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Neutron spin echo study of the dynamics of micellar solutions of randomly sulphonated polystyrene

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Abstract

The dynamics of phase separated micellar solutions of randomly sulphonated polystyrene ionomers in toluene were examined with neutron spin echo spectroscopy (NSE). The correlation functions demonstrated single exponential decays with a constant background offset. The relaxation rate (Γ) of the ionomer micelles at small length scales in the q range 0.075–0.16 Å^{-1} was diffusive ($\Gamma \sim q^2$) as expected for the collective breathing mode of a cross-linked gel. At intermediate length scales in the q-range 0.025–0.075 Å^{-1} the relaxation rates were non-diffusive ($\Gamma \sim q^{0.36}, q^{0.72}$), which is attributed to the hopping dynamics of the individual stickers inside the ionomer micelles ($\tau_{\text{sticker}} \sim 10$ ns). At large length scales the scattering due to the phase separated inhomogeneities of the micellar network did not relax on the time scales of the measurements (<20 ns), giving rise to a constant background on the correlation functions. This slow relaxation process may be due to the hopping dynamics of whole micelles previously observed in rheology experiments ($\tau_{\text{micelle}} \sim 0.05$ s). The NSE results are in agreement with a model developed in previous small-angle neutron scattering and rheology experiments for concentrated solution of ionomeric micelles. The NSE results for the associating ionomers are markedly different from the Zimm dynamics ($\Gamma \sim q^3$) previously observed for semi-dilute and cross-linked polystyrene polymers in a good solvent. The ionomeric cross-links thus have a large impact on the polymer chain dynamics at the nanosecond time scale.

Keywords: Ionomer; Neutron spin echo; Dynamics

1. Introduction

Linear ionomers in solution offer an ideal system to study the structure and dynamics of sticky polymers [1]. Previously we studied the behaviour of randomly sulphonated ionomers (1% monomer fraction containing stickers) using a combination of small-angle neutron scattering (SANS), static and dynamic light scattering, and bulk rheology [2]. Using these techniques we developed a model for the microphase separated micellar structure of the ionomers in solution. Toluene acts as a good solvent for the polystyrene backbone, providing well defined statistics for the sections of polymer chain between the stickers. The SANS experiments demonstrated two important static length scales in the polystyrene sulfonate (PSS) ionomer solutions; the polymer mesh size which followed the prediction for unmodified polystyrene chains obeying good solvent statistics (ξ), and a length scale (Ξ) due to the microphase separated structure of the micellar aggregates ($\Xi = (1/L_1 + 1/L_2)^{-1}$, Fig. 1). Linear rheology experiments show an almost perfect Maxwell type behaviour at low frequencies for the PSS ionomer solutions whose relaxation time decreases with concentration. This unusual behaviour (relaxation times normally increase with concentration for non-associating polymers [3])

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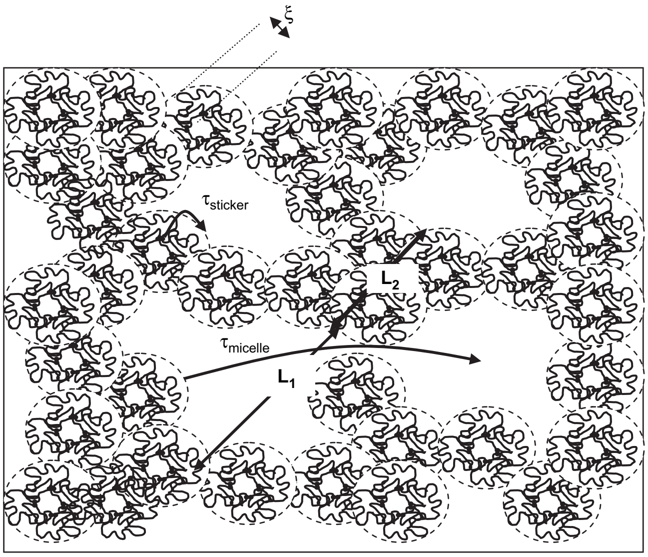

Fig. 1. Schematic diagram of the micro phase separated structure of random ionomer micelles. L_1 and L_2 are the average chord length of the polymer rich and depleted regions, respectively [2] ($1/\Xi = 1/L_1 + 1/L_2$). τ_{micelle} and τ_{sticker} correspond to the time scales for micelle hopping and sticker hopping, respectively.

was predicted by Semenov and Rubinstein using a dynamic scaling theory for micelle hopping of the associating polymeric aggregates [4]. Dynamic light scattering experiments at low PSS concentrations provided evidence for an open association model for the aggregation of the sticky micellar chains [2].

