

Telechelic ionomers studied by light scattering and dynamic mechanical measurements

Chassenieux Christophe⁽¹⁾, Johannsson Ragnar⁽¹⁾, Durand Dominique⁽¹⁾, Nicolai Taco⁽¹⁾, Vanhoorne Pierre⁽²⁾, Jérôme Robert⁽²⁾

⁽¹⁾ Laboratoire de Physico Chimie Macromoléculaire, URA CNRS, Université du Maine, 72017 Le Mans Cedex, France

⁽²⁾ Centre for Education and Research on Macromolecules, Inst, of Chemistry B6, University of Liège, Sart Tilman, 4000 Liège, Belgium

Abstract

The formation of a transient network by α,ω -sodium sulfonato polyisoprene (α,ω -NaPIPS) and α,ω -lithium sulfonato polystyrene (α,ω -LiPSS) in toluene is studied using static and dynamic light scattering and dynamic mechanical analysis. It is shown that at low concentrations aggregates are formed with increasing molar mass and polydispersity as the polymer concentration is increased. Above a certain concentration well below the overlap concentration of the polymer chains (C^*), a transient network is formed. This is characterised by a plateau modulus at high frequencies and a relatively narrow viscoelastic relaxation time distribution. The intensity auto-correlation function of the transient network shows two relaxational modes: a relatively fast diffusional mode close to the cooperative diffusional mode of semidilute solutions of the unfunctionalised polymers, and a slow broader mode which becomes independent of the scattering angle at concentrations close to C^* . The relation between this slow mode and the viscoelastic relaxation is discussed.

Keywords: Associative polymers; Dynamic mechanical analysis; Light scattering; Telechelic ionomers

1. Introduction

It is well known that the ionic groups situated at one or both ends of apolar polymers associate into multiplets when dissolved in apolar solvents, due to attractive interactions between dipoles [1]. Although the size and structure of the multiplets depend strongly on the particularities of the system (e.g. solvent, type of counter ion, type of ionic group, size and type of the polymer), for a given system the size of the multiplet is well-defined, with a narrow distribution around the average number of ionic groups per multiplet (n_m). The strength of the dipole interactions and thus the average life time of an ionic group in the multiplet can be tuned by changing the temperature, or by addition of polar additives. These features make telechelic ionomers good model systems for associative polymers in general. We believe that the conclusions based on the experimental observations presented here, are to a large extent valid for associative polymers in general and for telechelic polymers especially. Here we present the results of an investigation of high molar mass telechelic ionomers using static light scattering (SLS), dynamic light scattering (DLS) and dynamic mechanical analysis (DMA). We have studied polyisoprene (PIP) and polystyrene (PS) of molar mass 10^5g mol^{-1} end-capped with sulfonate groups in Spectra grade toluene. A study of the transient network formed by double end-capped PIP is described in detail elsewhere [2] and only the main results are repeated here. In this study we investigate the formation of the transient network by a study of the aggregation of single and double end-capped polystyrene in dilute solutions by SLS and DLS. Due to the low scattering contrast this cannot be done for PIP.

2. Experimental

2.1. Materials

α,ω -sodium sulfonate polyisoprene (α,ω -NaPIPS), α,ω -lithium sulfonate polystyrene (α,ω -LiPSS) and ω -lithium sulfonate polystyrene (ω -LiPSS) were synthesised by living anionic polymerisation as described elsewhere [3]. The molar mass and polydispersity index were determined by size exclusion chromatography (SEC), (see Table 1). Due to the high molar mass, the functionality could not be determined by titration. However, when the functionalised polymers are passed through the SEC columns single end-capped polymers are strongly retarded and double end-capped polymers are

irretrievably adsorbed into the column material. From this observation we conclude that the functionalisation is almost complete for the systems studied here, which is also expected from direct measurements on lower molar mass polymers synthesised by the same method.

Table 1
 Sample characteristics

	$M_w(\text{g mol}^{-1})$	M_w/M_n
α, ω -NaPIPS	1.0×10^5	1.3
α, ω -LiPSS	0.9×10^5	1.4
ω -LiPSS	1.2×10^5	1.4

2.2. Sample preparation

The end-capped PIP contained traces of a high molar mass contaminant. In order to free the sample from spurious scatterers the polymer was first dissolved in Spectra grade THF. In this solvent α, ω -NaPIPS does not associate and can be filtered through 0.2 μm Anatope filters. The optical cleanliness after filtration was checked by DLS. The THF was subsequently removed by evaporation under vacuum, after which Spectra grade toluene was added to obtain the desired concentration. End-capped PS was directly dissolved in toluene. The samples were slowly rolled for 24 h to obtain homogeneous solutions.

