Experimental Evidence of Slow Dynamics in Semidilute Polymer Solutions

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ABSTRACT: The semidilute and concentrated solutions have been extensively investigated, but many questions are still unsolved. The present work, by means of photon correlation spectroscopy investigation on PMMA/acetone solutions, aims to add new information to the comprehension of the existence of a long time contribution in the autocorrelation functions in semidilute solutions together with the fast diffusive modes. On the basis of our results we follow the idea of the intervention of elastic and stress relaxation of the network constituted by the entangled polymer chains. Moreover, we think that the observation of the slow modes can be attributed not only to the existence of entanglements but also to the effect that the monomer structure produces on the entanglement phenomenon itself.

Introduction

Recently, many studies on the static and dynamic properties of binary systems have been carried out in a very wide range of concentration values. Although thermodynamic and dynamic behavior of these systems in the diluted regime is well characterized, the semidilute and concentrated solutions constitute a still open question. They represent a many-body problem in which it is necessary to take into account not only the direct intermolecular interactions but also the effect of the long-ranged hydrodynamic component on the collective motions. As far as the colloidal suspensions at high concentration are concerned, however, it is possible to apply different models, such as, for example, the Baxter adhesive hard sphere[1] and to obtain information on the structural and diffusive properties of the colloidal particles as well as on the hydrodynamic interactions.[2]

For the existence of chain overlaps and entanglements, the polymer solutions in the concentrated regime are more complex than the colloidal suspensions; moreover, the solvent quality's role, which affects the dimension of a polymer chain in dilute solutions, in the semidilute regime is more delicate. It seems that the effect of good solvent quality approaches that of the Θ solvent condition increasing concentration above the semidilute regime.[3] Finally, in the intermediate scattering functions of many entangled polymeric solutions, there is the evidence of long time *q*-independent processes together with the fast diffusive ones. It is the widely held view that the fast modes are related to the relative random motions of blobs in the entangled polymer network and the slow modes are not to be attributed to the diffusion of clusters or to the coil self-diffusion as was first supposed, but to the presence of viscoelastic effects. This interpretation is founded on the fact that by varing concentration the nondiffusive slow modes are very similar to those observed in a polymer melt. A large number of semidilute polymer solution studies have been developed on the basis of two main theories: the transient network gel by de Gennes[4,5] and the Wang's hydrodynamic theory[6−8] based on a completion of the statistical mechanical approach of Bearman−Kirkwood.[9] The first one relates the presence of the slow modes to the viscoelastic nature of the transient network, formed by polymer entanglements, which relaxes its elastic stress induced by the concentration fluctuations. Within the anology with a polymer melt, the fast process is due to the concentration fluctuations of the polymer subsystem, while viscoelastic modes originate from density fluctuations of the entire system. But density fluctuations may relax by the much faster motions of solvent molecules; however, if partial specific volumes of solvent and polymer differ, fluctuation in polymer density may not fully relax by the fast motion of the solvent molecules. For these reasons Wang formulated his theory, showing that the coupling of concentration fluctuations to the relaxation stress modulus arises naturally when there exists a difference in specific volumes of the polymer and solvent components. However, because Brown and Stepanek[10] found the slow modes also for polymer solutions in which solute and solvent have the same density, Wang with Ackasu and Klein[11] revised Wang's model and found that there was an additional component, not present in the original theory, causing viscoelasticity effects on the decay of concentration fluctuations of the polymer component even if the specific volumes of solute and solvent are identical.

Although up to now numerous developments have been made in the semidilute and concentrated regime of polymer solutions, through for example recent works by Genz,[12] Schweizer,[13] and Ackasu et al.[11] as well as numerous experimental results,[14−17] the problem is far from a comprehensive resolution. For example, so far it is not possible to provide an underlying microscopic understanding of the physical origin of the *q* independence of the slow modes and the effects of temperature.

