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Scaling properties and ordering phenomena of star polymers in solution

D. RICHTER, O. JUCKNISCHKE, L. WILLNER, L.J. FETTERS*, M. LIN*, J.S. HUANG*, J. ROOVERS**, C. TOPOROVSKI** and L.L. ZHOU**

Institut für Festkörperforschung, Forschungszentrum Jülich, 5170 Jülich, Germany

** Exxon Research and Engineering Corporation, Annandale, New Jersey 08801, U.S.A.*

*** Institute for Environmental Chemistry, National Research Council of Canada, Ottawa, Ontario, K1A 036, Canada*

Star polymers are prototype systems both for tethered chains as well as for branched polymers. In this study we present a thorough investigation of the single star form factors in dilute solutions spanning a range of functionalities from 8 to 128. Using the zero average contrast method the form factor determination was also extended into the semidilute regime. As a consequence of their very inhomogeneous monomer density distribution star polymers exhibit osmotic repulsion leading to ordering phenomena in the neighborhood of the overlap concentration. We present a detailed investigation of such ordering phenomena in star polymer solutions with varying functionality and molecular weight. In all cases we observe an interparticle structure factor which is most pronounced at the overlap concentration ϕ^* . The ordering tendency increases with increasing functionality. These results are compared with current theoretical predictions.

1 Introduction

Star polymers are built from linear polymers joint covalently to a common center. If they are monodisperse both with respect to functionality and arm length they are called regular stars. The conformation of star shaped polymers has been theoretically examined by Daoud and Cotton [1] and Birshtein and Zhulina [2] relating to scaling theories. Thereby the analogy to semidilute polymer solutions is used where the screening effects of the excluded volume interaction are described by a screening length ξ , defining the so-called block structure [3]. As a consequence of the spatially inhomogeneous density distribution in star molecules, however, an inhomogeneous blob structure evolves with blob sizes growing from the center to the rim. Witten et al [4] investigated theoretically the concentration dependence of the osmotic pressure in star polymer solutions around the overlap concentration ϕ^* . The main outcome of their considerations is the prediction of a repulsive interaction between stars resulting from the large osmotic pressure inside a star molecule. Other than linear chains which interpenetrate easily, star polymers are expected to exhibit ordering phenomena in the neighborhood of the overlap concentration due to this osmotic repulsion. Depending on functionality, liquid-like ordering or even formation of a macrocrystal could be expected. The structure factor $S(Q)$ for such a system should display a peak, indicating the preferred spatial distance between the particles. The width and height of this peak depending on functionality, molecular weight and concentration, should reveal detailed information on the ordering process. Precise experiments in this field became possible due to the progress in anionic polymerization techniques which today allow the synthesis of monodisperse stars up to functionalities of 128 [5,6].

Here we present investigations on single star properties including measurements of the star form factors, varying the functionality and the molecular weight. Applying the zero average contrast method we also addressed the form factor as a function of concentration. The second objective were the ordering phenomena occuring around the overlap concentration ϕ^* [7].

2 Experimental

We studied star molecules with functionalities between 8 and 128. Their molecular characteristics are presented in table I. The 8 and 18 arm stars were made from polyisoprene (PI) while the 32, 64 and 128 arm stars were built from polybutadiene (PB). All stars were synthesized by anionic polymerization using organolithium initiators. The linking agents were chlorosilenes. The details of the polymer synthesis have been described elsewhere [5,6]. The stars were characterized by size exclusion chromatography (SEC), low angle laser light scattering (LALLS) and osmotic pressure measurements.

