5b). Oppositely, in the case of isotropic interactions of single-core stars there was observed a growth of isotropic globular (droplet-like) clusters (Figure 5a,c).

In dilute solution ($c = c_1$) the double-core stars demonstrate highly developed large-scale correlations (asymmetric peak, maximum at $R \sim 400$ nm). This is typical for coil-like structures but differs qualitatively from the picture of correlations for single-core stars. The anisotropic ordering of double-core stars is described by the function including the contributions of interior correlations between units in gaussian chains [12] as well as their cross-correlations

$$R^2\gamma(R) = \alpha_G \cdot R \cdot \exp(-R/R_C) + \alpha_1 \cdot R^2 \cdot \exp[-(R-L_1)^2/2\delta_1^2] + \alpha_2 \cdot R^2 \cdot \exp[-(R-L_2)^2/2\delta_2^2]. \quad (4)$$

The first term is related to a chain having correlation radius R_C (coefficient α_G is proportional to polymer content and squared contrast factor). The second and the third terms represent the events of chains' interpenetration and contacts with probabilities being proportional to the parameters α_1, α_2. It means the existence of spatial correlations between centers of mass of coils at characteristic distances $L_1 = H/2 = 3R_C/\sqrt{2}$, $L_2 = H = 3\sqrt{2}R_C$ where $H = 3\sqrt{2}R$ is the averaged squared end-to-end distance in chain. The parameters $\delta_{1,2}$ are the dispersions of L_1, L_2. We have applied the condition $\delta_1 = \delta_2 = R_C$ to minimize the number of free parameters of function (4) (α_G, R_C, $\alpha_{1,2}$) by approximation.

As a result of data analysis we have found that at low content ($c = c_1$) the double-core stars form specific superstructures being the chains in gaussian conformation (superchains, correlation radius $R_C = 425 \pm 10$ nm) weakly interacting in dilute solution. The latter is clear visible from the comparison of areas (S_G, S_1, S_2) under the peaks corresponding to the 1st, 2nd and 3rd term of function (4). The ratios $n_I = S_1/S_G = 0.22$ and $n_C = S_2/S_G = 0.23$ give the average numbers of superchains penetrating into a given superchain and contacting it. Totally in dilute solution the probability of interaction of a superchain with another one is equal to $n_I + n_C = 0.45$.

By the increase of polymer content ($c = c_2$) the radius of superchains as well as a probability of interactions become larger, $R_C = 602 \pm 10$ nm. On the average each particle is associated with $(n_I + n_C) = 1.69$ similar particles ($n_I = 0.73$, $n_C = 0.96$). So the triads of superchains dominate in solution.

Oppositely to double-core stars the single-core ones form extended globular (droplet-like) clusters. In the first approximation they are described by the correlation function of uniform sphere (5)

$$R^2\gamma(R) = \alpha_S R^2[1-(3/4)(R/R_S) + (1/16)(R/R_S)^3] \quad (5)$$

Here R_S is the radius of spherical cluster. The coefficient α_S depends on the number and mass of clusters. At low content of polymers ($c = c_1$) hybrids form the clusters (radius $R_{SH} = 1727 \pm 20$ nm) only slightly larger than that of 6-arm stars

($R_{S6S} = 1651 \pm 20$ nm), although the correlation peak for hybrids has the amplitude ~2 times higher (Figure 3a). Thus, the ability of hybrids to be associated is stronger than that for single-core 6 arm polystyrenes. The radii of globular clusters are comparable with the diameter of double-core stars' superchains, $H_D \approx 3\sqrt{2}R_C \approx 1700$ nm, i.e. the coils of double-core stars are twice compact than single-core stars' structures. However, at the enhanced concentration ($c = c_2$) this trend is reversed, and hybrids' solution is more homogeneous. Their cluster size becomes smaller, $R_{SH} = 1547 \pm 20$ nm, whereas the radius of 6-arm PS-stars is increased, $R_{S6S} = 2199 \pm 50$ nm, as well as the amplitude of correlation peak (Figure 3b). Like 6-arms stars the double-core stars demonstrate an active trend to be self-assembled at higher content when the coil diameter changes from $H_D \approx 1700$ nm (low concentration c_1) to $H_D \approx 2500$ nm (moderate concentration c_2).

Conclusion

Neutron scattering analysis of structure and self-assembly of stars of various functionality and type of core allowed us to recognize the mechanisms of stars ordering determined by the character of their interaction (isotropic, anisotropic). As we established, a double centre plays a crucial role in stars association into chain-like superstructures. However, this is not possible for stars with a highly symmetric single core.

On the other hand, a self-organization of hybrids does not reveal any significant deviations from the behavior of 6-arm PS-stars. Neither a chemical nature of arms (polar, non-polar) nor their numbers (6 or 12) do not influence radically on stars' assembly that depends mainly on the structure of core the modification of which may create the new abilities of regulation of stars' assembly.

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