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Neither Gaussian chains nor hard spheres – star polymers seen as ultrasoft colloids

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Abstract In dense solution high functionality star polymers show ordering phenomena which give rise to a well-pronounced peak in the static structure factor, $S_{\text{exp}}(Q)$, observed by small-angle neutron scattering. The concentration dependence of $S_{\text{exp}}(Q)$ gives evidence for unusual phase behaviour as predicted by theory. In addition, the dynamics of the star polymer solutions is dominated by an increasing amount of structural arrest with increasing concentration. The mean square displacement obtained from neutron spin-echo spectroscopy is compared to the blob size obtained

from dynamic light scattering. Thermal energy enables each star core to perform restricted motion over a spatial extent equal to the blob size of the surrounding dense star polymer solution.

Key words Star polymers · Small-angle neutron scattering · Neutron spin-echo spectroscopy · Liquid-state theory · Pair potential

Introduction

Recently we introduced star polymers as a new class of ultrasoft colloids showing both polymer-like and colloidal characteristics. This hybrid character gives rise to some unusual phenomena in the structural properties [1–4] as well as in the dynamics of dense star polymer solution [5, 6]. However, all these studies were limited to low functionality star polymers and/or concentrations below the overlap concentration, $c^* = 3/(4\pi R_{\text{g}}^3) \times (M_{\text{w}}/N_{\text{A}})$.

Here, we present new results concerning the structure and dynamics of star polymer solutions which have overcome these limitations. The article is divided as follows. In the first part, we present small-angle neutron scattering (SANS) data of a 57-arm polybutadiene (PB) star polymer in a good solvent up to a concentration well above c^*. The experimental data are analysed using the microscopic pair potential introduced by Likos et al. [1] and are finally compared to the phase diagram of Watzlawek et al. [3]. In the second part, we discuss the microscopic

dynamics of an 18-arm polyisoprene (PI) star polymer as investigated by neutron spin-echo (NSE) spectroscopy. To cover the slowed-down dynamics at the peak position in the static structure factor, Q_{m}, [6], the dynamic time range of NSE is extended for the first time up to 350 ns using a long wavelength of 19 Å at IN15(ILL). Finally, we draw some conclusions emphasizing the exceptional position of star polymers as a connecting link between polymer physics and colloidal science.

Experimental

The molecular characteristics of the polymers investigated are summarised in Table 1. The partially labelled high functionality PB star was prepared by anionic polymerization following an established procedure [7, 8]. The synthesis of the arms started with deuterated PB and secondary butyl lithium as initiator and proceeded with protonated PB. The still-living polymer chains were coupled to the linking agent, a 4G-chlorosilan dendrimer. The result of the synthesis is a labelled multiarm star which has a protonated core and a deuterated shell. Due to steric hindrance during the coupling [9], the synthesis results in a small polydisper-

Table 1 Molecular characteristics of the star polymers investigated

Sample	Monomer	f	M_w (g/mol)	M_w/M_n[a]	R_g (Å)	c^* (g/cm³)	R_h[b] (Å)
S18	Isoprene	18	139,700[c]	1.01	72.0[d]	0.149	80.5
S64	Butadiene	57	467,800[e]	1.01	105.5	0.158	124.5

[a] Gel permeation chromatography
[b] Dynamic light scattering
[c] Low angle laser light scattering
[d] Interpolated from literature data [17, 18]
[e] Small-angle neutron scattering

sity in f, which gives a mean functionality, f_{mean} of 57. The partially labelled 18-arm PI star could be prepared nearly monodisperse and is the same as that described in Refs. [1, 5]. Using fully deuterated methylcyclohexane, the solvent and the deuterated shell scatter neutrons in the same way and in the experiments only the protonated core is visible.

The SANS experiments were performed using the KWS1 instrument at Forschungszentrum Jülich and the PAXY instrument at LLB, Sacclay. NSE spectroscopy data were obtained using the NSE instrument at FRJ-2, Jülich, and at IN15, ILL, Grenoble.