Table 1: Molecular characteristics of the investigated star molecules

Polymer	$M_W [10^{-3} g mol^{-1}]$	$M_n(\text{arm}) [g mol^{-1}]$	$R_g [\text{\AA}]$	
			Zimm	Kratky
PB 128	840	6 800	111	109
PB 6415	725	12 100	-	124
PB 6406	395	6 330	113	97
PB 3205	169	5 400	89	72
PB 3210	301	9 500	100 (LS ¹)	98
PB 3220	644	19 400	145 (LS)	153
PB 3237	1 330	37 400	224 (LS)	222
PI 18	138	7 500	82	75
PI 8	61	7 500	69	67
PI 18 D	-	8 400	-	-

¹LS: Lightscattering

Neutron small angle scattering experiments were performed using the D17 small angle camera at the Institut Laue-Langevin in Grenoble and the 30 m machine at the National Institute of Standards and Technology in Gaithersburg. The polymer solutions were made from deuterated methylcyclohexane using monomer concentrations between $0.001 < \phi < 0.3$. The solutions were investigated in 2 and 5 mm quartz cells, such that the transmission was always higher than 50%. The experiments were performed at various sample detector distances and wave lengths, accessing a Q -range between $0.005 \leq Q \leq 0.11 \text{\AA}^{-1}$. Scattering due to the empty cell and the solvent as well as the calculated incoherent background, caused by the protonated polymer, were subtracted and standard correction procedures leading to absolute normalization were applied [8].

3 Single Star Properties

Fig.1 displays the normalized form factors $P(Q)$ which have been obtained from a Zimm extrapolation of scattering data obtained from low concentration ($\phi \leq 0.5\%$) star polymer solutions. The abscissa, thereby, is scaled with the respective radii of gyrations. While at high Q all data collapse on a single curve, displaying power law behavior, at low Q with increasing functionality, the observed intensity increases steadily.

Due to the large molecular weight of some of the stars, it was not always possible to determine the radius of gyration R_g by a Zimm extrapolation. As an approximative procedure we therefore

derived R_g from the position of the maximum in the Kratky plot of the scattering data. For Gaussian stars this maximum position relates directly to R_g [9]. Assuming that this relation still holds for stars in good solvents we determined our R_g values. Table I compares the thus obtained R_g data with those from a Zimm procedure where it was possible. As can be seen both approaches lead to very similar results.

The Daoud-Cotton model predicts for the scaling behavior of the radius of gyration

$$R_g^2 \sim N^{2\nu} f^{1-\nu} \quad (1)$$

where N is the degree of polymerization per arm, f the functionality and ν the Flory exponent. Figures 2 and 3 scrutinize this prediction on the basis of our results. For the $f = 32$ arm star fig.2 displays the dependence of R_g on the degree of polymerization and compares it with the theoretical prediction of equ.(1) (solid line). Fig.3 investigates the dependence on functionality. For this purpose $R_g^2/N^{2\nu}$ is plotted versus f . In order to make the PB and PI data comparable we furthermore corrected for the ratio of the respective values of the characteristic ratio C_∞ (PI: $C_\infty = 5.1$, PB: $C_\infty = 5.5$). In both cases the theoretical predictions represented by the solid lines agree very well with our experimental results.

Figure 1: Normalized zero concentration form factors for the investigated star molecules versus $Q \cdot R_g$ (from above: $f = 128, 64, 32, 18, 8$).

Figure 2: Dependence of R_g on the arm length for the $f = 32$ star. The solid line represents the prediction of equation 1.

We now consider the shape of the form factors $P(Q)$ in more detail. As can be seen from Fig.1 the Q -dependence of the form factor displays three different regimes. At low Q the intensity is given by the coherent superposition of the scattering from all the monomers within the star. The intensity there is given by $N \cdot f$. The power law tails at high Q originate from the polymer structure within the blobs. In this regime the intensity resulting from different blobs superimposes incoherently. In between these asymptotic regimes the intensity drops by a factor of $f^{3/2}$. This factor can easily be rationalized in considering the idea of coherent and incoherent superposition of scattering. At low Q the intensity is given by

$$I(Q \rightarrow 0) \sim \left[\left(\frac{R_g}{\xi} \right)^3 (\xi/\sigma)^{1/\nu} \right]^2 \quad (2)$$

the first factor giving the average number of blobs and the second factor the number of monomers

within a blob. σ thereby denotes the segment length. At the crossover to single blob scattering which occurs at $R_g \cdot Q \sim f^{1/2}$ ($\xi \propto R_g \cdot f^{-1/2}$) we have

$$I(Q R_g \approx f^{1/2}) \sim \left(\frac{R}{\xi}\right)^3 (\xi/\sigma)^{2/\nu} \quad (3)$$

The ratio of both is proportional to $f^{3/2}$. Fig.4 displays the experimental result for this ratio, the solid line giving the predicted $f^{3/2}$ dependence. Obviously, the step in $P(Q)$ follows very nicely the above prediction.