2.3. Instrumentation

The frequency-dependent shear modulus was measured on a Rheometrics RDA II apparatus with plate—plate geometry. The response was found to be linear for deformations less than 40%. All measurements were done in the linear response regime at a deformation of 5%.

SLS and DLS measurements were done using an ALV-5000 multibit, multitaup full digital correlator in combination with a Malvern goniometer and an Ar-ion laser emitting vertically polarised light with a wavelength of 488 nm.

All measurements were done at $20 \pm 0.1^\circ\text{C}$ unless otherwise specified.

3. Results

3.1. Static Light Scattering

SLS and DLS measurements were done on α, ω -LiPSS over a wide concentration (C) range. For weakly interacting systems, the excess scattering intensity ($I - I_{S0}$) is related to the weight average molar mass of the particles (M_w) [4]:

Kc

$$= M_w^{-1}(1 + B_2C)/P(q)$$

$R\theta$

Here K is a contrast factor which depends on the refractive index increment and $R\theta = R_{t01} [(I - I_{S0})/I_{t01}]\theta$ is the Rayleigh ratio at scattering angle θ using toluene as a reference. B_2 is the second virial coefficient and $P(q)$ is the particle form factor which depends on the scattering wave vector $q = (4\pi n/\lambda) \sin(\theta/2)$ with n the refractive index and λ the wave length of the incident light. If q^{-1} is much larger than the overall size of the particles, $P(q)$ is close to unity. Values of $Kc/R\theta$ extrapolated to $q = 0$ are plotted in Fig. 1 as a function of the concentration for both single and double end-capped PS. At low concentrations interparticle interactions are negligible and $Kc/R\theta$ corresponds to the inverse of M_w . For both single and double end-capped, aggregates of four polymer chains are formed at low concentrations above the critical association concentration (CAC). If we assume that at these low concentrations the aggregates formed by ω -LiPSS contain mainly only one multiplet, we find an aggregation number of 4 for the single multiplet. This means that the number of ionic groups per multiplet (n_m) can have any value between 4 and 8 depending on how much back-folding occurs. For ω -LiPSS $CAC \approx 0.2 \text{ g l}^{-1}$ while for α, ω -LiPSS it is less than 0.01 g l^{-1} . In the case of α, ω -LiPSS the aggregation number does not depend on the concentration.

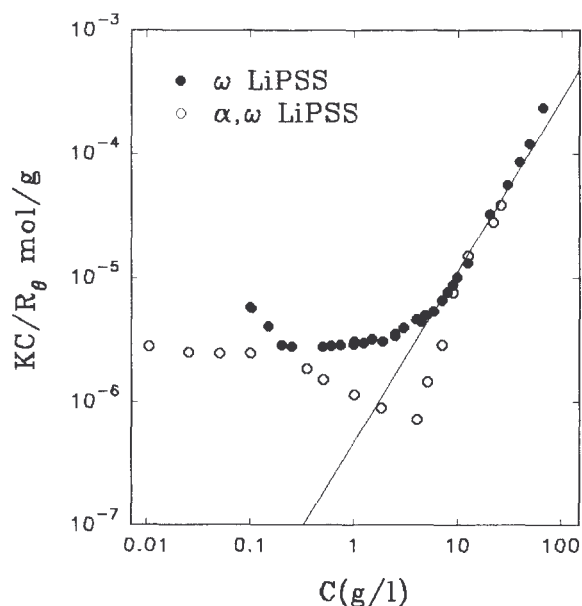


Fig. 1. Concentration dependence of $KC/R\theta$ for α,ω -LiPSS (open circles) and ω -LiPSS (filled circles) in toluene. The solid line is the result for semidilute PS in toluene.

The increase of $KC/R\theta$ at higher concentrations is due to inter-particle interactions. In the case of α,ω -LiPSS the aggregation number increases steadily with increasing concentration. The increase of $KC/R\theta$ at higher concentrations is again due to inter-particle interactions which dominate the increase of M_W at higher concentrations. At the highest concentrations the values of $KC/R\theta$ are close to those of semidilute linear and star-shaped PS solutions in good solvents [5].

