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Dynamics of star polymers: Evidence for a structural glass transition

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The dynamics of an 18-arm poly(isoprene) star polymer ($M_n^{arm}=7360$ g/mol) is investigated by dynamic light scattering and viscometry. Above the overlap concentration c^* the intensity autocorrelation functions show a two-step decay, which implies the existence of long range correlations, $\xi \approx 100$ nm. A similar length scale can be derived from the q dependence of the static scattering intensity, which reveals a strong excess scattering at low q. These experimental results are an indication for a structural glass transition at higher concentrations as known from colloidal systems.
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Due to their unique properties, in recent years star polymers have attracted the interest of experimental and theoretical physicists; for a recent review, see Grest *et al.* [1]. Star polymers can be considered as hybrids between polymerlike entities and colloidal particles, thereby connecting two important areas of research: polymers and colloids. Which of the two limits dominates depends crucially on the arm number. The structural properties of single stars have been intensively investigated [2] and the obtained results can be well explained by theory [3,4]. Moreover, solutions of star polymers show ordering phenomena at the overlap concentrations $c^*=(3/4\pi R_g^3)(M_w/N_A)$, with R_g the radius of gyration, M_w molecular weight, and N_A Avogadro number, which give rise to a peak in the static structure factor [5]. With increasing arm number f, there is a crossover from a liquidlike structure to crystallization, which occurs at $f=64$ and indicates the colloidal limit.

Much less work has been performed, however, on the dynamical properties of star polymer solutions, in particular in the concentration range above c^*. The pioneering work of Adam *et al.* [6] was mainly focused on the short time regime and to our knowledge no further studies were performed on star polymer solutions at higher concentrations. Linear polymers interpenetrate each other easily and above c^* there exists only one characteristic length, the screening length of the excluded volume interaction or the blob diameter $\xi(c)$, and one characteristic dynamical process, the blob or collective diffusion. For star polymer solutions on the contrary, there are two further length scales: (i) the mean interparticle distance $d \approx \langle n \rangle^{-1/3}$, with n the average number density, and (ii) a characteristic length $\chi(c)$ separating the outer regions of the stars, where arms of different stars already overlap, from the core region [3]. Thus, we may consider the star solutions as colloidallike star cores of size χ separated by a distance d in a sea of blobs of size ξ. All three lengths have their maximum value at $c=c^*:\xi \leqslant \chi \leqslant d \approx 2R_g$.

In this paper we present a dynamic light scattering study [7,8] of an 18-arm poly(isoprene) (PI) star polymer solution over a large concentration range and compare the obtained correlation functions with those from a corresponding solution of linear PI chains. We find two dynamical regimes: (i) Polymerlike relaxation dynamics at short times with a collective response following the renormalization group theory [9,10] independent of the polymer architecture, and (ii) at long times above c^* a very well separated second slow dynamic regime reveals itself in star polymer solutions. This slow diffusive process is connected to low angle excess scattering and indicates long range, slow density fluctuations, with $\xi_{slow} \gg R_g$, reminiscent of features of the glass process [11].

Dynamic light scattering (DLS) probes the relaxation of concentration fluctuations in polymer solutions on mesoscopic time and length scales. The measured intensity autocorrelation function $g^2(q,t)=\langle I(q,0)I(q,t)\rangle/\langle I\rangle^2$ is related in a homodyne experiment to the normalized field autocorrelation function $g^1(q,t)=S(q,t)/S(q,0)$ by the Siegert-relation: $g^2(q,t)=1+f_c|g^1(q,t)|^2$, with scattering vector $q=(4\pi n/\lambda)\sin(\Theta/2)$ and f_c an experimental factor. The intermediate scattering function $S(q,t)=1/\langle\rho\rangle \int_V[\langle\rho(0,0)\rho(r,t)\rangle-\langle\rho\rangle^2]e^{iqr}d^3r$ is the Fourier transform of the density correlation function of the scattering medium, where $\rho(r,t)$ is the local density at position r at time t in the sample. The DLS measurements were performed on a standard setup (ALV-125 compact goniometer, Ar$^+$ laser with $\lambda=514.5$ nm, ALV5000E correlator). The relative macroscopic viscosity of the solutions was determined by viscometry [12] (Ostwald capillar viscometer). Shear rate independence was checked by using different capillari radii. The star polymer (S18) was synthesized by anionic polymerization following an established procedure [13,14]. (For other reasons, the outer part of the star polymer is deuterated.) The linear poly(isoprene) (PI25) was purchased from PSS in Mainz, Germany. For a detailed characterization of the polymers, see Table I.