Figure 3: Scaling behavior of the radius of gyration as a function of functionality. The solid line represents the prediction of equation 1.

Figure 4: Ratio of the form factor at $Q = 0$ and the form factor at $Q \cdot R_g = f^{1/2}$ (see text). The solid line gives the theoretical $f^{3/2}$ prediction.

In order to carry on further we now model the scattering profile analytically. Fig.5 displays the form factor of the 128 arm star together with that of a sphere having the same radius of gyration. Obviously, the star form factor bears some resemblance to that of the sphere. We note particularly the evidence for the third maximum of the sphere form factor in the star data. The large discrepancy from the Q^{-4} sphere envelope at high Q arises from the polymer scattering in this asymptotic regime. We now approximate the pair correlation function for the star by a product of a shape function $\Omega(r)$ and the pair correlation function of a polymer $g(r) \propto r^{1/\nu-3}$. The form factor then is given by the square of the Fourier transformed of this product.

$$P(Q) \simeq \int_0^\infty \Omega(r)g(r)e^{iQr}d^3r \quad (4)$$

In Fourier space this results in the convolution of the two Fourier transformed functions including a $\delta(Q)$ arising from the average density. Considering the very different width of the two contributions we can replace this convolution by a sum of the two Fourier transformed. Approximating now $\Omega(Q)$ by the Guinier expression $\exp -\frac{1}{3}Q^2 R_g^2$ and Fourier transforming the polymer

pair correlation function including an exponential screening term $e^{-r/\xi}$, we arrive at an expression recently given by Dozier et al [10].

$$P(Q) = Nf \exp -\frac{1}{3}Q^2 R_g^2 + \frac{4\pi\alpha}{Q\xi} \frac{\sin(\mu \tan^{-1}(Q\xi))}{(1 + Q^2\xi^2)^{\mu/2}} \quad (5)$$

with $\mu = 1/\nu - 1$ and $\alpha \sim (\xi/\sigma)^{1/\nu} \sim Nf^{-1/2}$. Fig.6 displays the obtained fits to the data. We note that the fitted parameter α is proportional to the molecular weight and α/N is proportional to $f^{-1/2}$ as required. Furthermore, the screening length is compatible with the required $f^{-1/2}$ dependence.

In order to learn about the concentration dependence of the form factors we performed an experiment under zero average contrast conditions [11]. For this purpose identical hydrogenated and deuterated polyisoprene stars were prepared. These stars were dissolved in a mixture of hydrogenated and deuterated methylcyclohexane. By contrast variation the minimum of the scattered intensity was determined (44% protonated solvent) and under these conditions the experiments were performed. For zero average contrast all interstar interferences cancel and provided that both stars are identical the single star form factor as a function of concentration can be obtained.

Figure 5: Experimental form factor for the $f = 128$ arm star. Solid line: form factor of a sphere with the same radius of gyration.

Figure 6: Fit of eq.(5) to the form factors for the different star molecules (from above: $f = 128, 64, 32, 18, 8$).

Fig.7 presents the results. With increasing intensity the scattering shifts outwards to higher Q signifying a shrinking star. As may be seen from the master curve in the insert, by shifting the abscissa all curves collapse to a single master curve. The shift factors determine very precisely the relative changes of the radius of gyration. Fig.8 displays the obtained concentration dependent R_g . Above the overlap concentration which occurs at about $\phi^* = 10\%$ we observe a power law shrinking with an exponent close to $-1/8$. Considering the Daoud-Cotton scaling model we would expect the following. Very close to the overlap concentration $R_g \propto \phi^{-3/4}$ is predicted while for larger concentrations $R_g \propto \phi^{-1/8}$ should be observed. The second scaling law coincides with that for linear polymers. Our data do not show any sign of the first law but agree well with the $\phi^{-1/8}$ scaling. Thus, the stars in this respect behave like linear chains.