3.2. DLS

The intensity auto-correlation functions, $g_2(t)$ obtained from DLS were analysed in terms of a continuous distribution of relaxation times:

$$g_1(t) = \int_0^{\infty} A(\tau) \exp(-t/\tau) d\tau,$$

where $g_1(t)$ is the normalised electric field correlation function related to $g_2(t)$ via the so-called Siegert relation [6]. The REPES routine was used to obtain $A(\tau)$ without assuming a specific shape [7]. Relaxation time distributions are shown in Fig. 2 for a number of concentrations of α,ω -LiPSS in toluene. At concentrations below 5 g l^{-1} , $A(\log \tau)$ is a single-peaked distribution while at higher concentrations the correlation functions are clearly characterised by at least two relaxational processes.

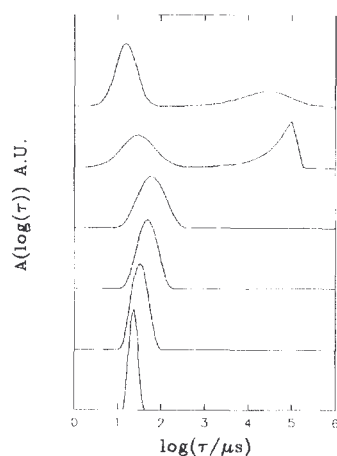


Fig. 2. Relaxation time distributions obtained from DLS at different concentrations of α,ω -LiPSS in toluene. From bottom to top $C = 0.05, 0.1, 1.0, 2.5, 12.5$ and 25 g l^{-1} .

The REPES routine represents the slower and broader mode in terms of multiple peaks. For this reason we have fitted the correlograms assuming for $A(\tau)$ the sum of a log—normal distribution to represent the fast mode, and a generalised exponential distribution [8] to represent the slow mode. This model fits the data very well. Details of the fit procedure are given in Ref. [2]. Starting from very dilute solutions, the average relaxation time increases and the distribution broadens with increasing concentration. The relaxation times are q^2 -dependent and can be used to calculate an apparent diffusion coefficient, $D_a = [q^2\tau]^{-1}$. At concentrations above 5 g l^{-1} , the faster mode is again q^2 -dependent. The q -dependence of the slow mode weakens with increasing concentration and becomes (q -independent at concentrations above 20 g l^{-1} over the q -range accessible to light scattering. At these higher concentrations additional even slower relaxations appear. The relative amplitude of these very slow and therefore ill-defined relaxations increases strongly with increasing concentration and decreasing scattering wave vector. We believe that they are caused by large-scale inhomogeneities in the samples which become increasingly viscous. In the analysis, the correlograms were cutoff at times shorter than the relaxation time of these very slow modes and their contribution was treated as a floating baseline. The z -average apparent diffusion coefficient is plotted in Fig. 3 as a function of the concentration. The data are compared with results from ω -LiPSS. For the latter system only single, relatively narrow, q^2 -dependent relaxation time distributions are observed over the whole concentration regime, except at very high concentrations for which we observe an additional slow q^2 -dependent relaxation. The relative amplitude of this mode increases strongly with increasing concentration and decreasing scattering wave vector. This mode is possibly due to a small amount of large particles, but we have as yet no explanation for their appearance. In the calculation of $KC/R\theta$ we have subtracted the contribution of this mode. At low concentrations the diffusion coefficient is consistent with that of a star-like polymer with four arms.

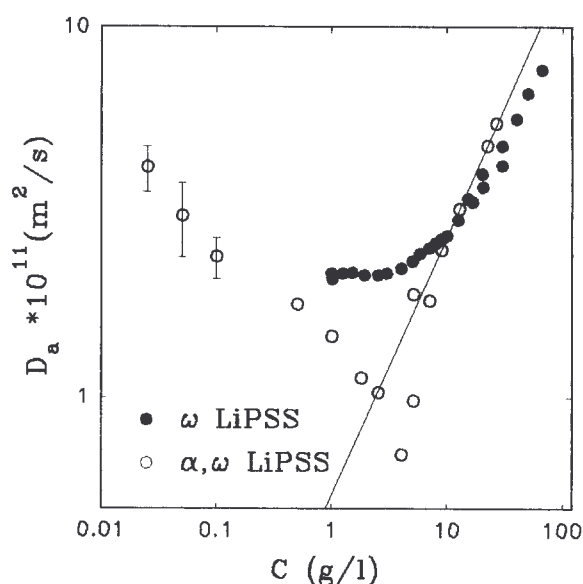


Fig. 3. Concentration dependence of the apparent diffusion coefficient of α,ω -LiPSS (open circles) and ω -LiPSS (filled circles) in toluene. The solid line is the result for semidilute PS in toluene.