The aim of the present work is to add new information by means of a deep experimental study. We will show the results of photon correlation spectroscopy measurements on dilute and semidilute solutions of poly(methyl methacrylate) (PMMA) in acetone. In addition, measurements on solutions of poly(ethylene oxide) (PEO) in water are reported and compared with those of PMMA/acetone and those found in the literature. The wide molecular weight range investigated allowed us to determine the good solvent quality of acetone for PMMA in the dilute region and the presence of repulsive

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interactions between the polymer chains. As the concentration is raised to the semidilute regime, the time correlation function cannot be considered a single exponential, and the existence of two distinct processes at very different time scales becomes more and more pronounced. In the frame of the present work we will show our experimental results suggesting that the existence of these modes can be led back to the polymer chain entanglements, and we will consider the possibility that the monomer structure constituting the chain can have an influence on the slow modes.

Samples and Experimental Setup

PMMA samples, furnished by Aldrich Chemical Co., are highly monodisperse and have molecular weight values that range from 10^4 to 8×10^5. The solutions were prepared using acetone as solvent, and care was taken in order to stabilize them. It was also necessary to filter the solutions in recirculation, by means of a Teflon Amicon Millipore filter of 0.45 μm. The investigated concentration range depends on the molecular weight because of the high viscosity of the samples and the solubility limit.

QELS measurements were performed by means of the photon correlation spectroscopy (PCS) technique, using a standard scattering apparatus with a photon counting optical system and a Brookhaven BI-2030 correlator to analyze the scattered light. This technique allows to investigate molecular motions on a time scale ranging from fractions of microseconds to few seconds, so it is really suitable for the investigation of the slow modes. As exciting source, the 4880 Å vertically polarized line of a unimode Ar^+ laser Innova model 70, working in the power range 50−400 mW, was used. The scattered light, by means of an optical fiber, was detected essentially in a 90° scattering geometry by a photomultiplier tube connected with the correlator. In some case we checked the q dependence of the correlation functions. Samples were mounted in a thermostat with a temperature control better than ±0.02 °C. The investigated temperature range was 30−50 °C.

Theoretical Background

A PCS apparatus allows to measure the normalized autocorrelation function of the total scattered intensity $I_S(q,t)$:[18]

$$g_2(q,t) = \frac{\langle I_S(q,0)\, I_S(q,t)\rangle}{\langle I_S(q)\rangle^2} \tag{1}$$

In the case of particle *motion independence* the central limit theorem ensures that the scattered field will obey to a Gaussian distribution, and the Siegert's relationship can be applied:

$$g_2(q,t) = 1 + \alpha |g_1(q,t)|^2 \tag{2}$$

where α is a constant which depends on the number of the selected coherence areas (and hence on the experimental setup) and $g_1(q,t)$ is the normalized field autocorrelation function, defined as

$$g_1(q,t) = \frac{\langle E_S(q,0)\, E_S^*(q,t)\rangle}{\langle |E_S(q)|^2\rangle} = \frac{\langle E_S(q,0)\, E_S^*(q,t)\rangle}{\langle I_S(q)\rangle} \tag{3}$$

For diffusing monodisperse spherical scatterers, the normalized intensity−intensity correlation function takes a simple exponential form: $g_2(t) = 1 + \alpha \exp[-2\Gamma t]$, where Γ, the half-width at half-maximum of the optical spectrum, for $qR_H < 1$ is related to the diffusion coefficient, D, by the relation $\Gamma = Dq^2$.[19]

In the very dilute limit, the theory of Brownian motion relates the measured D to the self-diffusion coefficient at infinite dilution D_0, which is connected to the center of mass motion of the isolated coil and allows to evaluate the hydrodynamic radius, R_H, of the particles by the Einstein−Stokes relation:

$$D_0 = \frac{K_B T}{6\pi\eta R_H} \tag{4}$$

where η is the viscosity coefficient of the continuous medium.[18]