Results and discussion

Small-angle neutron scattering

For analysing our SANS data the same procedure as described in detail in Ref. [1] was applied. That is, starting from a pair potential, $V(r)$, for star polymers which reads as follows

$$\frac{V(r)}{k_B T} = \begin{cases} (5/18)f^{3/2}[-\ln(r/\sigma) + (1 + \sqrt{f}/2)^{-1}] & (r \leq \sigma); \\ (5/18)f^{3/2}(1 + \sqrt{f}/2)^{-1}(\sigma/r) \\ \times \exp[-\sqrt{f}(r - \sigma)/2\sigma] & (r > \sigma) \end{cases}$$

(1)

and applying the Rogers–Young closure [10] and associated Monte Carlo simulations we obtain information about the pair structure of the liquid, in particular the centre-to-centre structure factor, $S(Q)$, of the stars. In attempting to fit the experimental data for the total scattering intensity, $I(Q)$, with the theoretical predictions based on an analytic pair potential, we must take into consideration the fact that the star size itself has a dependence on the concentration. Whereas in a previous study [1] this could be done using experimental data for $\sigma(\Phi)$, in the present study we have to use σ as (the only) adjustable parameter [11].[1]

A representative fit for a volume fraction, Φ, of 18.75%, i.e. approximately $1.2\Phi^*$, is shown in Fig. 1. It can be seen that the fit is quite satisfactory for the whole Q range. The insert of Fig. 1 shows how σ varies with increasing Φ. Obviously, there are three different regions:

1. Up to $\Phi \approx 0.5\Phi^*$, σ stays nearly constant at about 150 Å.
2. A steep decrease up to $\Phi \approx 1.2\Phi^*$.
3. A much less pronounced Φ dependence is reached for the highest volume fractions under study.

The Daoud–Cotton [12] scaling approach for star polymers predicts exactly these three different concentration regimes for high functionality star polymers. The proposed power laws $\sim\Phi^0$, $\sim\Phi^{-3/4}$ and $\Phi^{-1/8}$ are also shown in Fig. 1. Although not completely convincing, the observed Φ dependence agrees reasonably with these power laws.

For discussing in more detail the observed structures it is recommended to refer directly to $S(Q)$ rather than to $I(Q)$. The experimental static structure factor, $S_{exp}(Q)$, of the high functionality PB star polymer at Φ^* is compared to that of the 18-arm PI star polymer used in the previous study in Fig. 2. $S_{exp}(Q)$ is obtained assuming a decoupling between the form factor and the structure factor, i.e. $I(q) = V_W P(Q)S(Q)$, where $P(Q)$ is the intramolecular form factor.[2] For $f = 57$, $S_{exp}(Q)$ shows two well-developed maxima, indicating the high degree of structural order. From the peak height of the first maximum, we can estimate that we are already close to a phase transition to a crystalline phase [13]. The insert of Fig. 2 shows the dependence of the peak height, S_{max}, of the first maximum on the volume fraction. S_{max} itself shows a first maximum exactly at Φ^* as predicted by theory [14]. After a short monotonous decrease S_{max} starts to fluctuate strongly between $1.2\Phi^* \leq \Phi \leq 2\Phi^*$ until it finally increases again monotonically. These fluctuations can be interpreted as a precursor of a reentrant melting as predicted in the phase diagram of dense star polymer solutions [3]. This reentrant melting should take place exactly in the Φ region where S_{max} shows its unusual behaviour. The fact that no Bragg peaks are observed in the SANS data, as expected for a crystalline phase, can be attributed to the small polydispersity of our star polymers, which was also not taken into account in the phase diagram. To summarize this part, the agreement obtained between our SANS data

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[1] Zero-average contrast experiments on similar star polymers have shown that R_g stays constant with increasing concentration, but some changes took place an smaller length scales. Probably the size of the outermost blob changes, which could not be resolved within experimental errors.

[2] This assumption is still valid in our case at high volume fractions. Due to the fact that only the inner quarter of each star is protonated, i.e. visible for the neutrons, the form factor of this part is not affected by any overlap of the outer regions of the stars.

