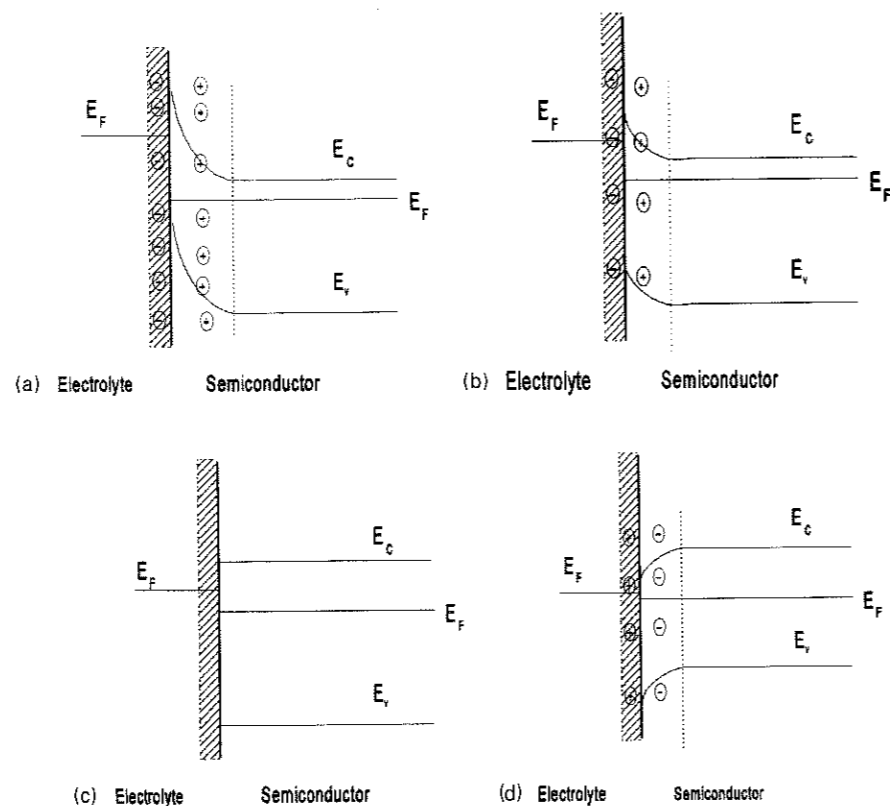


Fig. 4 Schematic representation of the proposed mechanism for the observed slow OH⁻ consumption in our TiO₂/water interface. E_F : Fermi energy level; E_c : Energy associated to the floor of the semiconductor conduction band; E_v : Energy associated to the top of the semiconductor valence band



Finally, the proposed mechanism justifies the observed pH drop, an object of future work for its validation with a quantitative support. In ref. [7] the electrolyte/semiconductor interface is considered to have a behaviour which is in agreement with the one proposed here. We remark again that the effect of the CO₂ is probably superimposed to the one described, which the authors consider as the dominant mechanism for the observed OH⁻ slow consumption.

The procedure followed for the determination of the PZC, has been useful for our semiconducting particles of titanium dioxide and may also be a good method for other semiconductor suspensions.

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Structure and dynamics of star polymers

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Abstract The structural and dynamical properties of an 18-arm poly(isoprene) star polymer ($M_n^{\text{arm}} = 7360 \text{ g mol}^{-1}$) are investigated by experiment and theory. Light scattering techniques reveal the existence of static and dynamic long range correlations ($\xi \approx 100 \text{ nm}$) above the overlap concentration c^* , which are an indication for a structural glass transition at higher concentrations. Combining statistical-mechanical theories and small angle neutron scattering (SANS), it is shown that the effective pair potential between star polymers is exponentially decaying for large distances and crosses over, at a density-

dependent corona diameter, to an ultra-soft logarithmic repulsion for small distances. Finally, neutron spin echo spectroscopy (NSE) is used to investigate the influence of interstar entanglements on the internal dynamics of the star polymer. Hence, star polymers can actually be viewed as hybrids between polymer-like entities and colloidal particles establishing an important link between these different domains of physics.

Key words Star polymer – colloids – neutron scattering – light scattering – liquid state theory – Monte Carlo simulations

Introduction

Regular star polymers consist of a well-defined number f of flexible polymer chains tethered to a central microscopic core. By enhancing this functionality (or arm number) f which governs the interpenetrability of two stars, one can continuously switch from unbranched polymer chains ($f = 1, 2$) to a colloidal sphere ($f \gg 1$). Hence, star polymers can actually be viewed as hybrids between polymer-like entities and colloidal particles establishing an important link between these different domains of physics. Moreover, star polymer solutions reveal quite a number of novel structural and dynamical properties which occur neither in single-chain polymers nor in suspensions of colloidal spheres, for recent reviews see [1, 2].