As a matter of fact, polymeric solutions, expecially at high concentration and with polymers at high molecular weight, are polydisperse, so $g_1(t)$ becomes nonexponential because of the presence of a relaxation times distribution originating from the distribution of particle sizes. Consequently, in such a case a standard cumulant analysis is more suitable:[20]

$$\ln(\alpha^{1/2}|g_1(t)|) = \ln \alpha^{1/2} - \langle\Gamma\rangle t + \frac{\mu_2}{2} t^2 - \frac{\mu_3}{6} t^3 + ... \tag{5}$$

Here $\langle\Gamma\rangle$ is the first cumulant, related to the effective diffusion coefficient by $\langle\Gamma\rangle = D_{eff} q^2$, and μ_n is the nth moment of the distribution. In particular, the second distribution moment, μ_2, is related to the polydispersity of the sample, defined as $\mu_2/\langle\Gamma\rangle^2$.

From a general point of view, $D_{eff}(q)$ is an *effective* q-dependent diffusion coefficient which depends on the particle equilibrium distributions ($S(q)$) as well as on the hydrodynamic interactions ($H(q)$):[21]

$$D_{eff}(q) = D_0 \frac{H(q)}{S(q)} \tag{7}$$

In the limit $q \to 0$, the effective diffusion coefficient is identified with the collective diffusion coefficient, defined by the generalized Stokes−Einstein relation $D_c = (\partial\Pi/\partial c)_T(1/\xi)$, with $(\partial c/\partial\Pi)_T$ the osmotic compressibility and ξ the frictional coefficient.

Above the overlap concentration $c^* = 3M(N_A 4\pi R_H{}^3)^{-1}$ (where M is the molecular weight and N_A the Avogadro number), which defines the semidilute regime, entanglements cannot be neglected and influence the overall dynamics of the polymer chains. The evidence of the entanglements effect occurs in the presence of two distinct contributions in the intensity autocorrelation function. In particular, the high-frequency limit of the spectrum is represented by a fast diffusive mode (q^2 dependent) attributed to the relaxation of the cooperative motions of the polymer chains forming a sort of network. In the low-frequency limit the concentration fluctuations decay through structural relaxation of the network itself and are manifested in an additional component in the correlation functions.[22−25] The occurrence of these slower modes (where it exists), which have a very broad distribution and are q-independent, depends on the polymer molecular weight as well as on the concentration.

Following the de Gennes and Brochard theoretical description,[22] the correlation function can be written as