Fig. 1 Experimental (*points*) versus theoretical results (*solid line*) for the total scattering intensity, $I(Q)/\Phi$, of 57-arm polybutadiene stars at a volume fraction, Φ, of $18.75 \approx 1.2\Phi^*$. Also shown is the star form factor obtained from extrapolation to zero concentration (*dashed line*). *Insert*: concentration dependence of the star radius, σ, used as an adjustable parameter in the fit. The *solid line* shows the proposed scaling laws of Ref. [12] (see text)
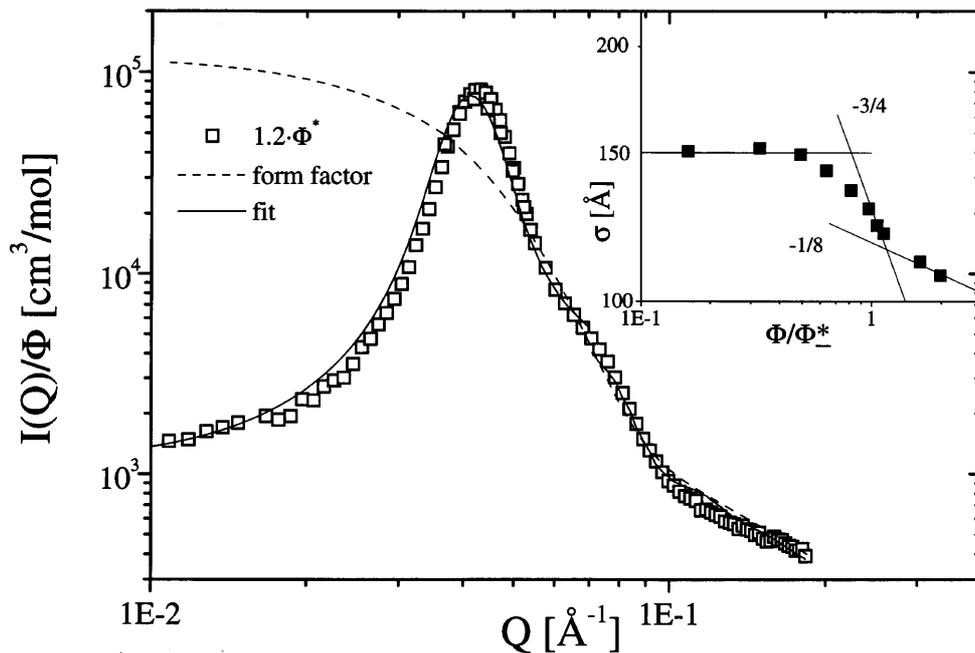
Fig. 2 The static structure factor, $S_{exp}(Q)$, obtained by small-angle neutron scattering is shown for star polymers of varying functionality, f, at their overlap concentration, c^*. With increasing functionality the degree of order increases substantially. From the height of the first maximum we can estimate that we are already close to a phase transition to a crystalline order for $f_{mean} = 57$. The *insert* shows the unusual concentration dependence of the peak height of the first maximum, S_{max}. The *dotted lines* indicate the region where reentrant melting is expected in the phase diagram [3]
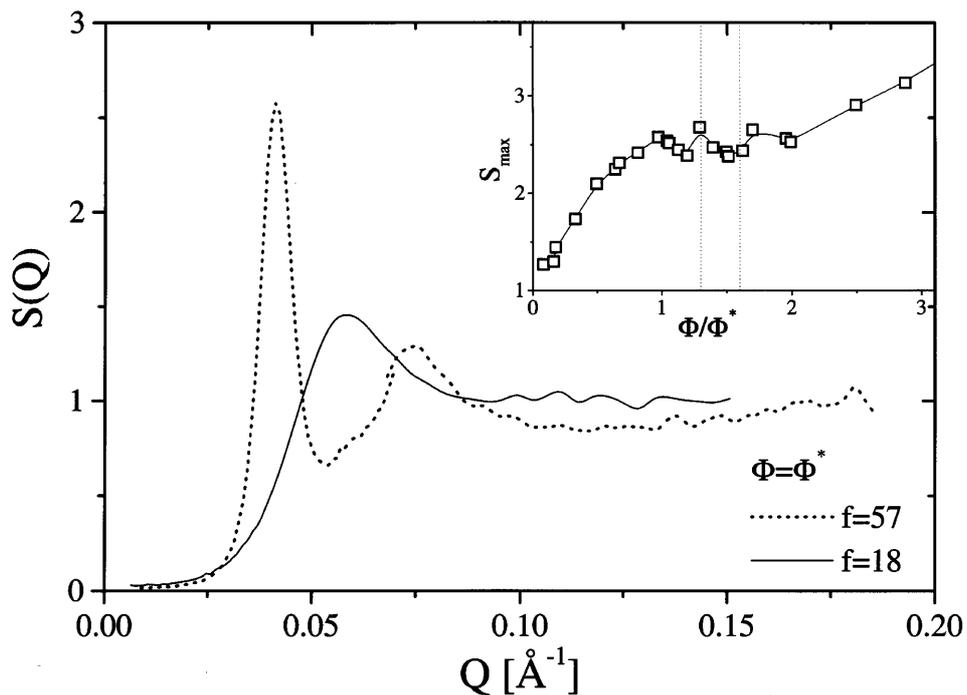
and predictions from polymer scaling theory as well as from a colloidal approach emphasizes the hybrid character of star polymers as a connecting link between polymer physics and colloidal science.