4 Approach to Semidilute Solutions

Fig.9 presents the Q -dependent intensities, normalized to the volume fraction for the 18-arm star. With increasing concentration at intermediate Q -values, a peak develops indicating preferred interstar distances in this concentration range. The observation of such a peak is the central result of the studies at intermediate concentrations. It immediately indicates the presence of ordering in

Figure 7: Form factors for the $f = 18$ arm star as a function of monomer concentration. Insert: master curve which can be obtained by shifting the abscissa.

Figure 8: Radius of gyration for the $f = 18$ arm star as a function of monomer concentration. The solid line presents the $R_g \propto \phi^{-1/8}$ power law.

Figure 9: Normalized intensities obtained from the $f = 18$ arm star as a function of concentration (concentrations from above: $\phi = 0.2\%, 0.4\%, 1\%, 1.5\%, 2.5\%, 4.9\%, 7.4\%, 9.9\%, 14.6\%, 19.2\%$).

Figure 10: Structure factor for the $f = 64$ arm star (PB/64 15). The concentrations from the left are: 2.8%, 5.3%, 7.8%, 10.3%, 13.0%, 15.0%, 20.2%.

such solutions. At low Q the intensity drops sharply indicating the increasing osmotic pressure Π in the solution ($I^{-1}(0) \propto d\Pi/d\phi$). At high Q all measured intensities approximately follow the same Q -dependence. The results for stars with higher functionality show even more pronounced peak structures reflecting the higher degree of order. The interstar structure factor $S(Q)$ was evaluated on the basis of

$$S(Q) = I(Q)/(\phi V_W P(Q)) \quad (6)$$

Thereby $I(Q)$ is the normalized intensity and V_W the polymer volume. $P(Q, \phi)$ was approximated by the zero concentration form factors $P(Q)$. This procedure bears some uncertainties since, as we have seen for the 18-arm star, some shrinking is observed above ϕ^* . Thus, the data beyond the overlap concentration may be affected by a changing form factor. However, since the form factors are smooth, the shrinking effects are expected to mainly cause errors in the normalization of $S(Q)$ but not to distort it. Fig.10 displays the such evaluated structure factors for 64-arm star solutions (PB-6415). From low to high concentration we observe the gradual build-up of the peak structure culminating at 10.3% where it reaches nearly 3. Towards higher concentrations it diminishes again. Calculating the overlap concentration from $\phi^* = V_W/(4/3 \cdot \pi R_g^3)$ we arrive at 11% (Zimm value for R_g). We note that beyond the first maximum no further peak structure develops.

The peculiar behavior of star molecules around ϕ^* originates from the crossover from a very inhomogeneous monomer density distribution in dilute solution to a homogeneous distribution in semidilute solution resembling that of linear polymers. Comparing stars and linear chains in dilute solution, the osmotic pressure in both cases is proportional to the number of molecules in solution. In semidilute solution where the branches of different stars or linear polymers respectively interpenetrate, a more or less uniform segment distribution arises. There, the osmotic pressure is given by the number of blobs in the system $\Pi \sim kT \cdot \xi^{-3}$. Around ϕ^* a transformation occurs from a state where with respect to the osmotic pressure all arms of one star act as one entity to another state, where each arm does not know any more to which star it belongs and acts separately. As a consequence a sudden increase of the osmotic pressure is expected. This extra osmotic pressure is the basis of the repulsion between polymer stars. Witten et al. have worked out a scaling theory and predict that the jump in the osmotic pressure should be proportional to $f^{3/2}$. Accordingly, the peak height in $S(Q)$ should follow the $f^{3/2}$ scaling. Furthermore, the ordering effect of self similar stars should not depend on the molecular weight of a given star.

Fig.11 displays the structure factor $S(Q)$ for the different stars at the overlap concentration ϕ^* demonstrating the build-up of structure in going to higher functionality. While for the 8-arm star the peak in the structure factor is barely developed with increasing f the peak height increases and sharpens up. The relative peak height $S(Q_{max})/S(0)$ as a function of functionality follows the predicted $f^{3/2}$ behaviour. Within experimental accuracy the results follow the predicted scaling law. In order to scrutinize the stated independence of the ordering phenomena on molecular weight, Fig.12 displays the structure factors for the 32-arm stars covering a molecular weight range of more than a factor of 7. Clearly the observed structure factors display all the same height indicating identical ordering effects.