The neutron spin echo (NSE) technique has been extensively used with semi-dilute solutions of polymers in good solvents [5,6]. NSE allows the dynamics of polymers to be probed at the nanometer length scale (4.2–31.4 nm) and at very fast time scales (1–20 ns). Unlike dynamic light scattering, NSE can be used to probe concentrated solutions, since multiple scattering effects are reduced. The dynamics of the blobs of flexible polymer chains in semi-dilute solutions are typically found to be Zimm-like at length scales smaller than the chain mesh size [3] i.e. the chains experience unscreened hydrodynamic coupling between their monomers with the relaxation rate (Γ) proportional to the momentum transfer cubed (q^3). There have been fewer NSE studies with chemically cross-linked polymer gels. A cross-over between a collective gel diffusive mode at low q and Zimm hydrodynamics at high q is seen with the poly(dimethylsiloxane) gels of Hecht et al. [7]. Again in the low q Guinier regime collective gel diffusion is observed with cross-linked polyfluorosilicone gels [8]. A study was made of the physical gelation of atatic polystyrene in carbon disulfide where a significant slowing down of the cooperative diffusive motions of the chains was observed at the gel point [9]. Diffusive internal motion was observed in a PNIPAM polymeric microgel crystal [10], illustrating the close connection between polymer gel and colloidal gel hydrodynamics [11]. Non-ergodicity of the correlation functions due to the combination of a frozen and a thermal fluctuating part of the chain dynamics has been observed in a poly(N-isopropyl acrylamide) gel [12].

In this article we present evidence for diffusive dynamics of ionomeric gels at small length scales and sub-ballistic dynamics of individual chain stickers at larger length scales. The physical dipolar cross-links between the ionomer chains thus have a large impact on the resultant polymer chain dynamics and NSE should prove to be a powerful tool for the investigation of this behaviour.

2. Method

Neutron spin spectroscopy (NSE) as employed in the current work is the spectroscopic counterpart of SANS. The analysed scattering intensity is the SANS intensity and in the investigated q-range it predominantly results from the coherent scattering contrast between the protonated polymer and the deuterated solvent. NSE measures the spatial Fourier transform of the polymer density–density correlation; the intermediate scattering function $S(q,t)$. It is calculated from the Fourier transform of the scattering function $S(q,\omega)$ in the time frequency domain. The latter is performed by the mechanism in which the NSE spectrometer generates its signal. The NSE experiments have been performed at the FRJ2-NSE in the ELLA guide hall at the DIDO reactor in Juelich. The neutron wavelength was 8 Å and the Fourier time range $0.1\ \text{ns} < t < 22\ \text{ns}$. The q-range was covered by settings of the scattering arm of $q = 0.05\ \text{Å}^{-1}$, $0.08\ \text{Å}^{-1}$, $0.11\ \text{Å}^{-1}$, $0.14\ \text{Å}^{-1}$ each of these nominal q-values pertains to the center of the area detector which covers $\sim \pm 0.02\ \text{Å}^{-1}$. A posterior analysis allows good statistics to be off set (summing the whole detector) against improved q-resolution by treating up to four separate detector zones separately. The samples were placed into $3 \times 3\ \text{cm}^2$ HELLMA quartz cells with 2 mm or 4 mm thickness and held at an ambient temperature of 296 K. The background from a quartz cell filled with a pure solvent has been subtracted [13].

2.1. Samples

The two polystyrene samples ($M_w = 158\ \text{kg mol}^{-1}$ and $87\ \text{kg mol}^{-1}$; the polydispersity was 1.55 for both the samples with no important variation after the sulfonation) were prepared by bulk free-radical polymerization using benzoyl peroxide as initiator. For homogeneous sulfonation, the method developed by Makowski et al. was used to obtain the poly(styrene-*co*-styrenesulfonic acid) samples [14]. To determine the acid content, the samples were dissolved in a benzene/methanol (9/1 v/v) mixture to make 5% (w/v) solution, and titrated with standard methanolic NaOH to the phenolphthalein end point. The neutralization of the acid groups was performed by the addition of a predetermined quantity of methanolic CsOH solution to a 5% (w/v) acid copolymer solution in a toluene/methanol (9/1 v/v) mixture. The concentration of the polymers in solution is reported in moles of monomer per litre of solution (M). The ionomers were dissolved in deuterated toluene in all of the experiments. All the samples examined corresponded to 1% sulfonation. The samples for NSE experiments were prepared at 10% w/w polymer/solvent. Toluene has a viscosity of 0.5911 cP and 0.3270 cP, at 20 °C and 80 °C, respectively.