In dilute solution the intensity autocorrelation functions (ICFs) of both polymers reveal only one relaxation process at all scattering vectors q. Cumulant analysis [15] gives a normalized second cumulant $\sigma^2/\Gamma^2 \leqslant 0.027$ (PI25) and $\leqslant 0.025$ (S18) characteristic for a narrow molecular weight distribution. The concentration dependence of the mutual diffusion coefficient $D_m=\Gamma/q^2$ in dilute solutions can be described by a virial expansion [8], $D_m(c)=D_0(1+k_d c)$, with D_0 the diffusion coefficient at infinite dilution. For PI25 this linear regime extends to $c=8.05\times10^{-2}$ g/ml; that is, $\sim 1.9c^*$. For the star polymer S18, in contrary, a significant departure from linear behavior is already found at concentrations $\geqslant 7.40\times10^{-2}$ g/ml, i.e., $\sim 0.5c^*$ (see Table I).

This different behavior of the two polymers becomes

TABLE I. Characterization of the investigated polymers.

Sample	M_w[a] (g/mol)	M_w/M_n[b]	R_g[c] (nm)	$c^*=\frac{3}{4\pi R_g^3}\frac{M_w}{N_A}$ (g/cm^3)	D_0 (cm^2/s)	k_D^Φ	$R_h=\frac{k_BT}{6\pi\eta_0 D_0}$ (nm)
S18	139 700	1.01	7.2	0.149	3.51×10^{-7}	26.9	8.05
PI25	25 600	1.02	6.2	0.0432	7.10×10^{-7}	10.6	3.98

[a] Low angle laser light scattering.

[b] Gel permeation chromatography.

[c] Interpolated from literature data [2,26].

more and more pronounced by a further increase of the polymer concentration. In Fig. 1 the ICFs for the star polymer at $c \geqslant c^*$ are shown together with that of the linear polymer at the highest concentration. For the linear polymer PI25 the shape of the ICFs do not change with increasing concentration. Even at $c=0.31$ g/ml ($\sim 7.2c^*$) there is a nearly single exponential decay ($\sigma^2/\Gamma^2 \leqslant 0.033$). On the other hand, σ^2/Γ^2 increases with increasing polymer concentration for the star polymer and finally a second, 4 decades slower relaxation process evolves at $c \geqslant 0.152$ g/ml. This additional relaxation process (slow mode) is a characteristic feature of star polymer solutions above c^* [16]. Its characterization and relation to the special molecular architecture will be the central issue of this paper.

The amplitude of the slow mode increases with decreasing scattering vector and increasing polymer concentration. All ICFs are fully relaxed, neither a decrease of the coherence factor f_c nor a dependence on scattering volume is observed, i.e., there is no indication of nonergodic behavior [17]. A CONTIN [18] analysis reveals two narrow peaks in the relaxation frequency distribution. In addition, the data can be well described by a sum of two Kohlrausch-Williams-Watts functions [19]; see Fig. 1. The narrow distribution found by CONTIN is reflected in the q-independent high stretching exponent $\beta_{slow} \geqslant 0.9$ value from the fitting procedure ($\beta_{fast} \geqslant 0.95$ at all q vectors and concentrations) [20]. The q dependence of both processes is shown in Fig. 2. Although the scatter in the data of the slow mode is somewhat stronger, fast and slow mode can be attributed to be q^2 dependent, i.e., originating from diffusive processes.

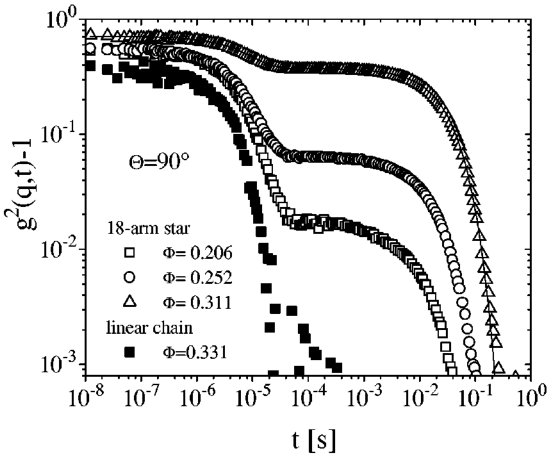

FIG. 1. Intensity autocorrelation functions for the star polymer at $c \geqslant c^*$ are shown together with that of the linear polymer at the highest concentration. The solid line is a fit to a sum of two KWW functions, $\beta_{slow}=0.97$; see text.