$$g_1(q,t) = A_1 e^{-\Gamma_1 t} + A_2 e^{-\Gamma_2 t} \tag{8}$$

where $\Gamma_1 = D_g q^2$ and $\Gamma_2 = D_c/(D_g \tau_R)$, τ_R being the

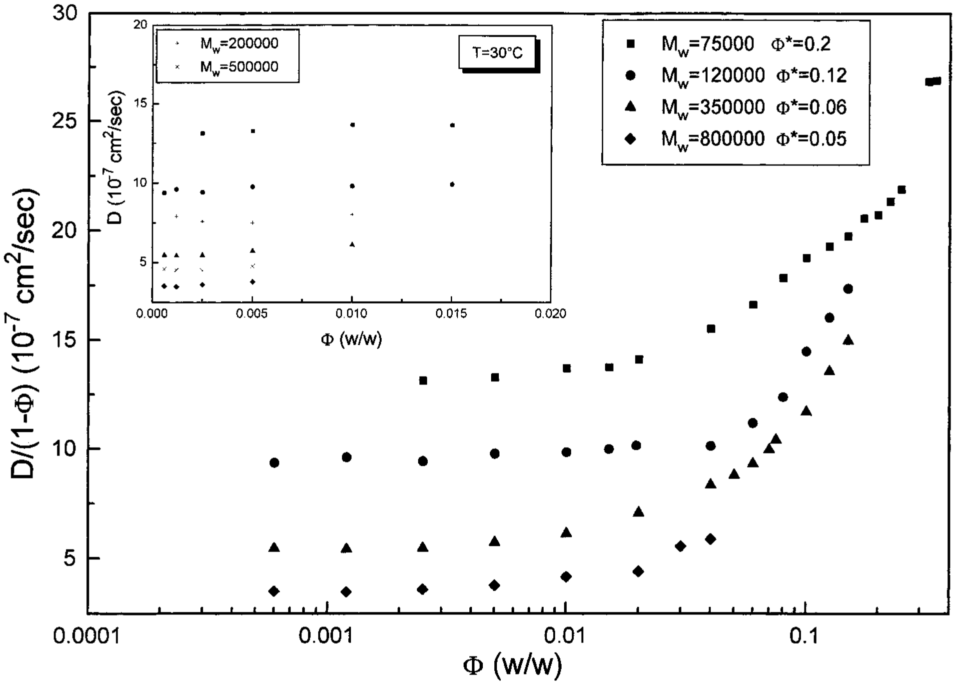

Figure 1. Plot representing the collective diffusion coefficient over the investigated concentration range, including both the dilute and semidilute regime at $T = 30$ °C. In the inset only the diluted region is reported.

characteristic lifetime of the network contact point and D_g the diffusion coefficient of the transient gel.

Introducing a wave vector $q^+ = (\tau_R D_g)^{-1/2}$ for which the diffusion time on a scale $(q^+)^{-1}$ is τ_R, the $q \ll q^+$ region defines the liquid regime where the time decay and the amplitudes in the normalized autocorrelation function $g_1(q,t)$ reduce to: $\Gamma_2 = \Gamma_{2c} = D_c q^2$; $\Gamma_1 = (\tau_R)^{-1}$; $A_2 = 1$ and $A_1 = 0$. Therefore, the time dependence of $g_1(q,t)$ is a single-exponential function: $g_1(q,t) = e^{-\Gamma_{2c}t}$.

The gellike regime is found in the opposite limit $q \gg q^+$. In such a case the faster relaxation mode is controlled by the equilibration between osmotic pressure and elastic stress and reflects the cooperative diffusion: $\Gamma_1 = D_g q^2$; the slower mode, $\Gamma_2 = D_c/(D_g \tau_R)$, is a q-independent structural relaxation and is related to the viscoelasticity of the entangled polymer solution. These are only approximate forms valid provided $D_g q^2 \gg (\tau_R)^{-1}$, namely for the time during which the polymer system can be considered as a permanent gel. The coupling of the viscoelastic mode alters the diffusion coefficient D_g of the fast diffusive mode. Since $D_g > D_c$, the collective diffusion is enhanced in the presence of viscoelasticity.

In view of these results the viscoelastic relaxation time plays a key role in the slow mode investigations. In fact, small viscoelastic relaxation times make the q^+ value higher than the q range investigated by QELS and allow to get information on the osmotic diffusion coefficient D_c in the liquid regime. On the other hand, for samples having long viscoelastic relaxation times, such that the corresponding q^+ value is lower than all the investigated q, the slow modes are detectable. The obtained diffusion coefficient D_g is concentration dependent and independent of the molecular weight; the long time decay, corresponding to a structural relaxation, instead, varies strongly with the molecular weight.

In the next section we will show the results of the study on PMMA/acetone solutions, showing the presence of the slow modes above a certain concentration value in a good solvent. A further study on PEO/water solutions, instead, did not show any presence of slow modes. This comparison suggests that in the viscoelastic effects, caused by entanglement processes, not only the polymer chain length plays the main role but also the monomer structure can affect this phenomenon.