At higher concentrations D_a increases in the same way as the co-operative diffusion coefficient of semidilute polystyrene in good solvents.

The apparent diffusion coefficient of α,ω -LiPSS decreases initially up to $C \approx 5 \text{ g l}^{-1}$. The decrease is due to an increase in the average size as interactions between the aggregates are negligible at low concentrations. The size growth cannot be explained by an increase in the number of ionic groups per multiplet, but is due to an increasing interconnection between more and more previously non-connected multiplets. The broadening of the size distribution suggests that the aggregation of multiplets follows the open association model. The fact that the diffusion coefficient at the lowest concentration is larger than for ω -LiPSS, which has the same aggregation number but for which back folding is not

possible, suggests that at least some back folding occurs for this system. Fluorescence measurements also indicate that back folding does occur in dilute solutions of telechelic ionomers [9]. At higher concentrations D_a increases again similarly to semidilute polystyrene in good solvents. At 5 g l^{-1} the correlogram can be analysed either in terms of a single broad distribution or as two distributions so two values are shown in the plot at this concentration.

For $C > 10 \text{ g l}^{-1}$ α, ω -LiPSS solutions, the slow mode shows a distinct ageing effect. The characteristic relaxation time of the slow mode (τ_s) defined as the peak position increases with ageing, see Fig. 4, but the q -dependence remains the same. The time needed to reach an equilibrium value increases strongly with increasing concentration, see Fig. 5. The equilibrium value extrapolated to $q = 0$ is independent of the concentration in the limited concentration range ($10\text{--}22 \text{ g l}^{-1}$) for which we were able to measure this value. An ageing effect has earlier been observed for the viscosity of solutions of α, ω -sulfonato polystyrene in toluene [10].

α, ω -NaPIPS shows a very similar behaviour at least for $C > 4 \text{ g l}^{-1}$ except that no ageing effect is observed for this system. At concentrations above 4 g l^{-1} , DLS gives a fast q^2 -dependent mode and a slower mode which becomes q -independent at $C > 9 \text{ g l}^{-1}$. At lower concentrations, accurate light scattering measurements are not possible because of the small refractive index increment of polyisoprene in toluene.

For both systems an Arrhenius temperature dependence is found for the slow relaxation with the activation energy 25 kJ mol^{-1} .

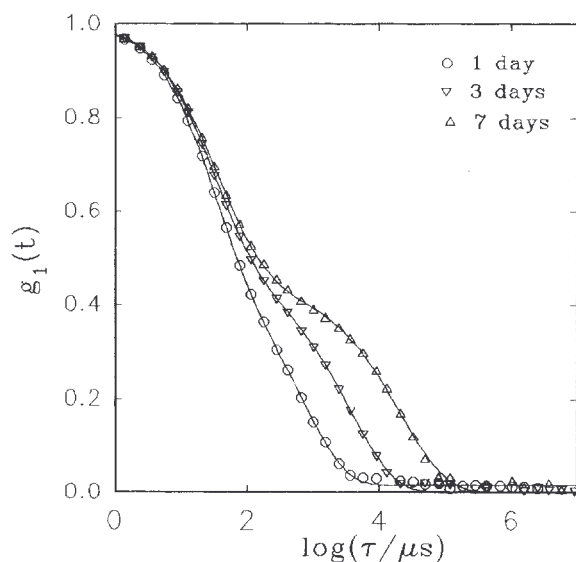


Fig. 4. Ageing effect of the normalised auto correlation function for α, ω -LiPSS in toluene at $C = 10 \text{ g l}^{-1}$. For clarity only one in five points is shown. The solid lines represent non-linear least square fits to the sum of a log-normal and a generalised exponential relaxation time distribution.