3. Results

Small-angle neutron scattering data is shown from polystyrene ionomer samples at 20 °C from the two molecular weights 158 kg mol^{-1} and 87 kg mol^{-1} (Fig. 2, [2]). Such data for well characterised randomly sulphonated polystyrene ionomers led us to develop a static structural model for ionomer micelles, which was subsequently found to be in agreement with a theoretical model of Semenov and Rubinstein for associating polymers (Fig. 1, [4]).

NSE correlation functions were collected at 19 separate q values ($q = 4\pi/\lambda \sin\theta/2$, θ is the scattering angle and λ is the wavelength) for both the samples at 10% w/w concentration. The intermediate scattering functions ($S(t,q)$) from the NSE data were found to be predominantly single exponential with a constant offset (Fig. 3). Data was therefore fit to the expression

$$S(t,q) = A_s(q) + A_f(q)e^{-\Gamma t} \tag{1}$$

where $A_s(q)$ is a constant q dependent background, $A_f(q)$ is the amplitude of the fast mode as a function of q, and Γ is the relaxation rate of the ionomer gel. The static scattering intensity ($I(q)$) could therefore be decomposed into an ergodic ($I_{erg}(q)$) and a non-ergodic component ($I(q) - I_{erg}(q)$) as a function of momentum transfer, Fig. 2, [7].

$$I_{erg}(q) = \frac{A_f(q)}{A_s(q) + A_f(q)} I(q) \tag{2}$$

At small length scales (between the mesh size (ξ) and the phase separated length (Ξ)) the dynamic modes are ergodic whereas at larger length scales there is a clear occurrence of both ergodic and non-ergodic modes (Fig. 2) i.e. a constant offset at long times. Such a behaviour has been observed previously in NSE experiments with poly(N-isopropyl acrylamide) gels [12].

Subsequently the relaxation rates extracted from the intermediate scattering functions were divided by q^2 to form the effective diffusion coefficient (D), $D = \Gamma/q^2$, and plotted as a function of the wave vector (q) to determine the nature of this dynamic mode (Fig. 4). The relaxation rates for the two molecular weights (87 kg mol^{-1} and 158 kg mol^{-1}) were in fair agreement at high q indicating that the mesh dynamics

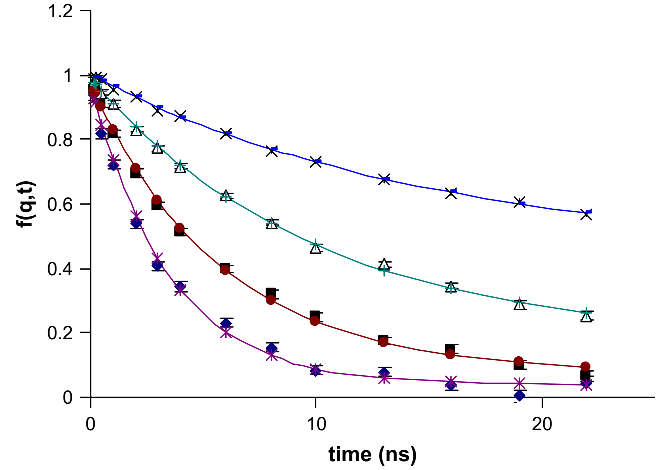

Fig. 3. Neutron spin echo correlation functions for PSS 158K at 10% w/w, 20 °C (diamonds $q = 0.14$ Å^{-1}, squares $q = 0.11$ Å^{-1}, triangles $q = 0.08$ Å^{-1}, and crosses $q = 0.05$ Å^{-1}). Error bars are shown on the figure derived from the neutron count statistics.