Results and Discussion

At low weight fraction, up to $\Phi \approx 1$ wt %, it is possible to fit the correlation function using a single exponential or for the samples at higher molecular weight the cumulant expansion, considering that more than one relaxation time can be present due to the polymer coils size distribution. The obtained translational diffusion coefficient as a function of concentration gives information about the intra- and intermolecular interactions. It is well-known, in fact, that the majority of linear polymers in solution are very flexible and that chains may be swollen or collapsed due to the repulsive or attractive forces among the monomers. The inset of Figure 1 displays the low-concentration behavior of the obtained collective diffusion coefficient as a function of weight fraction Φ for some (the qualitative behavior being the same for all the samples) of the investigated molecular weights. The increase of D at low Φ is represented by the relation[26] $D = D_0(1 + K_D\Phi)$, where K_D is called concentration coefficient giving information about the interaction character. This increase indicates a *swollen* ($K_D > 0$) state of the polymer molecules, namely the existence of repulsive interactions between monomers, and denotes that in the investigated temperature range acetone behaves as a good solvent for PMMA. Moreover, the evaluated K_D values are almost constant with molecular weight, as expected, indicating that the intrachain repulsive interactions which tend to swell the polymeric coil are independent of the chain length. The linear fit of the diffusion data allows also to evaluate the diffusion coefficient extrapolated at infinite dilution. This latter follows the Mark−Houwink (M−H) relation, $D_0 = aM_w^{-\nu}$, where ν, which depends on the nature of the solvent, is the universal scaling exponent determined by the interactions among the

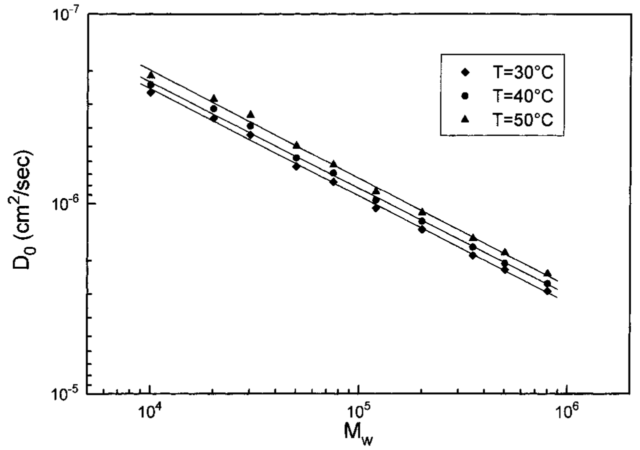

Figure 2. D_0 values arranged on the Mark−Houwink fit. The slope $\nu = 0.57$ indicates the good solvent quality of acetone.

Table 1. Hydrodynamic Radius Values for Different Molecular Weights and Temperatures

	R_H (Å)		
M_w	$T = 30$ °C	$T = 40$ °C	$T = 50$ °C
10 000	26.2	25.3	25.4
20 000	30.0	28.9	31.5
30 000	32.4	33.5	35.2
50 000	47.6	48.4	47.1
75 000	57.6	58.1	59.3
120 000	79.3	80.8	82.1
200 000	102.8	104.3	106.1
350 000	140.4	142.5	145.0
500 000	167.5	174.4	172.2
800 000	197.8	197.3	201.2

constituent monomers. Figure 2 shows that the data arrange on a straight line whose slope is $\nu = 0.57$, in excellent agreement with the theoretical value (0.6 according to the Flory model[27] or 0.588[28]), confirming the good solvent quality of acetone. Moreover, the D_0 data allow to evaluate the hydrodynamic radius, R_H, of the polymer coil according to the Einstein−Stokes relation; in Table 1 the radii are reported as a function of molecular weight and temperature.

As far as the temperature dependence of R_H is concerned, it seems that it increases with temperature systematically even if the variation is not great. This behavior can be interpreted by considering the net result of two effects. The enhanced thermal motions at higher temperatures lead to lower residence times of the solvent molecules in the solvation shell of the polymer; as a consequence, the average number of the solvent molecules moving together with polymer will be lower. On the other hand, temperature affects the solvent quality: when the temperature is raised, the intramolecular interactions tend to enhance the swelling of the polymer coil. Therefore, the observed increase of the hydrodynamic radius indicates that the diminishing of the solvent molecules in the solvation shell of the diffusing PMMA entities due to thermal effects is overcome by an increase in the dimension of the PMMA molecule due to the intramolecular repulsive interaction between the constituent monomeric unities.

