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Stretched-exponential relaxation of electric birefringence in complex liquids

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Abstract. The relaxation of electric birefringence is experimentally investigated in three distinct systems: critical binary mixtures, polydisperse micellar solutions and dilute polyelectrolyte solutions. The asymptotic behaviour is shown to be consistent with a stretched-exponential form $\exp[-(t/\tau)^\alpha]$. Most of the data are quantitatively explained by a simple model of parallel relaxation of many independent processes characterized by a wide distribution of sizes.

1. Introduction

In the past few years a great variety of experimental data for dielectric, magnetic, NMR, optical and mechanical relaxation phenomena in complex random systems [1–11] have been shown to obey, at least asymptotically, a behaviour of the type

$$R(t) = \exp[-(t/\tau)^\alpha] \quad \text{with } 0 < \alpha \leq 1 \quad (1)$$

which is known as a stretched exponential (SE). The similarity of relaxation processes in rather different random systems, such as glasses, spin-glasses, polymers, viscous fluids, disordered dielectrics and complex liquids, is striking and might indicate a common origin of such behaviour. We review in this paper our experimental work concerning the relaxation of electric-field-induced birefringence in critical binary mixtures [8, 12], micellar [10] and polyelectrolyte [11] solutions, placing particular emphasis on the latter system. We have found in all the investigated systems an asymptotic SE decay. A simple model based on the 'polydispersity' of the system can explain quantitatively most of the experimental results.

2. Stretched-exponential behaviour

The experimental results discussed in this paper are interpreted using a model which describes the overall relaxation of the system as a weighted superposition of many independent processes. The relaxation function $B(t)$ is written as

$$B(t) = \int_0^\infty P(m)S(m) \exp\left(-\frac{t}{\tau(m)}\right) dm \quad (2)$$

where m is the parameter (typically a size) which characterizes each individual process,

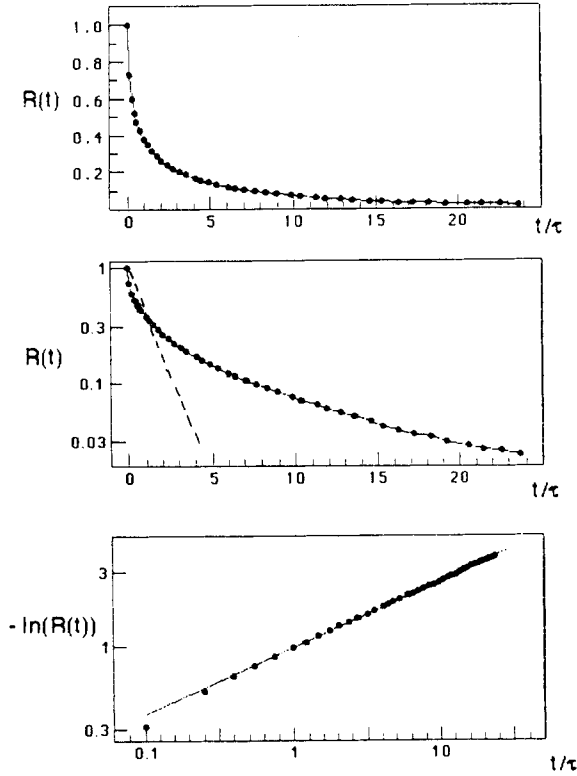


Figure 1. The normalized relaxation function $R(t)$ obtained in a TEB experiment on a polyelectrolyte solution. The upper plot is on a linear scale, the intermediate plot presents the same data on a semilogarithmic scale, and the lower plot presents $-\ln R(t)$ versus t/τ on a log-log scale.

$P(m)$ is the probability density of m , $S(m)$ is a signal function describing the contribution of each process to the observed signal, and $\tau(m)$ is the time constant of the exponential relaxation of process m . If we make the assumptions

$$P(m) \approx \exp(-Am^p) \quad S(m) \approx m^r \quad \tau(m) \approx m^q \quad (3)$$

where the exponents p, q, r are positive numbers and A is a constant, and we substitute (3) into (2), we can find an approximate solution to the integral by using the saddle-point approximation. The result is [12]

$$B(t) \approx t^\gamma \exp[-(t/\tau)^\alpha] \quad (4)$$

where

$$\alpha = p/(p+q) \quad \gamma = (2r+2-p)/(2p+2q). \quad (5)$$

In our discussion of the experimental data, we shall neglect the term t^γ which gives only logarithmic corrections to the dominant SE behaviour.

