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ORIGINAL CONTRIBUTION

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Coupling of concentration fluctuations to viscoelasticity in highly concentrated polymer solutions

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Abstract Photon correlation spectroscopy in the polarized geometry has been used to systematically investigate the complex dynamics of a highly concentrated entangled polymer solution in a nominally good solvent, poly(butylacrylate) in dioxane. In addition to the well known fast cooperative diffusion process, a slow virtually q-independent mode is detected, where q is the scattering wavevector, in agreement with previous experimental works on semidilute solutions. This mode is attributed to the viscoelastic nature of the transient physical network, formed by the entanglements, which relaxes its elastic stress induced by the concentration fluctuations, as confirmed by small amplitude oscillatory shear measurements; the latter reveal a terminal relaxation time comparable to the characteristic time of the slow relaxation process. Results, especially in terms of concentration and temperature dependence, are evaluated and discussed in view of the existing theoretical treatments in the field, predicting the existence of the slow viscoelastic relaxation. The relationship between dynamic light scattering and mechanical spectroscopy is established.

Key words Polymers – concentrated solutions – entanglements – dynamics – photon correlation spectroscopy

Introduction

Photon correlation spectroscopy (PCS) is a well established technique for studying the dynamics of solutions of linear flexible polymers over several decades in time, ranging from microseconds to seconds [1]. In the case of dilute solutions, the subject has been exhausted [2]. It is well known that for $qR_g < 1$, where q is the scattering wavevector and R_g the radius of gyration of the polymer coils, the concentration fluctuations decay exponentially with a rate $\Gamma = Dq^2$, where D is the translation diffusion coefficient of the monodisperse polymer chains. On the other hand, for $qR_g > 1$, smaller scale relaxations are detected [3]. In the limit of infinite dilution, the diffusion coefficient is related to the hydrodynamic radius of the coil, R_H.

As the concentration increases above the overlap concentration c^* ($= M/(4/3\pi N_A R_g^3)$, where M is the molecular weight and N_A is the Avogadro number), the semidilute concentration regime is reached; it is characterized by the overlapping of polymer coils and formation of the "entanglements" at concentration $c > c^*$. The situation is now much more complex, and the problem of polymer dynamics in the entanglement regime is far from being resolved. As a general observation, PCS experiments have revealed the presence of a slow, non-diffusive mode, in addition to a fast diffusive mode [4–8]; the latter is the cooperative diffusion (with coefficient D_c), which represents the relative random motion of blobs in the entangled polymer network, formed by the overlapping chains. A decrease of solvent quality (thus of temperature) will enhance the amplitude of this slow decay of concentration fluctuations. The key question here is what is the origin of the slow q-independent mode. A suggestion, based on the molecular weight dependence, that it is due to self-diffusion [6], has been dismissed in view of strong disagreement with pulsed-field-gradient NMR [9] and forced Rayleigh scattering measurements [10]. An alternative suggestion related to the presence of large clusters [11] has been also discarded, since "cluster modes" are diffusive and moreover are temperature-dependent [12]. Finally, several attempts to explain the dynamics of semi-dilute solutions, and in particular to relate the slow q-independent mode to the viscoelasticity of the entangled polymer solution have been made, and will be reviewed in the next section.

At much higher polymer content, in the highly concentrated regime towards the undiluted bulk state, the density fluctuations gain importance and can also couple to the concentration fluctuations, which decay through cooperative diffusion. In this case the faster q-independent mode is related to local segmental relaxations associated with the glass transition dynamics [13].

Dynamic shear mechanical measurements in the limit of linear viscoelasticity, indicate that a semidilute solution exhibits elastic gel behavior at short times and viscous behavior of long times, both in good and poor solvents. The two regimes are separated in time through the lifetime of the physical "transient network" (gel), formed by the entanglements [14]. Therefore, it is apparent that the slow relaxation mode detected by PCS may be associated to the viscoelastic terminal relaxation (e.g. reptational motion in the Doi–Edwards model) of polymer chains through the entanglement network. This was recently discussed by Koike et al. [15] who carried out PCS and rheological measurements in aqueous semidilute solutions of poly(vinyl alcohol); the characteristic times of the slow relaxation mode and the terminal relaxation, respectively, were in very good agreement. Similar results were obtained for the case of aqueous cationic surfactant solutions as well [16].

However, despite the above developments, there are a number of open questions which need to be clarified before this problem is fully understood. They relate to the effects of concentration in highly concentrated polymer solutions, the q-dependence of the slow mode and its physical origin, and the effects of temperature. In this paper we address these issues through a systematic experimental study of the dynamics of an entangled polymer solution in good solvent, by utilizing PCS in the polarized geometry and mechanical spectroscopy in the limit of linear viscoelasticity. In the remainder of this paper, a review of the existing theoretical treatments is first presented. Then, the experimental procedures and resulting data are discussed, with an emphasis on the slow q-independent relaxation process. Next, the results are evaluated and discussed by comparing optical and mechanical measurements, in light of the theoretical developments addressing the problem. It is confirmed that the slow mode is a viscoelastic relaxation process. Finally, the main conclusions of this investigation are summarized.

Theoretical background

de Gennes and Brochard [17] have presented a theoretical description of the dynamics of concentration fluctuations in semidilute polymer solutions including hydrodynamic interactions. In the case of Θ solvent, the polymer chain is self-entangled (in addition to the usual entanglements), and thus the characteristic mesh size is much smaller than the correlation length ξ of concentration fluctuations. In this "transient gel" regime, where $q\xi \ll 1$, they introduced the "two-fluid" model, i.e., they considered the polymer solution as consisting of two independent constituents, the solvent and the solute. Then, the macroscopic longitudinal displacement of a polymer chain $u(q, \omega)$, where ω is the frequency, is determined by the equation of motion, expressing a balance between restoring forces (arising from both osmotic pressure and elastic modulus of the chain) and frictional forces (viscous forces between solvent and polymer):

$$i\omega c u/\mu + [K + M(\omega)]q^2 u = 0 \, , \tag{1}$$

where μ is the effective mobility per monomer, K ($= c(\partial\Pi/\partial c)$, Π being the osmotic pressure) is the osmotic bulk modulus, and M is the longitudinal elastic modulus of the transient gel, which is frequency-dependent:

$$M(\omega) = M_g \left(\frac{i\omega\tau_R}{1 + i\omega\tau_R}\right) \, , \tag{2}$$