As the concentration of the polymer solutions reaches the semidilute region, the chains begin to overlap and entangle, and new dynamical processes involving interchain interactions and disentanglements begin to occur. As can be seen in Figure 1, which shows the concentration dependence of the collective diffusion coefficient normalized by $(1 - \Phi)$ at $T = 30$ °C, when Φ is further raised, $D' = D/(1 - \Phi)$ tends to become independent of molecular weight;[26] this region defines the semidilute regime.

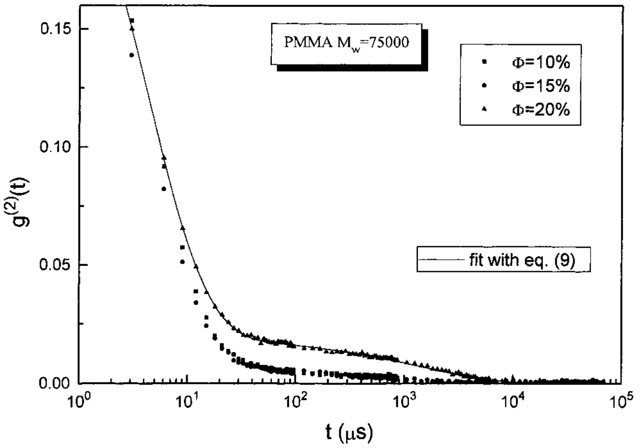

Figure 3. Long time contribution in the correlation functions for three concentration values at $T = 30$ °C.

For the concentration values above 10%, it is possible to see the most salient behavior of these solutions; in fact, the correlation functions show an evident net distinction between the fast relaxation modes, attributed to the collective diffusive process, and the slow modes.

Figure 3 shows that these slow modes become evident also below Φ^* but are more and more enhanced as the overlap concentration is reached. The time scales of slow processes differ 3 orders of magnitude from the fast ones.

Following the de Gennes and Brochard theory and considering that two decays contribute to the first-order correlation functions $g_1(q,t)$ (eq 8), the experimental intensity−intensity autocorrelation functions $g_2(q,t)$ have been fitted by the following relation:

$$g_2(t) = A_1 \exp\left[-2\left(\frac{t}{\tau_1}\right)^{\beta_1{}^{kww}}\right] + A_2 \exp\left[-2\left(\frac{t}{\tau_2}\right)^{\beta_2{}^{kww}}\right] + 2(A_1A_2)^{1/2} \exp\left[-\left(\frac{t}{\tau_1}\right)^{\beta_1{}^{kww}}\right] \exp\left[-\left(\frac{t}{\tau_2}\right)^{\beta_2{}^{kww}}\right] \quad (9)$$

We used the stretched exponentials, $A \exp[-(t/\tau)^{\beta^{kww}}]$, instead of pure exponentials because the slow relaxation modes are constituted by a broad distribution (see Figure 3 as an example). The fast modes are nearly exponential, the β_1 coefficient being always close to unity (0.9−1); furthermore, their amplitude is always higher than that of the slow modes.

Figure 4 shows, as an example, the q^2-dependence of the fast relaxation rate, confirming that we are dealing with diffusive motions. Figure 5, instead, shows that the slow processes time decay is q-independent, suggesting that these modes essentially originate from the viscoelastic nature of the relaxation due to the entanglement process.