NSE spectroscopy

Due to the applied matching conditions NSE experiments observe the collective motion of the star centres if

we measure close to the structure factor peak [15] (for our star polymer this occurs around $Q_m \approx 0.075$ Å^{-1} in the concentration regime of interest, see previous section).[3] The intermediate scattering function, $S(Q,t)$, is strongly modulated in the region around Q_m. To cover

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[3] In a very recent light scattering study Semenov et al. [15] observed precursors of the structural influence on star dynamics, but using light they could not achieve Q_m

Fig. 3 Normalized intermediate scattering functions, $S(Q,t)/S(Q,0)$, as obtained by neutron spin-echo (*NSE*) spectroscopy for an 18-arm polyisoprene star polymer at different volume fractions well above Φ^*. From *top* and *bottom* Φ = 30, 25 and 20%. Above Φ^* a concentration-dependent plateau is developed in $S(Q,t)$ near Q_m, the peak position in the static structure factor. *Solid line*: fit to Eq. (2). The dynamic time range of about 350 ns was achieved for the very first time using a long wavelength, 19 Å, at IN15(ILL)
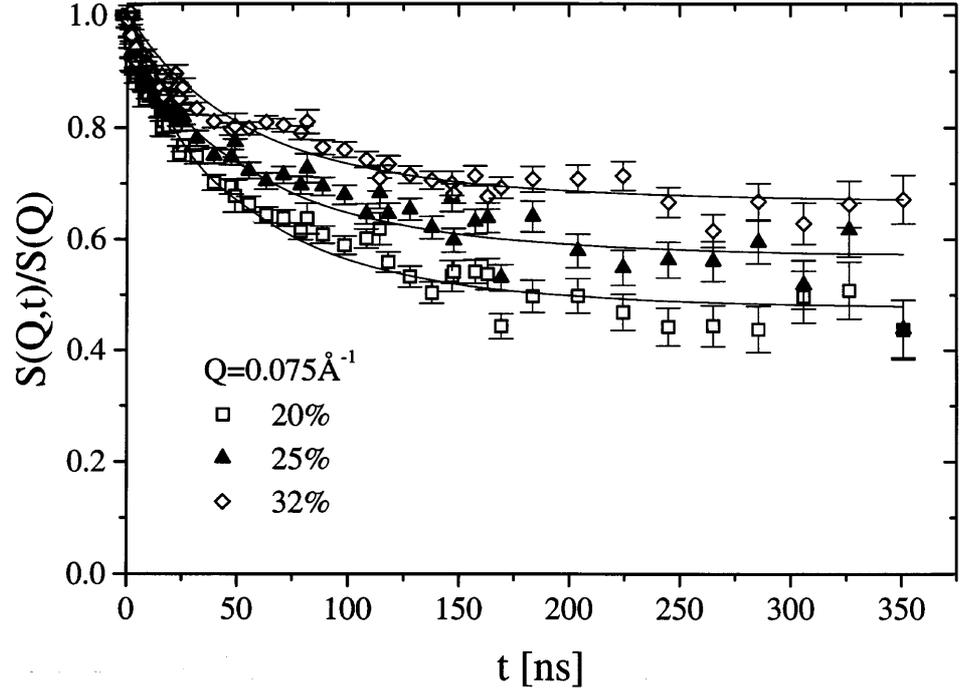
Fig. 4 Concentration dependence of the mean square displacement, $\langle r^2 \rangle^{1/2}$ of star cores obtained by NSE and of the blob size of the surrounding entangled star polymer solution, ξ, as obtained by dynamic light scattering (data taken from Ref. [5])
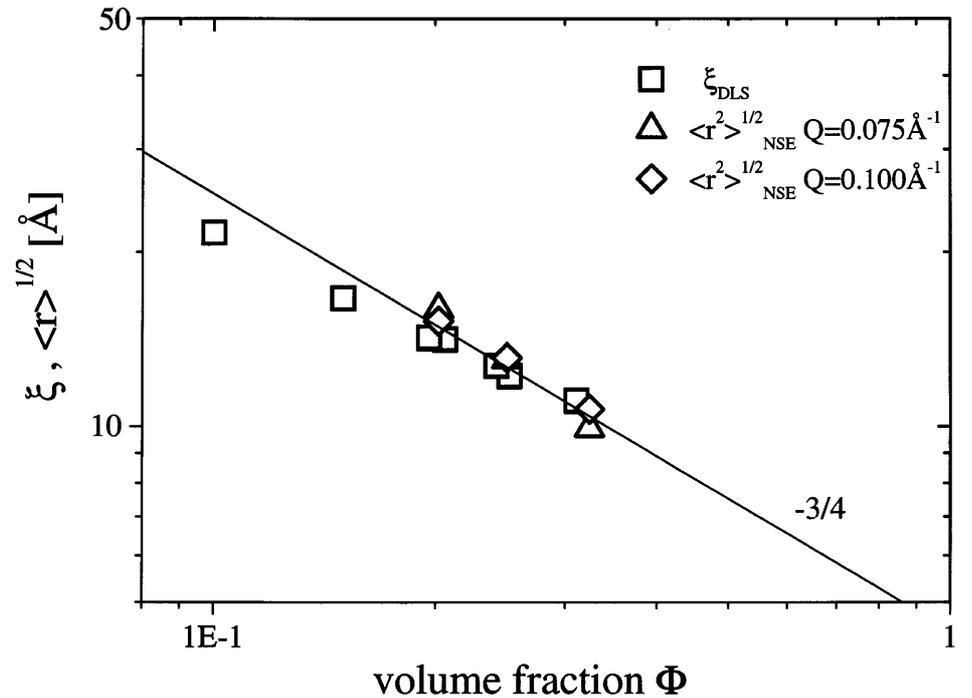
the slowed-down dynamics at Q_m, the dynamic time range of NSE was extended up to 350 ns using a long wavelength, 19 Å, at In15(ILL).