where τ_R is the characteristic lifetime of the network contact points. At low frequencies $\omega\tau_R \ll 1$ the polymer solution exhibits liquid-like behavior (hydrodynamic regime), with a characteristic rate $\Gamma = (\mu/c)Kq^2 = D_c q^2$; during the diffussion time $(D_c q^2)^{-1}$, the chains can disentangle. On the other hand, at high frequencies $\omega\tau_R \gg 1$, the polymer solution exhibits gel-like behavior with a characteristic rate $\Gamma = (\mu/c)[K + M_g]q^2 = D_g q^2$, where D_g is the gel diffusion coefficient; during the diffusion time $(D_g q^2)^{-1}$, entanglements may be considered to be "frozen" ($M_g \gg K$) and the concentration fluctuations relax as in a permanent gel. Further, at wavevectors q larger than a threshold q_g for which the diffusion time $(D_g q_g^2)^{-1}$ of the concentration fluctuations becomes τ_R, two relaxation processes govern the structure factor $S(q, t)$: the solvent moves through the chain and the chains disentangle at later times. The faster diffusive motion is controlled by the equilibration between osmotic pressure and elastic stress. The chain disentanglement (viscous relaxation of stress) is proportional to the characteristic time τ_R. In this case,

$$S(q, t) = A_1 e^{-\Gamma_1 t} + A_2 e^{-\Gamma_2 t} , \tag{3}$$

where subscript 1 denotes the "fast" mode, subscript 2 denotes the "slow" mode, with $A_1 + A_2 = 1$, and,

$$\Gamma_1 = D_c q^2 \quad \Gamma_2 = \frac{D_c}{D_g \tau_R} \approx \frac{K}{M_g \tau_R} \quad \text{and} \quad A_2 = \frac{D_g}{D_c} . \tag{4}$$

The slow process is a q-independent structural relaxation and related to the viscoelasticity of the entangled polymer solution. A first experimental confirmation of the presence of these two modes in polystyrene solutions in theta solvents was reported by Adam and Delsanti [18], who have also extended the above theory of deGennes and Brochard by relaxing the assumption of frozen gel ($M_g \geq K$); for the q-range of interest here the results were essentially the same as above, described by Eqs. (3) and (4).

Doi and Onuki [19] have recently presented a general phenomenological theory to account for the coupling between stress and diffusion in polymer solutions and blends in quiescent state and under the presence of flow. They used the two-fluid model of Brochard and de Gennes [17]. They argued that the stress $\sigma^{(n)}$ in entangled polymer systems is supported by chains, and if there is an imbalance in stress (because it is not acting equally on all chains) this creates a net force on the chains, resulting in their migration relative to the solvent. An important consideration is that since this stress arises from network deformations, it is determined by the gradient of polymer velocity only. The physical network extra stress is given by a constitutive equation [20]. By considering further a generalization of Brochard's mutual diffusion approach, i.e., accounting for the stress gradient in the diffusion equation by including the elastic energy of polymers in addition to the energy of mixing, Doi and Onuki assembled the important ingredients for the development of a general model for the effect of viscoelasticity on entanglement dynamics. Their calculation of the time correlation function of the concentration fluctuations under the assumptions $q\xi_b \ll 1$ (ξ_b being the blob size), $M_g(t) \approx M_g \exp(-t/\tau_R)$, $D_c q^2 \tau_R \gg 1$, revealed a structure factor of a similar general form to Eq. (3):

$$S(q, t) \approx A_1 e^{-D_c q^2 t} + \frac{\xi_{ve}^2}{D_c \tau_R + \xi_{ve}^2} e^{-t/\tau_R} \tag{5}$$

with ξ_{ve} being a characteristic length of the viscoelastic process, with $\xi_{ve}^2 = 0.65\, \xi_b^2 (\eta/\eta_S)$, where η and η_S are the solution and solvent zero-shear viscosities, respectively; this expression for ξ_{ve} is valid for entangled homopolymer solutions. The physical significance of ξ_{ve} is that it determines the strength (on a spatial scale) of dynamic coupling between concentration fluctuations and stress (viscoelasticity), which results in the presence of the slow structural relaxation process. The blob size is given by $\xi_b = 1.3\xi_H$ in the semidilute regime [21], with $\xi_H = k_B T/(6\pi\eta_S D_c)$ being the hydrodynamic correlation length (k_B is the Boltzmann constant and T the absolute temperature). The first decay is the short-time q^2-dependent relaxation. The second is actually q-independent. It is noted that under the assumption $\xi_{ve}^2 \ll D_c \tau_R$, the amplitude of this second slow process is essentially of the order of the shear modulus divided by the bulk modulus, which is much smaller than 1 for good solvents and of 0(1) for Θ solvents, again pointing to the enhancement of the effect in the latter case.

Semenov [22] has accounted for both the elastic deformation of the entanglement network and the entanglement dynamics of individual chains (some investigators have considered an undeformable network and attributed the relaxation of concentration fluctuations to the viscoelastic relaxation, e.g. reptation [23]). His generalized mean-field method for calculating the concentration time correlation function takes into consideration the volume interactions between the segments (which correspond to long-range forces betwen the segments of different chains or distant segments of the same chain), in addition to the "classical" entanglement interactions (which correspond to short-range forces between segments that prohibit them from intersecting each other). For concentrated polymer solutions, $S(q, t)$ is a three-step relaxation function:

$$S(q, t) = \frac{1}{v} [A_c g_c(q, t) + A_R g_R(q, t) + A_{rel} g_{rel}(q, t)] , \tag{6}$$

where v is the volume interaction parameter ($v = (1/cT)(\partial\Pi/\partial c)_T$); A_c, A_R, A_{rel} refer to the relative amplitudes of the cooperative, Rouse and terminal (longest) relaxation modes, respectively ($A_c + A_R + A_{rel} = 1$), and g_c, g_R and g_{rel} are the corresponding normalized decay functions. As a result of the initial deformation of the entanglement network, parts of the network are stretched and parts are compressed, i.e., the stress is nonuniformly distributed along tube axes in the entanglements [19]. The macromolecules will then tend to redistribute their links along the tubes in order to smooth out the stress, and this relaxation process is characterised by a Rouse time. At longer times, chain relaxation-type motions of the macromolecules along their tubes give rise to a relaxation process characterized by times of the order of the longest viscoelastic relaxation time. Depending on the value of the scattering wavevector relative to the size of the polymer chains (radius of gyration, R_g), the molecular weight and the entanglement molecular weight, either all three or only the cooperative and terminal relaxation modes are expected to be detectable.