The appearance of significant slow modes in PMMA/acetone solutions, namely under good solvent conditions, in contrast to what theory predicts, could be due to the fact that in the semidilute regime the solvent quality tends to the Θ condition. Most of the experimental work, in fact, deals with solutions of polymer in Θ solvent, but the present work and that one by Jian et al.,[14] who recently also found evidence of the slow modes in highly

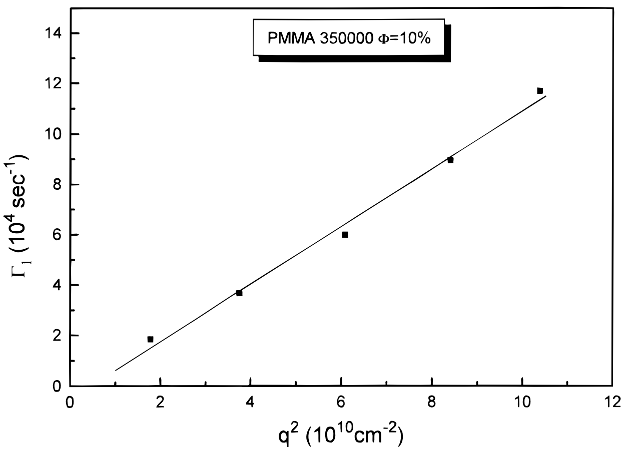

Figure 4. Mean rate decay of the fast modes at $T = 30$ °C.

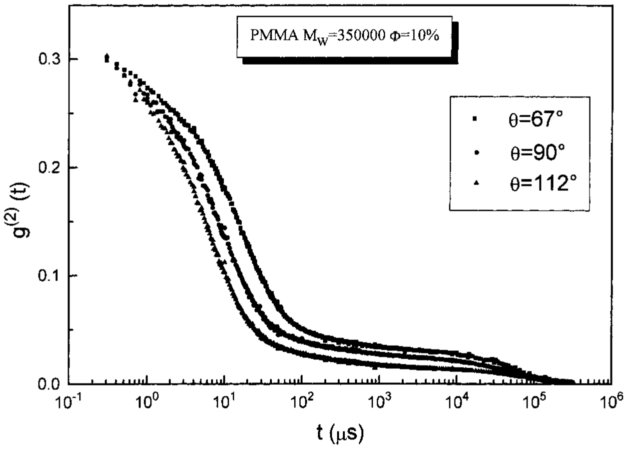

Figure 5. Experimental correlation function for a solution in the semidilute regime at three scattering angles and $T = 30$ °C.

concentrated solutions of poly(butylacrylate) in a good solvent (dioxane), show that this phenomenon is not peculiar of Θ systems.

In a recent work[29] Wang and co-workers made a comparison between the experimental correlation functions of two solutions of polystyrene in diethyl malonate (DEM) and in diethyl phthalate (DEP) far above the overlap concentration value. They attributed the absence of the viscoelastic modes in the PS/DEM solution to the zero value of the coupling parameter of Wang.[7,8]

As previously stressed, in order that the slow modes are detectable, it is necessary to reach substantial entanglements in the solutions. It has been highlighted[30] that there is a relation between the size of the polymer coils and the degree to which they entangle with each other and hence to their viscoelastic properties. For this aim it is possible to define an entanglement molecular weight, M_e, which depends on the polymer structure through

$$M_e \propto \left(\frac{\langle R^2\rangle_0}{M_W}\right)^{-3} \rho^{-2} \qquad (10)$$

where ρ is the density of the polymer and $\langle R^2\rangle_0$ the unperturbed (ideal) polymer size. Above this value the entanglement phenomena become significant.

All the samples investigated in this work are well above the entanglement molecular weight (M_e(PMMA) $\approx$ 10 000)[30] so that also at concentration values lower than Φ* there is evidence of viscoelastic effects. When the concentration increases above the overlap value, these effects are strongly enhanced. As far as the comparison with Wang's theory is concerned, Wang's coupling parameter β for PMMA/acetone solution takes nonzero values from 0.008 in one of the more dilute solutions of PMMA 75 000 (Φ = 2%) to 0.128 in the more concentrated one (Φ = 35%), according to Wang's theory, but our recent study on poly(ethylene oxide) ($M_e \approx$ 1400)[30] 8000/water solutions[31] does not show any presence of the slow processes up to a concentration of 50%. The coupling parameter value corresponding to this concentration ($\beta = 0.08$) is greater than that of the PMMA/acetone solutions in which the slow modes become evident. The well-known (see for example ref 32) good solvent quality of water for PEO makes this comparison suitable.