The normalized intermediate scattering functions, $S(Q,t)/S(Q,0)$, at $Q_m = 0.075$ are shown in Fig. 3 at three different volume fractions: $\Phi = 20, 25$ and 30% ($\Phi^* = 15\%$). It can clearly be seen that at each volume fraction a final plateau is reached at about 180 ns. Due to the increasing amount of structural arrest with increasing concentration, the height of the plateau depends on concentration. For quantitative analysis, the restricted motion of the star polymers can be approximated by the following intermediate scattering function (solid lines in Fig. 3):

$$S(Q,t) = \exp(-1/3\ Q^2\langle r^2\rangle)$$
$$+ [1 - \exp(-1/3\ Q^2\langle r^2\rangle)]H(Q,t)\ , \qquad (2)$$

with $H(Q,t)$ the Zimm dynamic structure factor [16] and $\langle r^2\rangle$ the mean square displacement or the average size of the star confinement. The values of $\langle r^2\rangle^{1/2}$ obtained of 15 Å are considerably smaller than the size of the star, $R_g = 75$ Å. The concentration dependence of $\langle r^2\rangle^{1/2}$ compared to that of the blob size, ξ, obtained from dynamic light scattering experiments is shown in Fig. 4 [5]. Obviously the star confinement relates to the ξ of the dense star polymer solution. The slope obtained is in reasonable agreement with the predicted value of $-3/4$ from scaling theory. Thus, the available thermal energy, kT, enables each star core to perform restricted motion over a spatial extent equal to the ξ of the surrounding dense star polymer solution. This relationship between kT and ξ is also known from solutions of linear polymers and emphasizes the hybrid character of star polymers. These results are a promising approach to elucidating the complex dynamics of dense star polymer solutions by combining SANS, NSE and dynamic light scattering.

Conclusions

The exceptional hybrid character of star polymers influences both their structural properties and their dynamics in dense solution. The colloidal aspect is more pronounced in the intermolecular properties of star polymers, for example, the centre-to-centre structure factor. $S_{exp}(Q)$ obtained by SANS can be described by a colloidal approach combining a new pair potential and liquid-state theory as known from hard-sphere systems. The observed agreement is, in particular, convincing due to the fact that we are starting from a microscopic level. The polymer aspect, on the other hand, is more pronounced in the single star properties. For example, the dependence of star size on concentration and the relationship between the dynamical confinement of a single star core and the blob size of the already entangled outer regions of different stars. All these results underline the importance of star polymers as a new class of colloids, which we would like to call ultra soft colloids.

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