In a different approach, Wang [24] has presented a hydrodynamic theory based on the statistical mechanical equation of Bearman and Kirkwood (BK) for a binary solution. Fluctuations in density and concentration produce random fluctuations in the dielectric constant of the medium. To account for the latter, which is a measure of the polymers' dynamics, it is necessary to start from the linearized hydrodynamic equations describing the polymer motion, supplemented by the constitutive equation of the viscoelastic fluid. The link to the dynamics of concentration fluctuations is provided by the BK equation. It is important to point out that the stress tensor of the polymer component is assumed to be related to the polymer solution velocity, rather than the velocity of the polymer component itself, as described by Doi and Onuki [19]. The result in the regime $qR_g < 1$ is that diffusion due to concentration fluctutations and viscoelasticity of the solution are connected through a coupling parameter, β. This parameter represents the increase of polymer solution density, ρ, with concentration, c, $\beta = (c/\rho)(\partial\rho/\partial c)_{T,P}$. When β is non-zero, a second slow q-independent viscoelastic mode appears in the light scattering spectrum, in addition to the fast cooperative diffusion mode. However, for $\beta = 0$, only the diffusive process is predicted. Recently it was recognized that the role of β is not always justified. For instance, Akcazu et al. [25] presented a different treatment of the coupling of diffusion to stress, which resulted in the prediction of a slow q-independent viscoelastic mode even for isopycnic polymer solutions ($\beta = 0$). Later, however Wang revisited the problem and argued for the original role of β, both theoretically and experimentally [26]. Furthermore, a systematic experimental investigation of the effects of β on the dynamics of concentrated polymer solutions in poor solvents indicates that even under $\beta \approx 0$ the slow viscoelastic mode is detected with substantial amplitude [27]. Despite this controversy, however, the theory predicts for $\beta \neq 0$ a dual structure factor of the type of Eq. (3). When the two processes are well separated in time, the amplitudes are given by:

$$A_1 = \frac{K}{\beta M_0 + K} \quad \text{and} \quad A_2 = \frac{\beta M_g}{\beta M_g + K} . \tag{7}$$

For $\beta = 0$, $A_2 = 0$. On the other hand, for a very concentrated polymer solution or a melt, $\beta M_g \gg K$, thus $A_2 = 1$, and the viscoelastic mode dominates the light scattering spectrum. Further, for $\beta = 1$, $A_2 = M_g/K$; this is a result identical to those of Brochard–de Gennes [17] and Adam–Delsanti [18], although derived from a completely different approach. Wang emphasized that his theory is more general, since it does not make use of the transient network. However, the slow mode has been observed only in entangled polymer solutions.

As a matter a completeness, the recent theoretical work of Genz [28] is included. She has developed a theoretical framework, based on the random phase approximation, in order to describe additional slow q-independent modes, which are due to the so-called memory effects, i.e., polymer viscoelasticity. In her microscopic approach for a polymer solution, the solvent is considered as an "inert" background, and thus the motion of polymer chains (or their statistical segments) dominates the dynamics. Long time effects are accounted for through generalized transport functions, which are determined from memory equations. When the time scales of the dynamics of internal motion inside statistical segments are well separated from the main chain motion, then high frequency processes are introduced by a friction constant, or a time-independent mobility function. This theory predicts the cooperative diffusion in the limit of short times, and the viscoelastic mode at longer times. Its main drawback is that it provides expressions for amplitudes and rates, which are related to complicated material properties and thus it is not very easy to compare against experiments.

In summary, a slow viscoelastic relaxation mode is predicted by two different approaches. It seems that the transient entanglement network ideas are physically more sound in explaining the coupling of concentration fluctuations to stress; the latter conclusion is supported by experimental results, as discussed in the sections below. Thus, these theories provide the framework for comparing dynamic light scattering and rheological experiments in concentrated polymer solutions and justify the investigation of the effects of solvent quality, concentration and temperature in highly concentrated systems.

Experimental

Materials

Solutions of polybutylacrylate (PBA) in dioxane were prepared by thermal polymerization directly in the measuring cells [29]. This procedure is the most reliable to yield high optical quality samples, which are suitable for photon correlation spectroscopy experiments, justified by the presence of only inherent scattering. The catalyst used was ditert-butyl peroxide at concentration 10^{-2} M with respect to the monomer. The polymerization proceeded for 72 hours at 60 °C and then for 48 hours at 80 °C. The conversion achieved was 96% for volume fraction of PBA $\phi = 0.1$, and increased with ϕ, reaching 99% for the bulk PBA. Solutions of various volume fractions were prepared, namely $\phi = 0.09, 0.17, 0.27, 0.36, 0.46, 0.56, 0.66, 0.77, 0.88$ and 1.00 (bulk). The corresponding molecular weight of the samples was about 100 000 (number of monomer units $N = 775$), and varied slightly with increasing concentration, the total increase being not more than a factor of 2 [29]. The entanglement molecular weight in the melt, M_e, estimated from viscoelastic measurements of the equilibrium plateau modulus, is about 14 000, and hence the concentrated solutions above about 27% are entangled. The glass transition temperature of the bulk PBA is − 50 °C.

Methods

Dynamic light scattering

Photon correlation spectroscopy (PCS) was utilized in the polarized geometry (VV). The correlation function $G_{VV}(q,t)$ of the VV light scattering intensity at different scattering angles θ was measured with an ALV-5000 full digital correlator, with a dynamic range $10^{-6} - 10^3$ s. The light source was an Ar^+ laser (Spectra Physics 2020) with 150 mW, single mode, at wavelength $\lambda = 488$ nm, and a Nd:YAG dye-pumped laser (ADLAS DRY 325) with 140 mW, single mode, at $\lambda = 532$ nm. At a given wavevector q, the measured homodyne intensity autocorrelation function $G(q, t)$ is expressed as [1]:

$$G_{VV}(q, t) = [1 + f^* | \alpha C(q, t)|^2] \, , \tag{8}$$

where $q = 4\pi n/\lambda \sin(\theta/2)$, n is the refractive index of the polymer, f^* is the instrument factor, α is the fraction of the total polarized scattered intensity arising from fluctuations with correlation times above 1 μs, and $C(q, t)$ is the normalized field correlation function. Before each measurement, the test samples were always left to equilibrate for at least 1 h. During the measurement the intensity of the scattered laser light remained constant. Usually, the analysis of the experimental correlation functions $C(q, t)$ was carried out by performing their inverse Laplace transform (ILT), using the program CONTIN [30]. This method assumes that $C(q, t)$ is represented by a superposition of exponentials

$$\alpha C(q, t) = \int_{-\infty}^{\infty} L(\ln \tau) \exp(-t/\tau) \, d(\ln \tau) \tag{9}$$

which describe a continuous spectrum of relaxation times $L(\ln \tau)$; the latter is used to determine the average characteristic relaxation times, τ. In some cases, however, the correlation functions were represented by the Kohlrausch–Williams–Watts (KWW) function:

$$C(q, t) = \exp[(-t/\tau)^{\beta_{KWW}}] \, , \tag{10}$$

where β_{KWW} is the shape parameter (usually $0 \leq \beta_{KWW} \leq 1$, with $\beta_{KWW} = 1$ corresponding to a single exponential relaxation mode). This method was chosen in order to get a direct estimate of the breadth of the relaxation modes detected. It is noted that the characteristic time τ determined from CONTIN corresponds to that from KWW for a given β_{KWW}. Measurements were performed at temperatures covering a range between − 40 °C and 40 °C. Several concentrations of PBA were measured, from 0.34% up to 100% (bulk) per volume using, either different samples (with slightly different molecular weight, as mentioned above), or one sample with successive dilutions with dioxane.