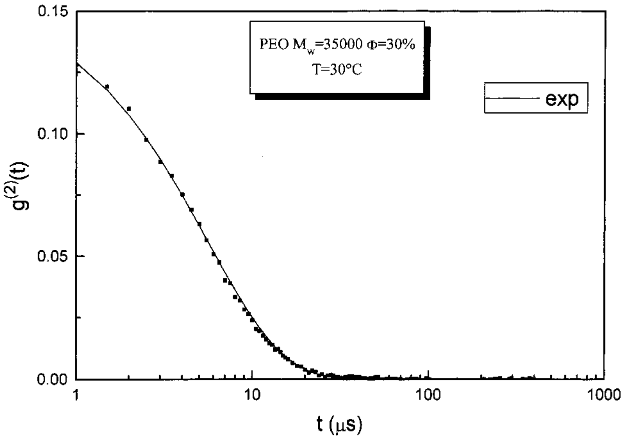

Figure 6. Plot showing that in the investigated PEO−water solutions the slow modes are not present.

If we consider that the polymer chain length plays the main role, the absence of the slow modes could be related to the fact that the PEO investigated sample has a too short chain. So, the minimum concentration value for the occurrence of slow modes could be higher than 50%. To check this hypothesis, we performed measurements on PEO 35 000 for which the polymerization degree ($n = 790$) is as great as PMMA 75 000, at a concentration of 30%, far above the overlap concentration. Also in this case we did not observe any presence of slow modes for PEO solutions, as shown in Figure 6.

This evidence can be due to the fact that there can be a relation between the side units of a polymer and the entanglement molecular weight M_e. The higher M_e value for PMMA than that for PEO implies a higher packing of PMMA entangled chains, giving rise to a higher viscoelastic relaxation time. As a consequence, at the same concentration, the value of q^+ for PMMA/acetone solutions is lower than that for PEO/water solutions at the same concentration; therefore, for the investigated q range it is possible to see the slow modes in the former solutions but not in the latter.

In view of these results, we think that the source of these viscoelastic effects in PMMA solutions cannot be attributed to the nonzero values of Wang's parameter, but it could be found in the topological constraint which becomes effective above a certain minimum concentration and polymer chain length necessary to produce entanglements and in the side chain effects of the monomer structure. Branched chains or bigger side units could increase the lifetime of the network and, hence, the viscoelastic relaxation time. The MMA unit, in fact, possesses side units bigger than those of the ethylene oxide, the latter having a linear conformation. When the entangled network is formed, smaller side units disentangle more easily than the bigger ones.

Further investigations, however, are in progress in order to understand better this phenomenon and to give more quantitative information about the relation between the chains side units and the occurrence of slow modes.

Concluding Remarks

An accurate study performed on dilute and semidilute PMMA/acetone solutions allowed to obtain information on the polymer coil dimensions, inter- and intramolecular interactions, and the presence of a long time contribution in the autocorrelation functions. This latter subject has been extensively studied recently, and it seems that the presence of these slow modes is to be attributed to the coupling between viscoelastic modes and concentration fluctuations. In particular, the occurrence of this phenomenon leads back to the elastic and stress relaxation effect of the network originating from by the entangled chains on the decay of concentration fluctuations.

The present work has shown that the slow processes can also not occur in circumstances in which they are expected. So, the entanglement effects, which are manifested above a certain minimum concentration and polymer chain length, could also depend on the monomer structure constituting the chain. In particular, the dimension of the side units can affect the entanglement and disentanglement phenomena and, hence, the elastic and stress relaxation of the network.

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