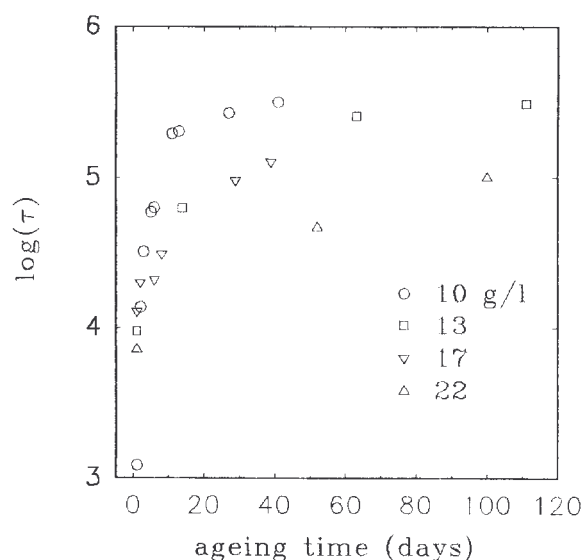


Fig. 5. Dependence on ageing of the slow mode observed in DLS for α,ω -LiPSS in toluene at different concentrations and $\theta = 30^\circ$.

3.3. Shear modulus

The loss, G'' , and storage, G' , shear moduli were measured in the linear viscoelastic regime as a function of the frequency. The frequency dependence for α,ω -NaPIPS at $C = 26 \text{ g l}^{-1}$ is shown in Fig. 6. The data are analysed assuming again a continuous distribution of relaxation times. As the distribution is rather narrow, the analysis is not very sensitive to the precise shape of the distribution and a simple log-normal distribution fits well, see solid lines in Fig. 6. The shape of the viscoelastic relaxation is independent of the concentration in the range investigated: 7-35 g l^{-1} . In Fig. 7 the viscoelastic relaxation time distribution is compared with spectra obtained from DLS at different scattering wave vectors on the same sample. The concentration dependence of the high frequency modulus, G_0 , is shown in Fig. 8. In Fig. 9 the concentration dependence of the relaxation time, T_V , is compared with the peak position of the slow mode obtained from DLS.

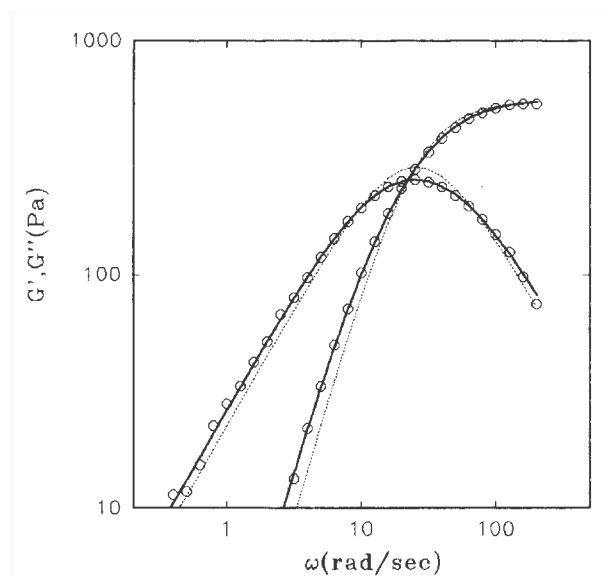


Fig. 6. Frequency dependence of the loss and storage moduli for α,ω -NaPIPS at $C = 26 \text{ g l}^{-1}$. The solid lines represent the results of fits assuming a log-normal relaxation time distribution. The dashed line represents a single exponential relaxation.

The latter could only be determined over a limited concentration range due to the dominant scattering of large scale inhomogeneities at high concentrations. Non-functionalised PIP shows a purely viscous response at these frequencies with very small shear moduli over the whole concentration range investigated. The strong increase of G_0 at $C > 5 \text{ g l}^{-1}$ can be understood in terms of the formation of a transient network of polymer chains connected via multiplets. The observed relaxation is determined by the finite life time of the ionic groups in the multiplet. The fact that τ_V does not vary systematically with C indicates that the multiplet structure is the same over the investigated concentration range. Similar viscoelastic behaviour has been observed earlier for other telechelic ionomers [1] and triblock copolymers for which the outer blocks associate [11]. If the network is affine, G_0 is proportional to the number of elastically active strands (ν) and then $G_0 = \nu kT$, with k the Boltzman constant [12]. The solid line in Fig. 8 gives G_0 assuming that all chains are elastically active. It appears that at higher concentrations almost all the chains contribute to the elasticity. We note that at these concentrations, entanglements are unimportant.

The temperature dependence of τ_V could be measured over a limited temperature range (15—45 °C) and was found to be the same as that of τ_S .

For α,ω -LiPSS the frequency dependence of the shear modulus is similar, but the values of τ_V depend on ageing.