Shear rheology

Small amplitude oscillatory shear measurements were carried out using a Rheometric Scientific RMS-800 rheometer in the parallel plate geometry (plate diameter was 25 mm and the gap was set to 0.5 mm). Isothermal frequency sweeps were obtained over the frequency range 0.01–100 rad/s, for temperatures between − 10° and 30 °C; temperature control was achieved with liquid nitrogen or air convection under nitrogen atmosphere. The time-temperature superposition principle was found to hold by shifting the moduli at various temperatures along the frequency axis; shift factors were fitted using the WLF equation [31]. The crossover between storage (G') and loss (G'') moduli in the terminal regime defines the characteristic longest relaxation time of the entangled polymer chains.

Results and discussion

As already mentioned, a prime concern was the optical quality of the samples; they were indeed of supreme quality for the light scattering experiments, as confirmed by the correlation functions obtained (see for example Fig. 2 below) and the high fraction of scattered intensity from the bulk PBA, arising from density fluctuations (about 0.5, in Fig. 2 below). This represents one uniqueness of this work and is also reflected in the quality of the correlation functions, which are discussed below. Further, the transition from dilute to semidilute regime was determined from the change of the scattered VV intensity at a scattering angle

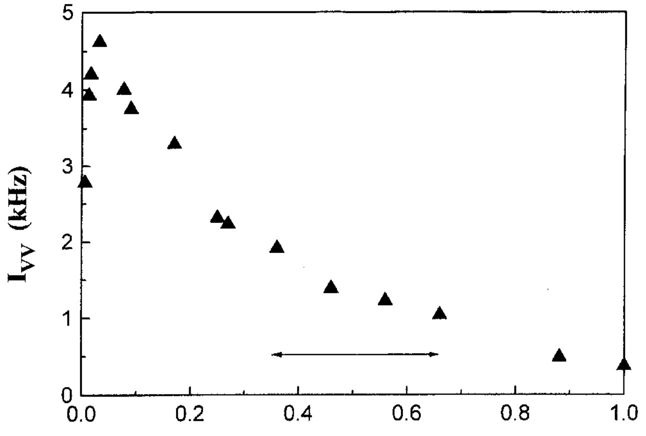


Fig. 1 Total polarized scattering intensity I_{VV} at an angle of 90° versus concentration of PBA in dioxane at 20 °C. The peak corresponds to the overlap concentration c^* (3.5%). The horizontal arrow indicates the range of concentrations studied by PCS with respect to the slow relaxation mode

of 90° with concentration, illustrated in Fig. 1. The concentration of maximum intensity is taken as the c^* (about 3.5% by weight). The results discussed here refer mostly to the range 36–66%, which fall well within the concentrated regime. Thus, the concept of physical entanglement network is relevant, and extends the concentration range of the previous experimental studies, which were mainly focused in the semidilute regime [15, 32].

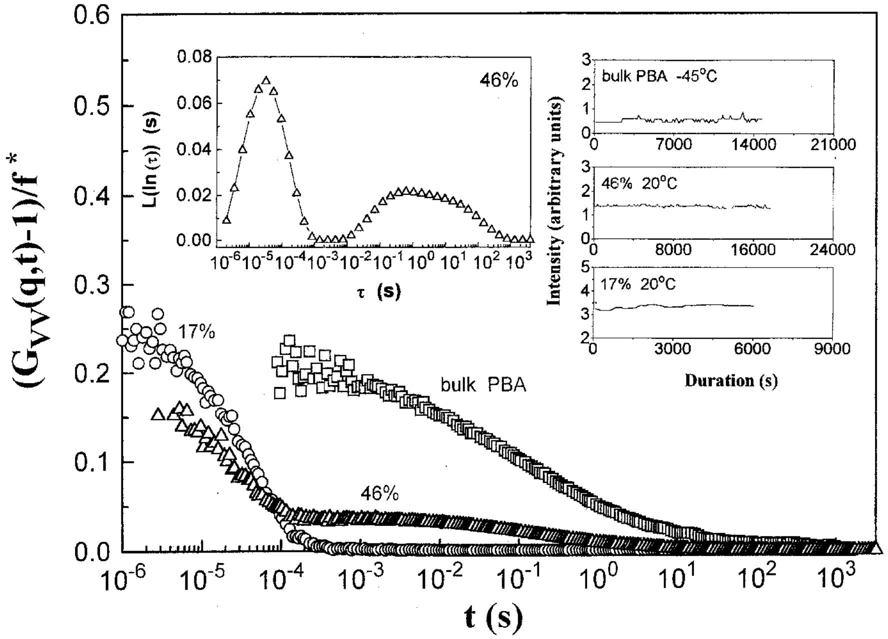
Before proceeding further, it is important to check the quality of the solvent. This task has been carried out by measuring the translation diffusion coefficient, D, of several mostly dilute PBA concentrations, from 0.3% to 9%, obtained from the original 17% sample by successive dilutions in dioxane; the experimental conditions were 20 °C, $\theta = 90°$, and $\lambda = 488$ nm. The concentration dependence of D in the dilute regime is given by:

$$D = D_0(1 + k_D c + \cdots)\,, \qquad (11)$$

where k_D is the concentration coefficient and c the concentration. This expression holds for good solvents with $k_D > 0$, whereas under Θ solvent conditions $k_D < 0$ due to increased interactions (e.g. friction) among chains. The results revealed a coefficient $k_D = 33.5\ \mathrm{cm}^3/\mathrm{g}$, which implies that dioxane is a good solvent for PBA. This result is in fairly good agreement with results from similar studies on polystyrene solutions in toluene [33].

Figure 2 represents the experimental net intensity correlation (normalized with the instrument factor f^*, which is a measure of the coherence area and calculated by means of a PS/CCl$_4$ standard) function at two concentrations: one corresponding virtually to the early stages of the semidilute regime $c = 0.17\ \mathrm{g/cm}^3$ (17%), and one corresponding to the concentrated regime $c = 46\% > c^*$, both at temperature 20 °C and scattering angle 45°. The correlation function of the bulk PBA is also included in this figure; it was obtained at much lower temperature (− 45 °C) and revealed only one process observed, the α-relaxation. The 17% solution exhibits a single relaxation process as well, corresponding to a cooperative diffusion. It is noted that measurements were also carried out at very low concentrations (below 3.5%), where a single process

Fig. 2 Net normalized intensity autocorrelation functions $[G_{VV}(q, t) - 1]/f^*$ (Eq. (8)) versus time, at a scattering angle of 45°, for the bulk (□) at − 45 °C, and two solutions (dilute to semidilute (○) 17% per weight, and concentrated (▲) 46%) at 20 °C. Right insets: corresponding traces of the scattering intensity. Left inset: Corresponding distribution of relaxation times (Eq. (9)) for the 46% solution