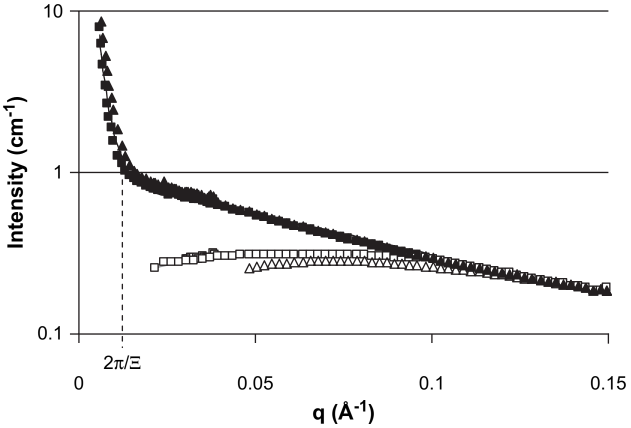

Fig. 2. The intensity as a function of momentum transfer is shown for small-angle neutron scattering experiments from PSS ionomers of two molecular weights 158K (filled triangles) and 87K (filled squares) at 10% w/w, 20 °C. The ergodic fraction of the static scattering signal deduced from NSE experiments is shown as open symbols. $2\pi/\Xi$ shows the q value associated with the micro phase separated mesh size. The fit of Eq. (3) to 87K PSS is shown by the continuous line.

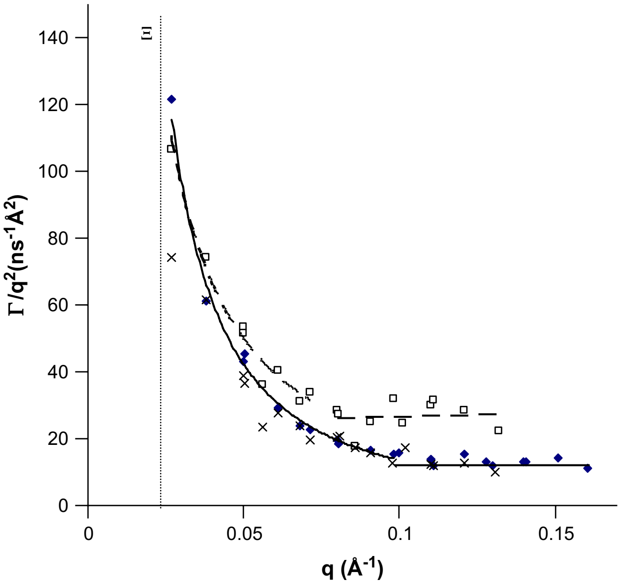

Fig. 4. Effective diffusion coefficients (Γ/q^2) as a function of momentum transfer (q). Squares indicate PSS 87 kg mol^{-1} at 80 °C, diamonds indicate PSS 87 kg mol^{-1} at 20 °C and crosses indicate PSS 158 kg mol^{-1} at 20 °C. The average chord length ($1/\Xi = 1/L_1 + 1/L_2$) for the micro phase separated structure is shown. The static correlation length (ξ) corresponds to 0.31 Å^{-1}. Continuous straight lines indicate diffusive motion of the ionomer gels at small length scales.

was independent of molecular weight ($D \sim M_w^0$). An increase in the temperature (80 °C) caused an increase in the sample dynamics, but did not significantly change the q dependence of the relaxation rates at small length scales ($\Gamma \sim q^2$). At small length scales diffusive behaviour was observed, whereas at large length scales relaxation rates become sub-linear in q ($\Gamma \sim q^{0.36}$ for PSS 87K and 158K at 20 °C, and $\Gamma \sim q^{0.72}$ for PSS at 80 °C).

4. Discussion

The static scattering intensity ($I(q)$) for small-angle neutron scattering experiments was shown in a previous article to follow the functional form

$$I(q) = \frac{I_1(0)}{\left(1+q^2\xi^2\right)} + \frac{I_2(0)}{\left(1+q^2\Xi^2\right)^2} \tag{3}$$

where ξ is the mesh size, Ξ is the micro phase separated length, and $I_1(0)$ and $I_2(0)$ are two constants [2]. This model provides a good fit to data such as that shown in Fig. 2, throughout the q range. The first term in Eq. (3) is due to the semi-dilute mesh of polystyrene chains in the ionomer micelles at short length scales and the second term is due to a micro phase separated micellar structure at larger length scales. For a semi-dilute polymeric solution or gel the relationship between the diffusion coefficient (D) and the dynamic correlation length (ξ_h) from a mode-coupling scaling theory is given by an expression identical to the Stokes–Einstein relationship [15]

$$D = \frac{kT}{6\pi\eta\xi_h} \tag{4}$$

where η is the viscosity of the solution and kT is the thermal energy. This relationship has been well tested for a large range of gelled/semi-dilute polymeric systems [16] and is in good agreement with experiment.