For linear polymers renormalization group theory [21] describes continuously the *crossover behavior* from single chain diffusion to collective, short time dynamics over the whole concentration range. The explicit concentration dependence (in terms of volume fraction Φ) found in our experiments is compared to a theoretical work of Shiwa *et al.* [9,10] in Fig. 3. Here the rescaled values $D_0/D(\Phi)$ are plotted against $k_d\Phi$. The use of $k_d\Phi$ as abscissa instead of the originally proposed ΦA_2 has been pointed out by Nystroem and Roots [22] and by Wiltzius *et al.* [23]. All data fall onto one universal master curve independent of the very different architecture of the two polymers. Moreover, there is an excellent agreement with the theoretical curve, also shown in Fig. 3. This theoretical result is a combination of the work of Shiwa (Eq. 5 in [9]) and Nystroem (Eq. 7 in [22]) and assumes the following form (for the derivation of the numerical factors, see the original works):

$$D_0/D(\Phi)=\frac{(1+0.8608k_d\Phi)^{3/8}}{1+1.3255k_d\Phi(1+0.8608k_d\Phi)^{1/4}}. \qquad (1)$$

Herein the numerator describes the hydrodynamic and the denominator the thermodynamic interactions. In Eq. (1) two correction terms have been neglected: (i) The so-called *enhancement factor* calculated by Shiwa, which describes the effect of hydrodynamic screening in semidilute solutions, and (ii) a correction of the exponents proposed by Nystroem and Roots [22]. Figure 3 is an experimental verification of the expected independence of collective dynamics from molecular architecture above c^* and supports the very local character of the fast mode.

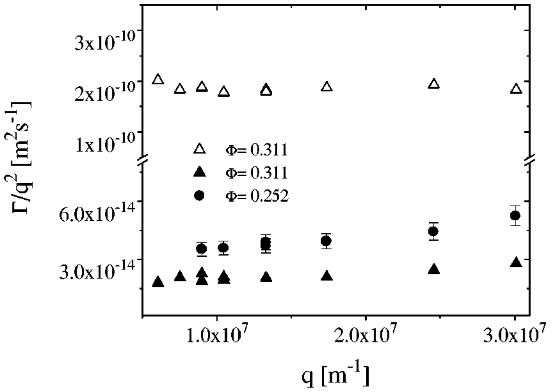

FIG. 2. Plotting Γ/q^2, Γ=relaxation frequency, as a function of scattering vector q reveals the diffusive character of the observed processes (open symbols, fast mode; closed symbols, slow mode).

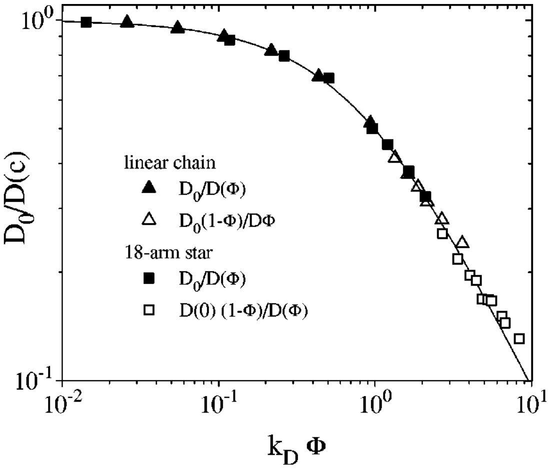

FIG. 3. Rescaled values $D_0/D(\phi)$ are plotted against $k_d\Phi$ for both polymers; solid line, Eq. (1).

Now we return to the slow mode. The most striking feature of this relaxation process obviously is its large separation from the fast process and the very well developed intermediate plateau regime of the ICFs. Of particular interest is the concentration dependence of the slow mode. Whereas its amplitude increases with increasing polymer concentration, the diffusion coefficient D_{slow} decreases, i.e., the process freezes. In Fig. 4 the reduced diffusion coefficient $D_0/D_{slow}(\Phi)$ is plotted against polymer volume fraction Φ together with the reduced macroscopic viscosity $\eta(\Phi)/\eta_0$, where η_0 is the solvent viscosity. Both magnitudes show the same scaling law above c^*, $\sim c^{2.2}$, but the ratio of the diffusion coefficients is two orders of magnitude larger than the ratio of the viscosities.