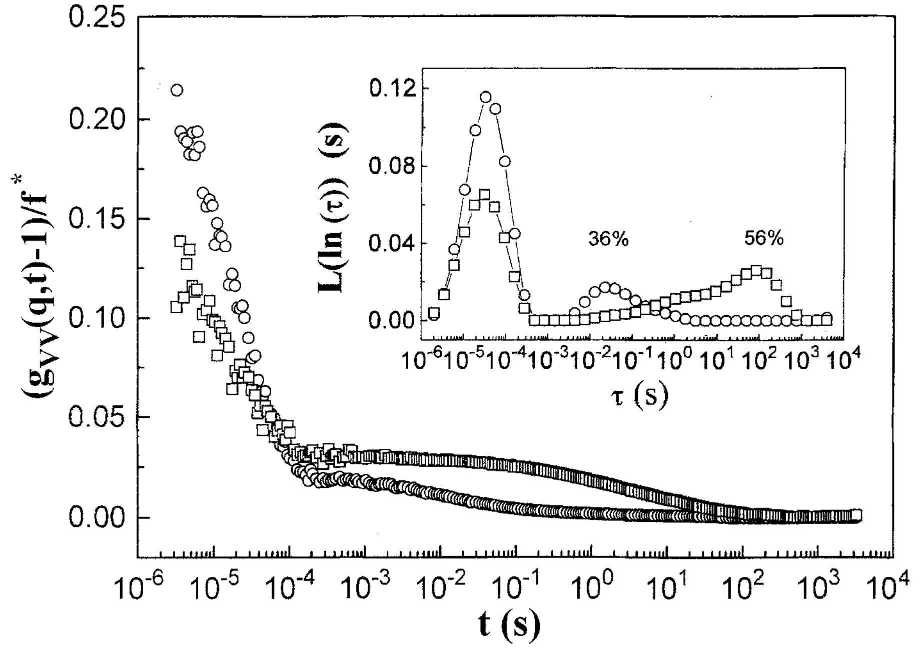


Fig. 3 Net normalized squared field correlation functions $[g_{VV}(q,t) - 1]/f^*$ versus time for two concentrated PBA/dioxane solutions, namely 36% (○) and 56% (□), at 45° and 20 °C. Inset: Corresponding distribution of relaxation times

was also observed. In the 46% solution, which is associated with the presence of entanglements, two relaxation processes are detected: the fast cooperative diffusion mode, which just appears in the time window of the correlator, and a much slower (by about 4 orders of magnitude) mode with a nonexponential shape; its amplitude is still lower compared to that of the fast mode. It is emphasized that the latter relaxation mode is a true one, and not an experimental artifact, as, for example, transient heterogeneities. This is confirmed by the quality of the samples discussed before, as well as the nearly constant intensity traces during the measurements of the correlation functions, shown as insets in Fig. 2. It is thus evident that in order to detect the slow mode under the present good solvent conditions (at least up to 10%), it is necessary to reach substantial entanglements in the solution. The left inset of Fig. 2 depicts the ILT analysis (Eq. (9)) of the 46% solution, signifying the difference between the fast and slow relaxation modes. It is clear therefore, that the slow process cannot be detected in the bulk in the experimental time window. Moreover, the fast process in concentrated solutions has nothing to do with the q-independent α-relaxation in the bulk; for the latter the KWW fit (Eq. (10)) revealed a shape parameter of $\beta_{\mathrm{KWW}} = 0.30$. The appearance of a clear slow mode with substantial amplitude under good solvent conditions, apparently contradicts previous claims that this essentially cannot be observed [18, 27]. Of course, it is not possible to assess at this stage how enhanced the amplitude would have been in a Θ solvent. Neither is it clear whether we are still under good solvent conditions in the highly concentrated regime, since Eq. (11) is valid only in the dilute limit; as the concentration increases, the solvent quality is expected to decrease due to more cancelations of segment–segment interactions.

In order to better appreciate the slow process, the square of the net field correlation function, normalized again with the instrument factor f^*, is depicted in Fig. 3, for the 36% and 56% solutions, again at temperature 20 °C and scattering angle 45°; the quality of the correlation functions is also confirmed by the intenstiy traces. It is now evident that the slow mode is very broad with characteristic time about 4 orders of magnitude longer than the cooperative diffusive process for the 36% solution, and nearly 7 orders of magnitude for the 56% solution; the shape parameter obtained from the KWW in the concentration range from 36% to 66% is nearly constant $\beta_{\mathrm{KWW}} \approx 0.37$. Further, from this figure, along with its inset depicting the distribution of relaxation times (from ILT), and in combination with Fig. 2, the effects of concentration become apparent (taking into account the small change of molecular weight from sample to sample, as already discussed). It is noted that it was not possible to measure the slow relaxation in solutions above 66%, since its decay time is longer than 10^3 s, the upper limit of the correlator. Even in the 66% solution, the slow process is not fully relaxed within the time window of the correlator.

Based on the theoretical approaches on the entanglement dynamics presented before, if the slow relaxation mode is associated with the viscoelasticity of the concentrated polymer solution, then it should be q-independent. This is indeed shown in Fig. 4, which depicts the intensity autocorrelation functions of a 46% solution at 20 °C and

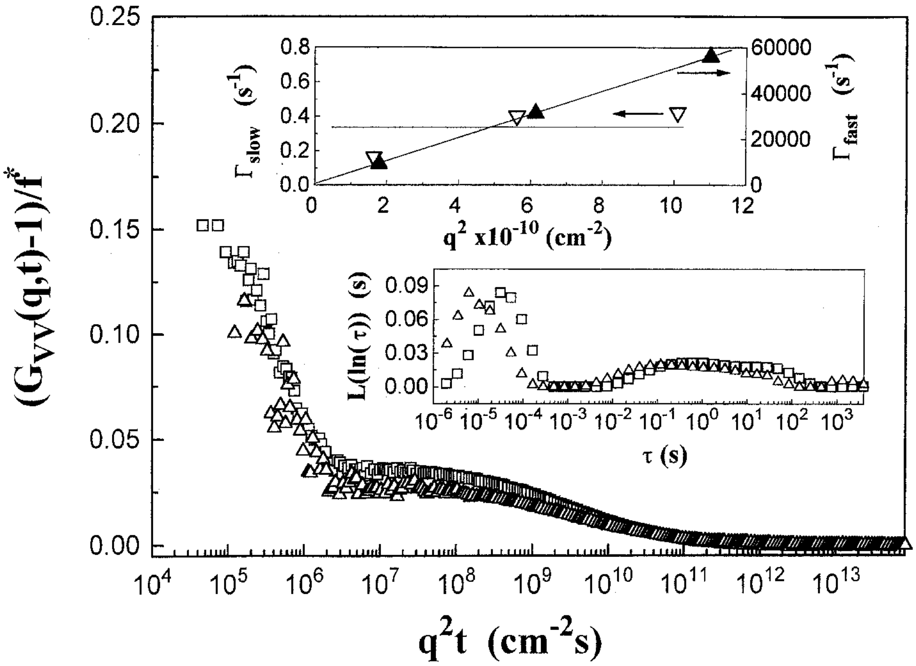


Fig. 4 Net normalized intensity autocorrelation functions $[G_{VV}(q,t)-1]/f^*$ versus time, for a 46% PBA solution in dioxane, at 20 °C and two different scattering angles, 45° (□) and 135° (△). Lower inset: Corresponding distributions of relaxation times. Upper inset: Relaxation rates of the fast cooperative (▲) and slow viscoelastic (▽) modes, as functions of q^2