We show in figure 1 a typical relaxation curve following an electric-field rectangular pulse which terminates at $t = 0$. With $B(t)$ the observed birefringence at time t , we define a normalized relaxation function $R(t) = B(t)/B(0)$. The upper plot presents the data on a linear scale. The intermediate plot presents the same data on a semilogarithmic scale: the decay is clearly non-exponential and shows a very long tail. In this plot the broken line corresponds to an exponential decay having the same time constant τ as the SE decay. The lower plot presents $-\ln[R(t)]$ versus t/τ on a log-log scale. The linearity of

the plot indicates a SE decay, the stretch exponent α being given by the slope of the straight line.

3. Experimental details

The transient electric birefringence (TEB) experiment consists of applying a rectangular pulse of electric field to the sample and observing the associated pulse of induced birefringence. We have focused our attention on the decay of the induced birefringence after removal of the applied electric field. A detailed description of our apparatus can be found in [13]. Here, we simply recall that the set-up includes a quarter-wave plate inserted between the Kerr cell and the analyser. For the experiments described in this article the optical path length of the cell is 60 mm, and the electrodes have a separation of 2–3 mm. Voltage pulses with heights of 0.2–5 kV cm⁻¹ and durations of 20–500 μ s were used. The output of the photodetector is sent to a transient digitizer and averager, the decay being sampled over 1000 points, with typically the last 100 points used to evaluate the baseline to an accuracy of better than 0.2%. The overall response time of the apparatus is less than 1 μ s.

The Kerr constant B is defined as $B = \Delta n / \lambda E^2$, where Δn is the induced anisotropy in the refractive index in stationary conditions, E is the applied electric field and λ is the wavelength of the probing light. For all the experiments described in this paper, we have verified that the shape of the birefringence transient does not depend on the applied field and that Δn is proportional to the square of the field.

4. Critical binary mixtures

We have studied two critical binary mixtures, both showing a lower consolute boundary: water and 2,6-lutidine [8], and water and 2-butoxyethanol [14]. We briefly discuss the results obtained with the latter system which has a critical point at 49.8 °C and contains 26 wt% butoxyethanol. Temperature control within the thermostatted cell was maintained to ± 0.01 °C. By fixing the concentration at the critical value, we have studied the temperature dependence of the electric birefringence measurements in a temperature range of 10 °C below T_c . We do not repeat here the description of the static data [12], but we limit our discussion to the dynamic behaviour. We have found indeed that the relaxation function is not exponential and shows asymptotically a SE behaviour. By making a log–log plot of the type shown in the lower part of figure 1, we find that the linear behaviour is followed over a larger and larger time range as T approaches T_c . The value of the stretch exponent α is 0.40 ± 0.05 , independently of the temperature distance from the critical point, for both the investigated critical systems. The time constant τ shows a power-law divergence as a function of the reduced temperature. A fit with the law $\tau \approx (T_c - T)^{-y}$ yields $y \approx 1.8$ for both systems.

To describe the observed birefringence transients we have used a dynamic droplet model [8], suggesting that the spectrum of relaxation times arises from the distribution of sizes of order-parameter fluctuations in the critical fluid. These fluctuations are distorted by the application of an electric field, in the same way as it occurs with aerosol droplets, and will relax back to equilibrium diffusively. If we assume that the role of the variable m in equation (2) is taken, in the critical fluid, by the size of the critical fluctuation, we can take, consistently with the static droplet model, a Gaussian probability density for $P(m)$ which means an exponent $p = 2$. The observed dependence of

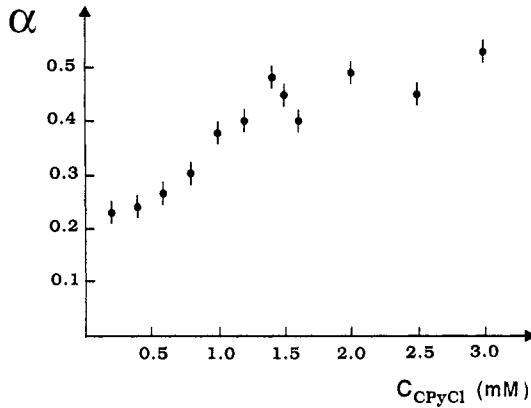


Figure 2. The stretch exponent α plotted as a function of the amphiphile concentration for a solution of polydisperse rod-like micelles.