Here we present a comprehensive study of the structural and dynamical properties of star polymer solutions, in particular in the concentration range above the overlap concentration $c^* = (3/(4\pi R_g^3)) \times (M_w/N_A)$. Using neutron (SANS, NSE) and light scattering techniques (SLS, PCS), combined with viscometry, it is possible to investigate a spatial and temporal range spanning from microscopic to macroscopic length and time scales. The experimental work is compared to new theoretical approaches using a recently proposed pair potential [3] as a description of the particle interaction. In the theoretical investigations, we use standard liquid-state theory techniques to obtain accurate data for the structure and thermodynamics of the fluid phase and density-functional theory to investigate the phase diagram of the system as a function of concentration and arm number.

Experimental

The partially labeled 18-arm polyisoprene (PI) star was prepared by anionic polymerization following an established procedure [4, 5]. The synthesis of the arms started with deuterated PI and secondary butyl lithium as initiator and proceeded with protonated PI. The still living polymer chains were coupled to the linking agent octadeca-chlorosilan. The result of the synthesis is a labeled 18-arm star with a near-monodisperse molecular weight distribution, which has a protonated core and a deuterated shell. Light scattering experiments were performed on a standard set-up (ALV-125 compact goniometer, Ar⁺-Laser $\lambda = 514.5$ nm, ALV5000E correlator). The SANS and NSE experiments were performed at the FRJ-2 reactor of the Forschungszentrum Jülich. 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 (For the light scattering experiments protonated methylcyclohexane was used). Samples covering polymer volume fractions ϕ in the range $5 \times 10^{-4} \leq \phi \leq 0.33$ were investigated.

Results and discussion

In a recent dynamic light scattering study [6] of PI star solutions ($f = 18$) we find two dynamical regimes: (i) Polymer like relaxation dynamics at short times with a collective response following the renormalisation group theory [7, 8] independent of the polymer architecture. (ii) At long times above c^* a very well separated second slow dynamic regime reveals itself in star polymer solutions, see Fig. 1. This slow diffusive process is connected to low angle excess scattering and indicates long range, slow density fluctuations, with $\zeta_{\text{slow}} \gg R_g$, reminiscent of features of the glass process [9]. Comparing the reduced diffusion coefficient D_0/D_{slow} and the reduced macroscopic viscosity η/η_0 ($D_0 =$ diffusion coefficient at infinite dilution, η_0 solvent viscosity), it is found that both show the same scaling law above c^* , $\sim c^{-2.1}$, but the ratio of the diffusion coefficients is two orders of magnitude larger than the ratio of the viscosities. These experimental results resemble properties that have been recently reported for a colloidal PMMA system [10]. Those 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. For the star polymer solution $q_m \approx 0.05 \text{ \AA}^{-1}$ is much larger than the q values covered in our experiment. Thus, the difference observed here cannot be explained in

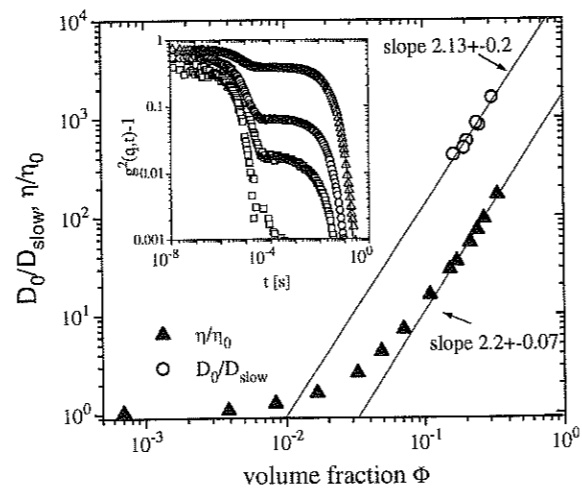


Fig. 1 The reduced diffusion coefficient D_0/D_{slow} is plotted against polymer volume fraction ϕ together with the reduced macroscopic viscosity η/η_0 ($D_0 =$ diffusion coefficient at infinite dilution, η_0 solvent viscosity). The inset shows the intensity autocorrelation functions for the star polymer at $c \geq c^*$ together with that of a linear polymer

this way but must relate in a different way to the colloidal character of the star solution.