two scattering angles, namely 45° and 135°, as functions of the reduced quantity q^2t; in such a representation, the q^2-dependent modes collapse in a single mastercurve, whereas actually the q-independent modes do not superimpose. It is thus clear from Fig. 4 that while the fast mode is q^2-dependent (cooperative diffusion), the slow one is truly nondiffusive. It should be noted, of course, that usually broad relaxation processes [13] are characterized by a very weak q-dependence for low light scattering q's, if at all, and the current work is no exception. The lower inset of Fig. 4 confirms this finding, as reflected in the distribution of relaxation times, from the ILT of the correlation functions. Furthermore, the characteristic times from the ILT analysis of the two processes are plotted as functions of q^2 in the upper inset of Fig. 4. From the above data it is established that within the q-range and time range of our PCS technique, and for the specific polymer system used, only two processes can be detected: the fast cooperative diffusion and the slow q-independent viscoelastic network relaxation. This result confirms the predictions of Semenov [22], according to which in the regime $\lambda_1 < q^{-1} < \lambda_2$ (with λ_1 and λ_2 being characteristic lengths determined below) only two relaxation processes are detectable, namely the cooperative diffusion and the slow chain relaxation process (for example, of the reptational type, assuming validity of the Doi–Edwards model); the Rouse relaxation is "mixed-up" with the cooperative diffusion, due to the similar characteristic length scales, reflecting similar relaxation times. Actually, the Rouse times from mechanical measurements (Fig. 5 below) lie in the range of the cooperative diffusion times of light scattering, confirming the prediction of only two distinctly different processes.

For the PBA/dioxane system of this work, $\lambda_1 = R_g(N/N_e)^{1/2} = 2.9 \times 10^{-6}$ cm and $\lambda_2 = N^{1/2}\ \lambda_1 = 8.1 \times 10^{-5}$ cm; thus, the above inequality is always valid for the q range of our light scattering experiments ($0.13 \times 10^6 - 0.32 \times 10^6$ cm^{-1}). A further assessment of the relation of the slow viscoelastic mode can be made by considering the two main theoretical alternatives offered, namely the idea of a physical entanglement network and that of coupling of concentration fluctuations to viscoelasticity through the parameter β. The latter was checked by measuring directly $\partial\beta/\partial c$ at 25 °C and over the concentration range from 9% to 25%; this increment was found to be -3.85×10^{-3}, resulting in a negligibly small value of $\beta = 9.82 \times 10^{-4}$ for the 25% solution. This suggests that Wang's argument concerning the necessity of nonzero β in order to detect the viscoelastic mode may not always hold, in agreement with the recent experimental results of Brown and Stepanek [27]; on the other hand, it should be mentioned that Wang et al. very recently reported on experiments with semidilute isopycnic polymer solutions (polystyrene in diethyl malonate), suggesting no slow viscoelastic mode [26b]. However, based on the molecular weight (185 000) and concentrations used (0.1% – 22.5%), nearly none of the solutions investigated was in the entangled state, with the exception of the highest concentration which can be considered are marginally entangled. This assessment was made by considering the expression

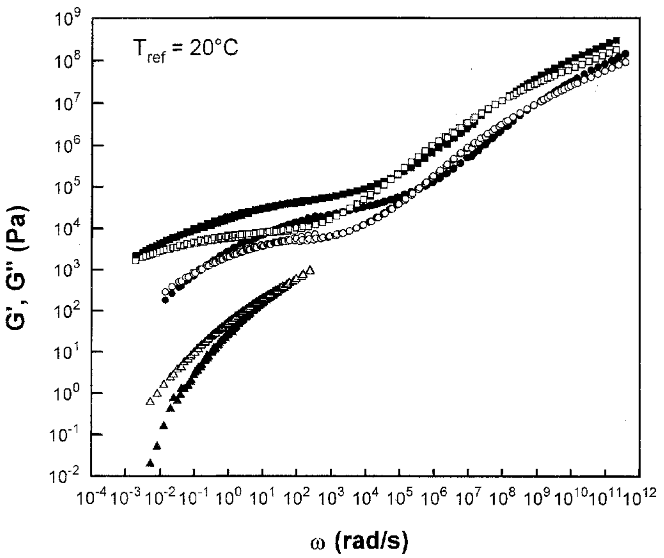


Fig. 5 Master curves of storage (G') and loss (G'') moduli for PBA/dioxane solutions at three concentrations, namely 27% (G': ▲; G'': △), 56% (G': ●; G'': ○) and 66% (G': ■; G'': □). Reference temperature is 20 °C

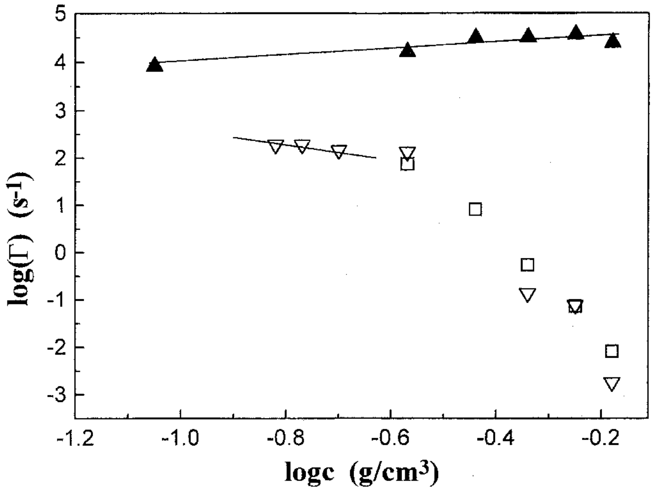


Fig. 6 Log–log respresentation of the relaxation rates of the fast cooperative (▲; scattering angle was 90°) and slow viscoelastic (□) modes, as functions of concentration, at 20 °C. Solid line through the cooperative rates represents the 0.75 scaling perdiction. Also included are the terminal relaxation times from rheology (▽). Solid line represents the 1.6 scaling law in good solvents

$M_e(c) = M_e c^{-d}$, with d between 1 and 1.3 [34]; $M_e(c)$ is the entanglement molecular weight at a given concentration c, and M_e the molecular weight of the bulk polymer. Therefore, there is evidence that the observed viscoelastic slow mode is the relaxation of the concentration fluctuations – induced elastic stress of the transient physical network, formed by the entangled polymer chains.