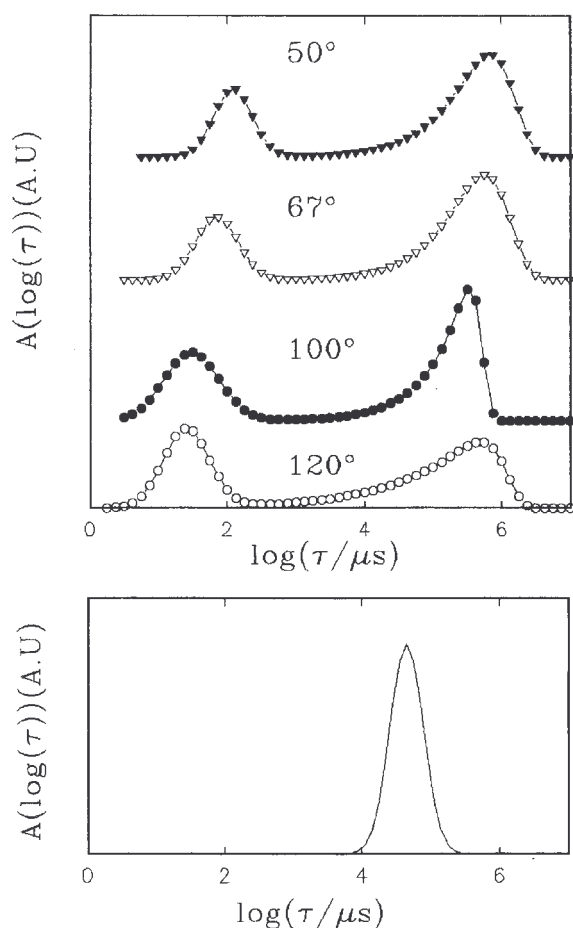


Fig. 7. Relaxation time distributions for α,ω -NaPIPS at $C = 10 \text{ g l}^{-1}$ obtained from DLS at different scattering angles (top) and from DMA (bottom).

4. Discussion

The experimental results suggest a relatively simple model for these telechelic ionomers in solution. At very low concentration, but above the CAC, they organise into well-defined multiplets with some extent of back folding.

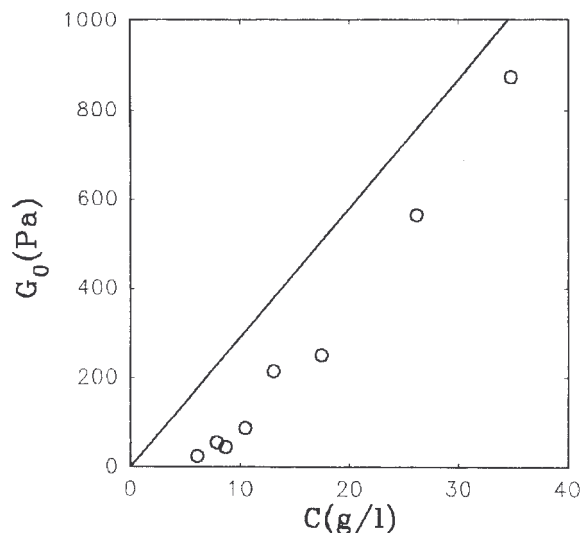


Fig. 8. Concentration dependence of the gel modulus. The solid line represents the theoretical result for an ideal affine network.

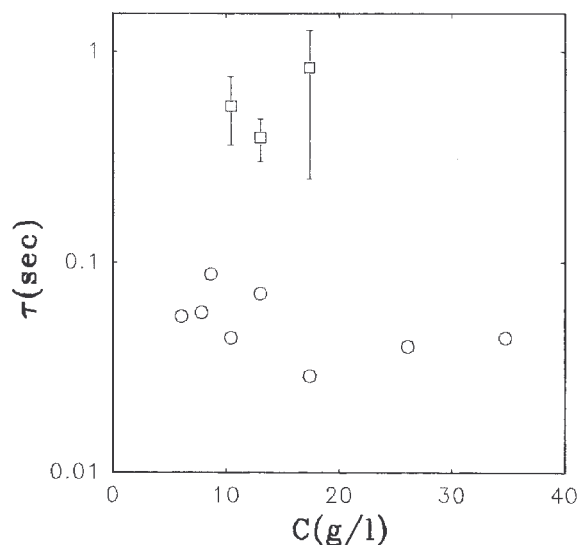


Fig. 9. Concentration dependence of the viscoelastic relaxation time (circles) and the q -independent relaxation time observed by DLS (squares). The error bars indicate the spread of the latter at different scattering wave vectors.