For describing the SANS data we make use of a pair potential [11] $V(r)$ for star polymers which reads as follows [3]:

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

The potential $V(r)$ is an interpolation between a Yukawa-form, suitable for $r > \sigma$, and a logarithmic behavior, appropriate for $r < \sigma$, shifted by a constant which is chosen in such a way that the potential is smooth at $r = \sigma$. The logarithmic form of the interaction sets in when two stars are separated by such a distance that the outermost blobs of the stars in the Daoud-Cotton model [1, 12] fully overlap, i.e., $\sigma/2$ is the distance from the center of the star to the center of the outermost blob. By geometry, the latter has a radius $R_b = \sigma/\sqrt{f}$. We now take the pair potential given by Eq. (1) and apply the Rogers-Young (RY) closure [13] and associated Monte Carlo simulations to obtain information about the pair structure of the liquid, in particular the center-to-center 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

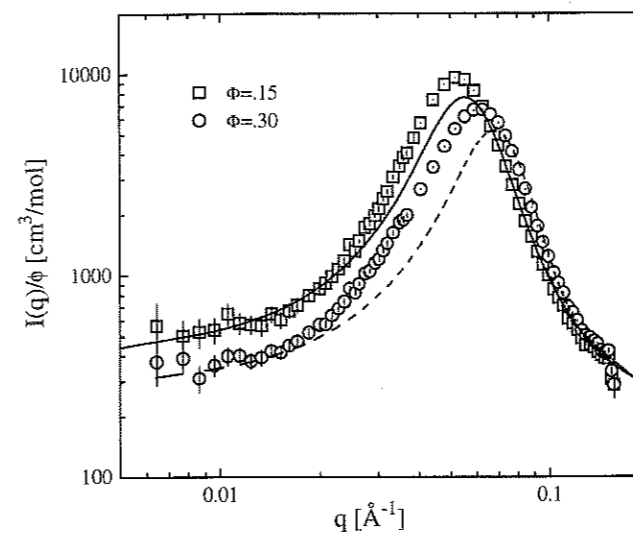


Fig. 2 Experimental (points) vs. theoretical results (lines) for the total scattering intensity $I(q)/\phi$ of 18-arm stars at various volume fractions ϕ . From top to bottom $\phi = 15$ and 30%

dependence on the concentration ϕ , as was earlier found experimentally [14, 15]. Accordingly, the length σ must also have a ϕ -dependence, $\sigma = \sigma(\phi)$. We fixed this dependence as follows: for the lowest concentration considered, $\phi = 2\%$ we obtain σ by optimizing the agreement between the theoretical prediction and the experimental results. For the potential given by Eq. (1), we obtain in this way $\sigma(\phi = 2\%) = 96 \text{ \AA}$. At the same concentration, the experimentally measured radius of gyration is $R_G(\phi = 2\%) = 76.1 \text{ \AA}$ [14, 15]. This fixes once and for all the ratio $\sigma/R_G \equiv \tau = 1.26$. For all other concentrations ϕ we set $\sigma(\phi) = \tau R_G(\phi)$, where $R_G(\phi)$ is read off from the experimental results [14, 15]. In this way we can say that our fit contains *no adjustable parameters* since σ does not vary arbitrarily with ϕ , but rather in a way dictated by the measured values of the size of the star. Moreover, the value $\sigma = 96 \text{ \AA}$ yields a theoretical prediction 70.63 \AA for the star radius which is within two error bars from the experimental result. In Fig. 2 we show representative results for $\phi = 15$, and 30%. It can be seen that the fit is quite satisfactory for the whole range of concentrations. In particular, the compressibility of the solution, being proportional to $I(q \rightarrow 0)$ is given correctly for all concentrations, as well as the general shape and wavenumber q_{max} at which the scattering intensity displays a maximum. The height of the peak is underestimated by the theory and the agreement worsens somewhat as the concentration grows. However, at high values of ϕ the decoupling between form- and structure factors implied in writing down $I(q) = V_W P(q) S(q)$ becomes questionable and this is a possible source of discrepancies between theory and

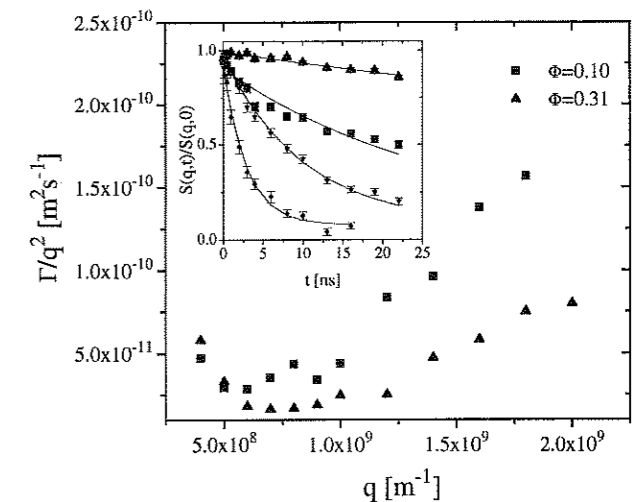


Fig. 3 The reduced relaxation frequencies Γ/q^2 show a minimum when plotted against scattering vector q . The insert show $S(q, t)$ obtained at a polymer volume fraction $\phi = 0.31$, from top to bottom: $q = 0.06, 0.12, 0.16, 0.2 \text{ \AA}^{-1}$

experiment. We emphasize that our logarithmic-Yukawa potential is the first that gives semi-quantitative agreement between theory and experiment for such a wide range of concentrations. Earlier attempts to fit the experimental results with a hard sphere - Yukawa interaction, for example, failed at and beyond the overlap concentration ϕ^* [16]. Indeed, the existence of a "soft core", such as the logarithmic term in our potential is crucial at high concentrations where the stars start interpenetrating.