In order to examine the relation of the slow relaxation mode in the light scattering spectrum to the terminal relaxation of the PBA/dioxane entanglement network, dynamic shear rheological measurements were carried out, as already discussed. Typical results are presented in Fig. 5, which depicts the master curves of G' and G'' as functions of frequency for three concentrations, namely 27%, 56% and 66%, with reference temperature 20 °C. First of all, it is pointed out that these measurements were carried out in solutions obtained from the original 77% with successive dilution. This means that the molecular weight was unchanged in all rheological data reported. Further it is noted that the principle of time-temperature superposition holds for all concentrations, as expected; shifting was done only along the horizontal (frequency) axis. It is clear that, within the frequency window of the instrument used, in the 27% solution the whole terminal relaxation process is detected, whereas in the more concentrated solutions only the Rouse-like and rubber plateau regions are measured, including the crossover between G' and G'' at the onset of terminal relaxation, which signifies the longest relaxation time. The shift factors were found to follow the WLF behavior. The corresponding times are in good agreement with the light scattering relaxation times of the slow mode (see Fig. 6 below).

A further analysis of the dynamics of the entangled polymer solutions is presented in Fig. 6, which depicts the relaxation rates of the two processes as functions of concentration. The much stronger dependence observed in the slow "viscoelastic" time, τ_R represents by itself another evidence of the assignment of this process to chain relaxation-like large-scale motion. Essentially there is a different scaling of the cooperative diffusion time, τ_c and τ_R with concentration [31, 35]:

$$\tau_c \sim c^{-\alpha} \quad \text{and} \quad \tau_R \sim c^{\gamma} \tag{13}$$

where $\alpha = 0.75$ for good solvents and 1 for theta solvents, while the corresponding values of γ are 1.6 and 3, respectively, without accounting for friction effects. It should be noted that the scaling for τ_c may not hold as the concentration increases in the highly concentrated regime, as already pointed out by other authors [13]. The actual data covering the whole concentration range (from 9% to 66%) scale with a slope approaching 0.75, suggesting good solvent scaling. The slope of the experimental τ_R at concentrations $c \geq 27\%$ is very large, nearly 10, and does not conform to the above scaling predictions. It represents a clear evidence that at these very high concentrations the viscoelastic behavior of the solutions is dominated by the polymer friction. To further confirm this statement, we carried out rheological measurements at lower concentrations, in the semidilute regime (from 15% to 20%); as can be seen in Fig. 6, the corresponding longest relaxation times scale

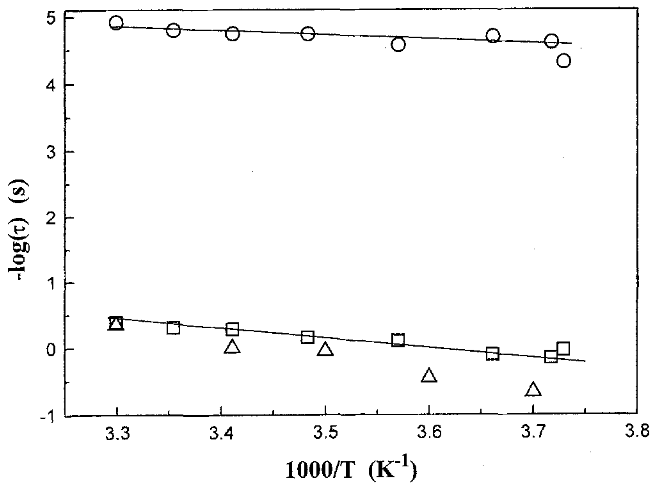


Fig. 7 Arrhenius plot of the relaxation rates of the fast cooperative (○) and slow viscoelastic (□) modes, for the 46% solution at a scattering angle of 90°. Also included are the shift factors α_T from rheology (△). Solid lines are drawn to guide the eye

with nearly the good solvent prediction, 1.6. Concerning the light scattering τ_R data, it is important to emphasize that the molecular weight varies a bit from concentration to concentration, due to the preparation procedure for each sample (thermal polymerization); thus, exact quantitative information on the scaling at very high concentrations cannot be extracted. Nevertheless, despite this inherent uncertainty, the good agreement with the rheological measurements mentioned above, reflected in the terminal relaxation times which are also shown in Fig. 6, as well as the drastically different concentration dependence of the two relaxation processes, are evident and worth noting. Despite the differences in molecular weights, both rheological and light scattering data clearly suggest that PBA/dioxane above 27% cannot be considered being under good solvent friction conditions (despite $D_c \sim c^{0.75}$), due to the increased segmental friction. Thus, irrespective of whether the solvent quality decreases or not at high concentrations (with respect to the measurements of solvent quality in dilute solution, mentioned before), it is apparent that the slow relaxation mode is dominated by segmental friction.

The temperature dependence of the dynamics was investigated for the 46% solution over the temperature range from $-5\,^\circ$C to 30 °C and at a scattering angle of 90°. First of all, the correlation functions obtained suggest that the viscoelastic mode is more affected than the cooperative diffusion mode. The amplitude of the former seems to increase with decreasing temperature, presumably due to a decrease of solvent quality, which enhances the light scattering signal, as discussed in the theoretical section. The relaxation rates (at a scattering angle of 90°) of both processes are depicted in the Arrhenius plot of Fig. 7. It is apparent that the temperature dependence of the slow mode is stronger compared to that of the fast one. In the latter, the increase of D_c with temperature is actually attributed to the corresponding decrease of solvent viscosity, which appears to affect the concentration dependence of D_c (Fig. 6). However, in the case of viscoelastic network relaxation, on top of that we have the chain friction responsible for its terminal relaxation (for example reptation). This is indeed reflected in Fig. 7, where the shift factors from the rheological measurements are also plotted and follow virtually the same trend. The data suggest the following scaling: $\tau_c \sim \exp(-818/T)$, and $\tau_R \sim \exp(-2270/T)$. The activation energy of the slow viscoelastic process is nearly three times as large as that of the fast cooperative one. It is further noted that although the light scattering slow τ_R data follow the shift factors closer than the τ_c data, there is a deviation especially at the lowest temperatures, as seen in Fig. 7; this can be explained by the fact that the PCS measurements at low temperatures are ambiguous, since the long-time relaxation tail of the correlation function is outside the window of the technique, thus introducing an uncertainty in the determination of τ_R.

The issue of time-dependence of the amplitude and relaxation time distribution of the slow relaxation mode, firstly addressed recently by Wang et al. [36], has been investigated by measuring the field correlation function of the same sample (46%) under the same conditions (20 °C, $\theta = 90°$) twice, with a time interval of 16 months. The results clearly show no time dependence whatsoever, in contrast to those of Wang et al. [36], and confirm the high quality of the carefully prepared and equilibrated samples, without the presence of clusters.