With increasing concentration these reversed micelles associate into larger aggregates following an open association model. At a particular concentration well below the overlap concentration of the polymer coils, the aggregates fill the whole space and a transient network is formed possibly via a percolation process. At this point, the gel modulus is still very low as not all aggregates are part of the network which itself may contain dangling ends. As the concentration increases further, more and more aggregates become part of the network and G_0 increases rapidly until all chains are elastically active. The fact that all chains contribute at higher concentrations implies that for all multiplets n_m is at least 3 for α, ω -NaPIPS and that there is no longer any back folding.

The slow q -independent mode observed in DLS is very probably related to the viscoelastic relaxation in view of the similar temperature dependence for the two modes. We can propose two possible explanations for the q -independent mode. The first is to assume that the system is homogeneous down to the scale of the correlation length, and to consider the viscoelastic relaxation in the expression for the correlation function. The general expression of $g_I(t)$ which includes viscoelastic relaxation is complicated, but is much simplified if the viscoelastic relaxation is single exponential and much slower than the co-operative diffusion [13]. In this case, two modes are expected in DLS: a fast q^2 -dependent

mode and a slower q -independent mode with a relaxation time close to the viscoelastic relaxation time. The relative amplitude of the slow mode is q -independent, but depends on the strength of the longitudinal gel modulus compared to the osmotic modulus. The shear gel modulus and the osmotic modulus are of the same order of magnitude for the systems investigated, so that the presence of a slow mode is consistent with this approach. However, τ_S is almost a factor 10 larger than τ_V which is not predicted by these theories. In addition, the DLS relaxation time distribution is significantly broader than the viscoelastic relaxation time distribution.

An alternative explanation would be that the slow relaxation is due to diffusion and/or restructuring of small scale inhomogeneities. If the diffusion is faster than the life time of the multiplets, the break-up of the multiplet becomes the limiting time step for the diffusion of such inhomogeneities and the relaxation time will be q -independent. If the relaxation is due to restructuring a q -independent relaxation is also expected. In both cases the characteristic relaxation time would be larger than τ_V and with a broader distribution as more than one escape of an ionic group from a multiplet could be involved in such a relaxation.

The transient gel is formed at a lower concentration for the end-capped PIP than for PS. This is probably due to the lower overlap concentration (C^*) of the PIP chains compared to that of the PS chains. If we define C^* as $(3M)/(4\pi R_g^3 N_A)$ with N_A Avogadro's number and R_g the radius of gyration we obtain for PS with $M = 10^5 \text{ g mol}^{-1}$ $C^* = 27 \text{ g l}^{-1}$ while for PIP with the same molar mass $C^* = 11 \text{ g l}^{-1}$. Here we have used the relation between the molar mass and the radius of gyration in good solvents for PS given in Ref. [14] and for PIP given in Ref. [15].

5. Summary

ω -LiPSS forms monodisperse aggregates in toluene with aggregation number 4 independently of the concentration for $C > 0.2 \text{ g l}^{-1}$. α, ω -LiPSS forms aggregates with an initial aggregation number 4 which grow in size and polydispersity when the concentration is increased. At $C > 5 \text{ g l}^{-1}$ a transient network is formed of which the shear modulus is characterised by a narrow relaxation time distribution. The gel modulus increases with increasing concentration. The characteristic relaxation time increases with ageing up to an equilibrium value independent of the polymer concentration. For α, ω -NaPIPS, no effect of ageing is observed. The gel modulus of this system at high concentrations is consistent with that of an affine network in which each polymer chain is elastically active.

DLS measurements of the transient network show two relaxational modes: a fast q^2 -dependent mode due to co-operative diffusion and a slower mode which becomes q -independent at $C > 20 \text{ g l}^{-1}$ for α, ω -LiPSS and $C > 9 \text{ g l}^{-1}$ for α, ω -NaPIPS. The viscoelastic relaxation and the q -independent mode observed in DLS have an Arrhenius temperature dependence with the same activation energy: 25 kJ mol^{-1} . Although the viscoelastic relaxation is almost a factor 10 faster than the q -independent mode observed in DLS, both relaxations are probably determined by the average life time of an ionic group in a multiplet.

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