Using $\eta(\Phi)$ a dynamic correlation length $\xi_{slow} = k_BT/6\pi\eta(\Phi)D_0$ of approximately 100 nm independent from volume fraction Φ can be derived. This length scale is one order of magnitude larger than the radius of the whole star polymer, which for our system amounts to $R_g = 7.2$ nm. Thus, the slow mode *cannot* be related to the lengths d and χ introduced by present theories [3].

Investigating now the static scattering intensity we find strong excess scattering at low q. An Ornstein-Zernicke plot of $I_{VV}(q)$ for the highest concentration $\Phi=0.31$ is shown in the inset of Fig. 4. Analysis of the data in terms of an Ornstein-Zernicke correlation function yields a static correlation length $\xi_{OZ}=104$ nm compared to $\xi_{slow}=116$ nm obtained from dynamic light scattering. Both results establish the existence of both static *and* dynamic long range correlations $\xi_{OZ}\approx\xi_{slow}\gg R_g$ in semidilute solutions of star polymers.

These new experimental results resemble properties that have been reported for glassforming liquids, i.e., molecular glassformers [orthoterphenyl (OTP)] [11], bulk polymers [poly(methyl-p-tolyl-siloxane) (PMpTS)] [24], and colloids [poly(methylmetacrylate) (PMMA)] [25]. All these systems exhibit qualitatively similar additional slow relaxation processes, which are characterized by a single exponential decay and a q^2 dependence. They occur in DLS experiments approaching the glass transition either in reducing the temperature versus T_g or in increasing the volume fraction in the colloidal case.

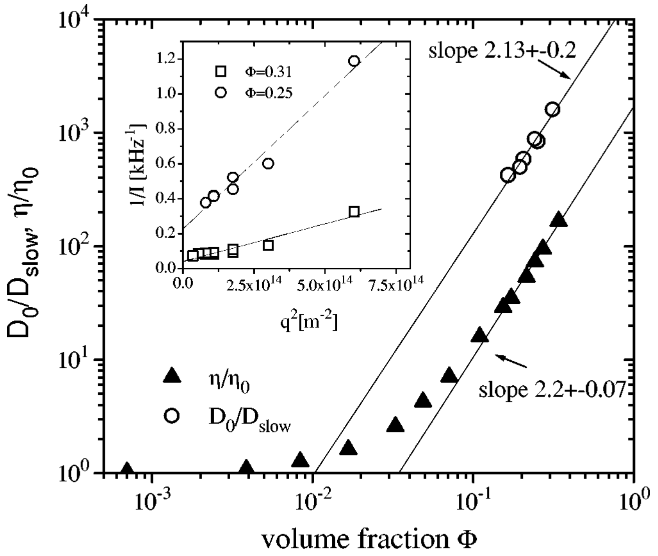

FIG. 4. Reduced diffusion coefficient D_0/D_{slow} is plotted against polymer volume fraction Φ together with the reduced macroscopic viscosity η/η_0 (D_0=diffusion coefficient at infinite dilution, η_0 solvent viscosity). The inset shows an Ornstein-Zernicke plot of the static scattering intensity I_{VV}.

For the colloidal PMMA system the authors interpreted the slow process as a structural relaxation. This was mainly concluded from the fact that long time diffusion and viscosity show exactly the same Φ dependence only, when the diffusion coefficient is measured at q_m, the peak position of the static structure factor [25]. For the star polymer solution $q_m\approx0.05$ Å^{-1} much larger than the q values covered in our experiment. Thus, the here observed difference cannot be explained in this way but must relate in a different way to the colloidal character of the star solution.

Our observations appear to have some close analogy to findings on OTP and bulk polymers by Fischer and coworkers [11,24]. There, these authors observed both a slow $q2$ dependent process in DLS as well as a q-dependent excess scattering in static light scattering. It has been suggested that the excess scattering and the ultraslow relaxation are characteristic features relating to long range density fluctuations inherent to any glassforming liquid [11]. In our study we appear to have observed this phenomenon in a colloidal-like system, where the glass transition is not driven by temperature but by concentration.

Thus, we conclude that the dynamics of star polymer solutions above the overlap concentration c^* reveal features of both (i) solutions of linear homopolymers and (ii) colloidal systems. The polymer aspect concerns the collective short time dynamics following the renormalization group description, which is shown to be valid independent of the polymer architecture. In addition long range density fluctuations giving rise to an *ultraslow* diffusive mode are observed. They stand for the colloidal aspect and indicate a nearby concentration driven glass transition. These results underline the importance of star polymers as a link between polymer and colloidal properties. Star polymers can be considered as a new class of colloids, which we would like to call *ultrasoft* colloid, due to the long range logarithmic interaction potential (see Ref. [4]).

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