Finally, for a more quantative test of the theoretical predictions, the relative amplitude of the slow mode was performed using the approach of Doi and Onuki [19]; the latter provides A_2 as a function of parameters which can be easily measured or determined independently, as seen in Eq. (5) above. The first important remark is that A_2 is q-independent. This was confirmed from our experiments at scattering angles of 45°, 90° and 135°, the measured $A_{2,\,\mathrm{expt}}$ ($= \alpha_{\mathrm{slow}}/(\alpha_{\mathrm{fast}} + \alpha_{\mathrm{slow}})$, α_{slow} and α_{fast} being the amplitudes of the slow and fast relaxation processes, respectively) was found to be 0.49, 0.50 and 0.47, respectively, i.e., constant within experimental error. Further, at 25 °C and a scattering angle of 135°, for concentrations 46% and 66%, the measured $A_{2,\mathrm{expt}}$ are 0.49 and 0.60, respectively. The corresponding predictions A_2 are 0.58 and 0.90, respectively. Given the experimental uncertainties, the uncertainties in the determination of quantities such as ξ_b, for eample, as well as the non-constant molecular weight, the agreement is quite satisfactory. Similar results are reported for the temperature dependence as well. More specifically, for the 46% solution, at a scattering angle of 90°, as the temperature varies from 0° to 14° to 30 °C, the measured A_2 varies respectively from 0.85, to 0.70 to 0.65. The corresponding predictions $A_{2,\mathrm{expt}}$ are 0.95, 0.87, and 0.56, respectively. It is interesting to note that the observed trend of enhanced amplitude of the slow mode at lower temperatures is nicely predicted by the theory. It may be related to the decreased solvent quality, or increased segmental friction, as the temperature is decreased. It is thus clear from the above results that the slow viscoelastic mode can be attributed to the relaxation of the transient entanglement network, which releases its elastic stress induced by the concentration fluctuations.

Summary

Photon correlation spectroscopy in the polarized geometry has been utilized in order to investigate the complex dynamics of highly concentrated polymer solutions. The appearance of a second slow q-independent relaxation mode, in addition to the fast cooperative diffusion process has been confirmed. A direct association between this mode and the terminal region in dynamic shear rheological measurements has been established. Therefore, this mode is of structural origin and due to the viscoelasticity of the transient physical network, formed by the entanglements. The latter result is also supported by theoretical treatments based on the idea of a transient physical entanglement network, which relaxes through the release of the elastic stress induced by the concentration fluctuations. The concentration and temperature dependencies, the former dominated by friction, of this mode are also consistent with rheology and these transient network ideas.

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References

1. Berne B, Pecora R (1976) Dynamic Light Scattering. Wiley, New York
2. Schaefer DW, Han CC (1985) In: Pecora R (ed) Dynamic Light Scattering. Plenum Press, New York
3. de Gennes PG (1979) Scaling Concepts in Polymer Physics. Cornell Univ Press, Ithaca, New York
4. Brown W, Nicolai T (1993) In: Brown W (ed) Dynamic Light Scattering. The Method and some applications (Brown W. ed.), Oxford, London
5. Nicolai T, Brown W, Hvidt S, Heller K (1990) Macromolecules 23:5088; Nicolai T, Brown W, Johnsen R, Stepanek P (1990) Macromolecules 23:1165
6. Amis EJ, Han CC (1982) Polymer Commun 23:1403; Amis EJ, Han CC, Matsushita Y (1984) Polymer 25:650
7. Koch T, Strobl G, Stühn B (1992) Macromolecules 25:6255
8. Wang CH, Zhang XQ (1993) Macromolecules 26:707
9. Brown W (1984) Macromolecules 17:66
10. Chang T, Yu H (1984) Macromolecules 17:115
11. Brown W, Nicolai T (1990) Colloid Polym Sci 268:977
12. Fischer EW (1993) Physica A 201:183
13. Floudas G, Fytas G, Ngai KL (1990) Macromolecules 23:1104; Floudas G, Fytas G, Fischer EW (1991) Macromolecules 24:1955; Gapinski J, Fytas G, Floudas G (1992) J Chem Phys 96:6311
14. Adam M, Delsanti M (1983) J Phys (France) 44:185; Adam M, Delsanti M (1984) J Phys (France), 45:1513; Adam M, Delsanti M (1977) Macromolecules 10:1229
15. Koike A, Nemoto N, Inoue T, Osaki K (1995) Macromolecules 28:2339; Nemoto N, Koike A, Osaki K (1996) Macromolecules 29:1445
16. Nemoto N, Kuwahara M, Yao M, Osaki K (1993) Langmuir 11:36; Buhler E, Munch JP, Candau SJ (1995) J Phys II France 5:765
17. de Gennes PG (1976) Macromolecules 9:587; de Gennes PG (1976) Macromolecules 9:594; Brochard F, de Gennes PG (1977) Macromolecules 10:1157; Brochard F (1983) J Phys (France) 44:39
18. Adam M, Delsanti M (1985) Macromolecules 18:1760
19. Doi M, Onuki A (1992) J Phys II – France 2:1631
20. Larson RG (1988) Constitutive Equations for Polymer Melts and Solutions. Butterworths, Boston
21. Nemoto N, Kishine M, Inoue T, Osaki K (1991) Macromolecules 24:1648
22. Semenov AN (1990) Physica A 166:263
23. Pincus P (1981) J Chem Phys 75:1996; Binder K (1983) J Chem Phys 79:6387
24. Wang CH (1991) J Chem Phys 95:3788; Wang CH (1992) Macromolecules 25:1524; Wang CH (1993) In: Brown W (ed) Dynamic Light Scattering. The Method and some applications. Oxford, London
25. Akcazu AZ, Wang CH, Klein R (1994) Macromolecules 27:2736
26. Wang CH (1995) J Chem Phys 102:6537; Wang CH, Sun Z, Huang QR (1995) J Chem Phys, submitted
27. Brown W, Stepanek P (1993) Macromolecules 26:6884
28. Genz U (1994) Macromolecules 27:3501
29. Brown W, Schillen K, Johnsen R, Konak C, Dvoranek L (1992) Macromolecules 25:802
30. Provencher SW (1982) Comput Phys Commun 27:229
31. Ferry JD (1980) Viscoelastic Properties of Polymers. 3rd ed, Wiley, New York
32. Wang CH, Zhang XQ (1995) Macromolecules 28:2288
33. Huber K, Bantle S, Lutz P, Burchard W (1985) Macromolecules 18:1461
34. Douglas JF, Hubbard JB (1991) Macromolecules 24:3163
35. Doi M, Edwards SF (1986) The Theory of Polymer Dynamics. Oxford, London; Schweizer KS, Szamel G (1995) Macromolecules 28:7543
36. Wang CH, Sun Z, Zhang XQ (1994) Makromol Symp 28:2288