Due to the applied matching conditions neutron spin echo experiments (NSE) observe the collective motion of the star centers if we measure close to the structure factor peak (for our star polymer this occurs around $q_m \approx 0.05 \text{ \AA}^{-1}$ in the concentration regime of interest, see previous section). With increasing scattering vector more and more contributions from internal segmental motions inside the core become visible. The reduced relaxation frequencies Γ/q^2 , where Γ is obtained from the initial slope of $S(q, t)/S(q, 0)$, show a minimum at the structure factor peak, see Fig. 3. This minimum is a characteristic feature of star polymer solutions. In dilute solution it arises due to the special molecular architecture of the star polymers [17]. Above c^* intermolecular interactions come into play and the observed phenomenon resembles the *deGennes narrowing* known from simple liquids. The depth of the minimum increases with increasing concentration. Moreover, in the high q -range a strong concentration effect is unexpectedly found, which might result from entanglements in the star shell affecting the internal motions of the core. For illuminating this hypothesis we have investigated the dynamics of a smaller star with size equal to the

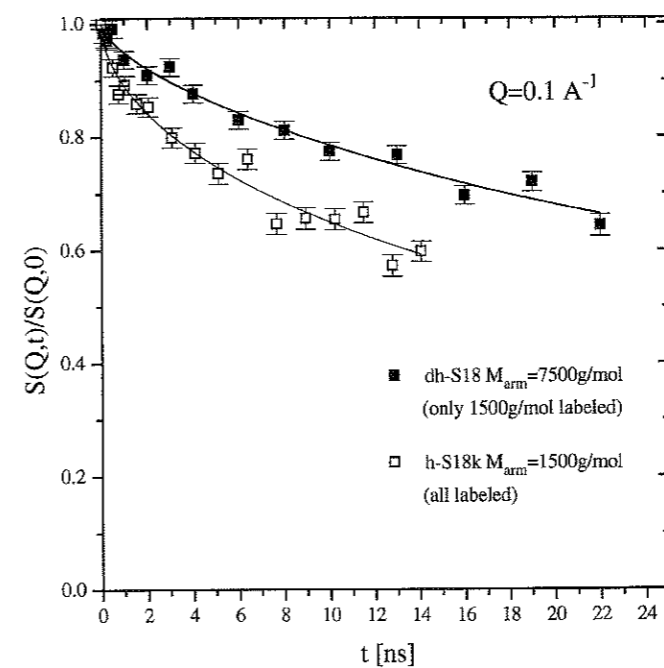


Fig. 4 NSE spectra for two star polymers with M_{arm}^{arm} well below (open symbols) and above (filled symbols) the entanglement molecular weight of polyisoprene $M_e \approx 5000$ g/mol; solid line: fit to a stretched exponential, see text

protonated core of the former one. Both stars have been dissolved separately in a matrix of a fully deuterated star ($M_n^{arm} = 7360$ g mol $^{-1}$, $\phi_{matrix} = 0.26$). Preliminary results from these experiments are shown in Fig. 4. As can be clearly seen, entanglements slow down the dynamics as expected. Both spectra have been fitted, after correction for

resolution and background, to a stretched exponential decay (Kohlrausch–Williams–Watts function); $S(Q, t)/S(Q, 0) = A \exp(-(\Gamma t)^\beta)$. Whereas the characteristic decay times $\tau = 1/\Gamma$ of both spectra are well separated, the stretching exponents are very similar, 0.60 ± 0.03 for h-S18k and 0.67 ± 0.04 for dh-S18. Thus, the lineshape seems to be not affected by the presence of entanglements.

Conclusions

Structure and 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 renormalisation group description, which is shown to be valid independent of the polymer architecture, and the influence of entanglements on the internal segmental motions. In addition long range density fluctuations give rise to an *ultra slow* diffusive mode observed by PCS indicating a nearby concentration-driven glass transition. Combining statistical-mechanical theories and SANS it is shown that the effective pair potential between star polymers is exponentially decaying for large distances and crosses over, at a density-dependent corona diameter, to an ultra-soft logarithmic repulsion for small distances. The latter two results stand for the colloidal aspects and 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 *ultra soft* colloid.

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