τ on $T_c - T$ is consistent with the choice $q = 3$, if we note that the measured exponent y is nearly 3ν , ν being the critical exponent for the divergence of the correlation length. Inserting the values chosen for p and q into equation (5), we derive the prediction $\alpha = 0.4$, in very good agreement with the experimental results.

5. Polydisperse micellar solutions

The interpretation of the results obtained with the critical systems suggests that any polydisperse system satisfying some simple general criteria (additivity of contributions, exponential form of the size distribution $P(m)$, power-law dependence of $\tau(m)$ on m) might show a SE relaxation. In order to test this prediction we have performed a TEB experiment on an appropriately selected colloidal solution, namely a polydisperse solution of rod-like micelles. It is known that ionic amphiphile solutions undergo, upon addition of salt, a transition from spherical to polydisperse cylindrical micelles. Since the conductivity of the solution must be very low in an electric birefringence experiment, it is necessary to choose a system which forms elongated micelles at very low concentrations (below a few mM) of both ionic amphiphile and salt. The system we have chosen was previously investigated by Hoffmann and co-workers [15], and consists of water solutions of cetylpyridinium chloride (CPyCl) with the addition of sodium salicylate (NaSal). We have performed measurements at 3 mM NaSal, in the amphiphile concentration range $0.2 \text{ mM} < c < 3 \text{ mM}$ (figure 2). We have found that, at all the investigated concentrations, the relaxation of induced electric birefringence follows asymptotically a SE behaviour. Typically, by making a plot of $R(t)$ of the type shown in the lower part of figure 1, a linear behaviour is observed over more than one decade in the reduced variable t/τ . The slope of the best-fit straight line is reported in figure 2 as a function of the amphiphile concentration. We see that α grows from about 0.24 at concentrations below 0.5 mM to about 0.5 for c larger than 1 mM. We have calculated the entanglement concentration c^* by using for the average rod length the experimental data of [15]. We find that $c^* \approx 0.6 \text{ mM}$.

The low-concentration results can be interpreted in the following way. On the assumption that interparticle interactions are negligible, $B(t)$ can be written as a sum of individual-particle responses and can be expressed as equation (2) with m here playing the role of the micelle aggregation number. The statistical model for the sphere-to-rod transition [16] predicts a probability distribution $P(m) = A \exp(-Am)$, where the

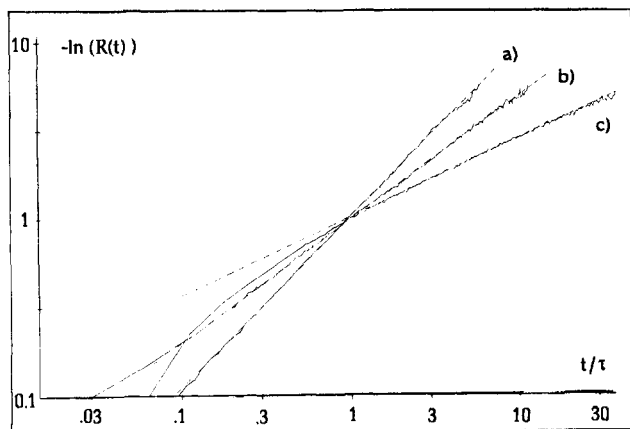


Figure 3. Relaxation function obtained with NaPSS solutions: curve a, $M = 1 \times 10^5$, $I = 0.05$ mM, $c = 5 \times 10^{-2}$ mg cm $^{-3}$, $\alpha = 1$; curve b, $M = 4 \times 10^5$, $I = 0.4$ mM, $c = 1 \times 10^{-2}$ mg cm $^{-3}$, $\alpha = 0.7$; curve c, $M = 1.2 \times 10^6$, $I = 1$ mM, $c = 2.5 \times 10^{-2}$ mg cm $^{-3}$, $\alpha = 0.43$.