Extrapolating the diffusion coefficient (D) of the ionomers at small length scales (Γ/q^2 is q independent) to zero q, we find that the diffusion coefficient is 5.53 Å^2 ns^{-1}, 9.0 Å^2 ns^{-1} and 24.7 Å^2 ns^{-1} for 20 °C 85K, 20 °C 158K, and 80 °C 85K, respectively. From Eq. (4) we can thus calculate the hydrodynamic mesh size (ξ_h) to be 65 Å, 40.4 Å and 32.0 Å for 20 °C 85K, 20 °C 158K, and 80 °C 85K, respectively.

Previous SANS measurements give the static correlation length (ξ) to be 20 Å at 10% w/w ionomer concentration, independent of the molecular weight of the chains, in reasonable agreement with the hydrodynamic mesh size from the NSE results. From the molecular weight independence of the relaxation rates at fast times we deduce that the correlation functions measured at small length scales correspond to the breathing modes of the semi-dilute mesh. However, at large length scales, this is not the case with the micellar system, since the results are non-diffusive, showing a much weaker scaling with q ($\Gamma \sim q^{0.73}$, $q^{0.36}$) and correspondingly faster dynamics. Cipelletti et al. [17] attributed ballistic colloidal motion ($\Gamma \sim q$) in DLS experiments to a broad distribution of random particle velocities and a characteristic velocity (v) of $1/\tau q$. The correlation functions such as those measured with NSE are sensitive to a constant velocity offset (convection in a single direction [18]) and such a motion can be unequivocally discounted from the analysis. However, similar to DLS we conclude that a random distribution of velocities (e.g. in a gas of micelles) would lead to a non-zero ballistic relaxation rate. The hopping time scale we are measuring (∼10 ns) is much faster than that observed for the terminal relaxation time in previous rheology experiments [2,4] (∼0.05 s). We thus attribute the non-diffusive behaviour of the relaxation rate from the random ionomer solutions as due to the sub-ballistic hopping dynamics of polymer chain sections attached to single stickers ($\tau_{\text{hopping}} \sim$ 10 ns, Fig. 1). The hopping behaviour of whole ionomer micelles has been clearly observed in the decrease in relaxation time with concentration in previous linear rheology experiments and this occurs at much slower time scales ($\tau_{\text{micelle}} \sim$ 0.05 s, Fig. 1) than the sticker hopping time, leading to the constant offset on the NSE correlation function.

The change in the cooperative dynamics of the gelled micellar network as a function of temperature cannot just be solely explained by the change in the temperature dependent factor, T/η, in Eq. (4) ($T_1/\eta_1/T_2/\eta_2 = 2.2$ for 85K at 20 °C and 80 °C, whereas the ratio of the two diffusion coefficients is $D_1/D_2 = 4.47$). We conclude that there is a significant change in the nature of the dynamics of the network with temperature, possibly due to the activated motion of the stickers.

NSE thus has provided evidence for hopping dynamics of the stickers of the ionomer chains at the 10 ns time scale. A more detailed study is required to fully describe the scaling of the dynamics with polymer concentration and temperature, but unusual phenomena are observed when compared with conventional gels and semi-dilute polymer solutions.

5. Conclusions

Neutron spin echo experiments can be used to probe the dynamics of sticky ionomer gels at ultra short times in concentrated solutions. The behaviour observed is in good agreement with a previous experimental model developed on the basis of SANS, linear rheology and developed separately in the theory of Rubinstein/Semenov [4]. NSE is sensitive to the hydrodynamics of the ionomer chains at length scales in the order of the static correlation length and indicates diffusive gel modes ($\Gamma \sim q^2$). At larger length scales sub-ballistic modes ($\Gamma \sim q^{0.72}$, $q^{0.36}$) are observed which are attributed to the hopping motion of polymer chain sections attached to individual ionomer stickers. An additional slow dynamic mode was measured at large length scales in the samples and is thought to be due to the relaxation of inhomogeneities in the micellar gel network, possibly by means of whole micelle hopping motions, as observed in previous linear rheology experiments.

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