5 Colloidal Approach

The theory of liquids and colloids [12] tries to relate the structure factor $S(Q)$ reflecting the pair correlation function in the system to the interparticle potential. Such calculations are performed on the basis of statistical mechanical procedures and in general require many approximations. In order to get a first idea about the ‘star liquid’ we have investigated the observed interstar structure factors in terms of two commonly applied models: (i) The hard sphere approach in terms of the Percus-Jevic

Figure 11: Structure factors at the overlap concentration ($\circ$ $f = 128$; $\blacktriangle$ $f = 64$; $\bullet$ $f = 18$; $\triangle$ $f = 8$).

Figure 12: Structure factor for $f = 32$ arm stars with different molecular weight (from the left M_N (arm): 37 400, 19 400, 9 500, 5 400).

[13] approximation and a soft Yukawa potential using the mean-spherical approximation (MSA) by Hayter and Penfold [14]. The hard sphere approach deals with one parameter, namely the diameter of the hard sphere R_h . For inter particle distances larger than $2 \cdot R_h$, the interaction energy is 0 while for distances smaller than $2 \cdot R_h$ it becomes infinitive. The soft potential Yukawa approach adds to the hard core a screened Coulomb tail.

$$\frac{V(r)}{kT} = \frac{2\gamma R_h}{r} e^{-r/\lambda} \quad (7)$$

where γR_h describes the strength of the potential and λ the range of the soft potential interaction.

A fit with the hard sphere potential gives unsatisfying results. The calculated structure factor does not describe the experimental profiles. Furthermore, the hard core radius changes continuously with the star concentration rendering this model as non-applicable. Fig.13 presents a fit with the Yukawa potential which below ϕ^* describes the observed structure factors reasonably well. We note that below ϕ^* the shown agreement can be obtained fixing both the screening length and the potential strength. In each case the monomer concentration was kept to the experimental value. For the screening length we find $\lambda = 25 \text{ \AA}$ which relates well to the outer blob diameter of $\xi \sim R_g f^{-1/2} \approx 20 \text{ \AA}$. Thus, the interaction range of the interacting stars correlates with the outer blob size. From the potential strength we can calculate the interaction energy at $r = 2R_g$. This interaction energy comes out to $0.3 kT$, which again relates well to the energy per blob, which is in the order of kT . Thus, approaching the critical overlap concentration, a soft potential model can consistently describe the interstar interactions revealing the appropriate structure factor. If we go to concentrations beyond ϕ^* the description in terms of a Yukawa potential breaks down. It cannot account for interstar interpenetration yielding an increasing screening length accompanied by decreasing interaction strength. Our efforts to describe the structure factors in terms of interstar interaction potentials are clearly only at the beginning and descriptions with more appropriate potentials should be tried in the future.

Figure 13: Structure factors for the 18 arm stars in comparison to the calculated structure on the basis of a soft Yukawa potential using the MSA approximation according to ref.14.

6 Summary and Conclusion

In this work we have investigated the form factor of single stars over a wide range of molecular weight and functionality. The neutron small angle data verify the scaling predictions for the radius of gyration, both with respect to molecular weight and functionality. Using the zero average contrast method the radius of gyration of a single star was also determined as a function of concentration. Here, the scaling behavior of linear chains was found. The experimental form factors can be very well interpreted in terms of the blob model. Studying the concentration dependence we have shown that other than linear polymers, which penetrate each other easily, the polymer stars assume a liquid-like structure close to the overlap concentration. For high functionalities, the large peak heights of the structure factors indicate solid-like structures. The dependencies of the peak heights on functionality and molecular weight agree well with the scaling predictions. Finally, an interpretation of the structure factor for 18-arm stars in terms of a Yukawa potential yields consistent results up to the overlap concentration Φ^* . Further work will have to be devoted in order to understand the interstar structure factors in terms of interaction potentials.

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