constant A depends on the specificity of the system, on the amphiphile and salt concentrations and on the temperature. The model used for the micellar shape is a cylinder of fixed diameter and variable length terminated with hemispherical caps. If we call m_0 the minimum aggregation number (corresponding to a spherical shape), we can say that, for $m \gg m_0$, m is proportional to the length of the cylindrical micelle. If the rods have sufficient rigidity, $\tau(m)$ represents essentially a rotational diffusion time. As such, it should be proportional to the cube of the rod length. This gives $q = 3$. By substituting the values of p and q into equation (5), we obtain $\alpha = 0.25$, in excellent agreement with the experimental result found in the dilute regime. It is possible that the analysis in terms of SE behaviour might represent a rather general and powerful method of characterizing relaxation phenomena in polydisperse systems, with α containing direct information on the shape of the size distribution function.

We see from figure 2 that α departs significantly from 0.25 when c becomes larger than c^* . This is expected because, when entanglement is present, it is meaningless to describe the dynamic response of the system as a linear superposition of the responses of individual micelles, one should instead use a description in terms of collective modes. It is, in any case, remarkable that the decay is asymptotically SE even for the entangled system. If we take a continuous distribution of relaxation times, $B(t)$ can be written as

$$B(t) \approx \int W(\tau') \exp\left(-\frac{t}{\tau'}\right) d\tau' \quad (6)$$

where $W(\tau')$ is an appropriate weighting function. By applying to equation (6) the same approach used for equation (2), we find that the result $\alpha = 0.5$ implies a weighting function of the type $W(\tau') \approx \exp(-\tau'/\tau)$.

6. Dilute polyelectrolyte solution

We have performed TEB measurements on aqueous solutions of the linear polyelectrolyte sodium polystyrene sulphonate (NaPSS) [11]. Previous studies of the same system by

Mandel and co-workers [17] have shown that the decay of birefringence after the application of an electric field pulse is non-exponential and can be fitted with the superposition of three or four exponentials. We have repeated the experiment with the aim of testing a different interpretation of those experimental data.

NaPSS presents a large specific Kerr constant for two reasons: there is a large contribution to the electric polarizability coming from the counterion cloud, and the monomer has a strong optical anisotropy. Our samples consisted of water solutions of nearly monodisperse ($M_w/M_n \leq 1.1$) NaPSS obtained as molecular weight standards from Pressure Chemical Co., Pittsburgh, PA, USA, and used without further purification. The five different molecular weights used are $M = 1.0 \times 10^5$, 2.0×10^5 , 4.0×10^5 , 7.8×10^5 and 1.2×10^6 . The ionic strength of the solution was varied by the addition of NaCl in the concentration range 0.2–4 mM. All solutions were prepared with deionized water and salt of analytical grade. The polyelectrolyte concentration c was chosen so as to explore only the dilute regime, in which the polymer concentration is smaller than the entanglement concentration c^* [18], where $c^* = M/N_A R_g^3$, R_g being the radius of gyration.

All the reported data refer to measurements performed in the Kerr regime, i.e. the regime in which the induced birefringence is proportional to the square of the applied field. We have verified that the shape of the birefringence pulse does not depend on the field strength and on the pulse duration T (provided that T is not small in comparison with the relaxation time τ) in the Kerr regime. An important feature of the Kerr regime is that it is a small perturbation regime, so that both static and dynamic behaviour of the polymer solution are controlled by the properties of the unperturbed system.

Figure 3 shows $R(t)$ for three different polymer solutions, plotted as a function of the scaled time $t/\tau(L, I)$ where $\tau(L, I)$ is the fitted relaxation time for each polymer system, varying both with the extended polymer length L and with the ionic strength I of the solution. All the three relaxation functions are very well described by a SE form, except, perhaps, for the initial part, as can be seen from the linear behaviour of the plots in figure 3. More generally, we have found that, for all the investigated NaPSS solutions, the relaxation function follows SE behaviour. Table 1 presents the best fit values of α and τ for solutions of different polymer lengths and/or different ionic strengths. We have also reported in table 1 the average relaxation time $\langle \tau \rangle$ calculated as

$$\langle \tau \rangle = \int_0^\infty R(t) dt. \quad (7)$$

Note that, for a pure SE, $\langle \tau \rangle = \alpha^{-1} \Gamma(\alpha^{-1}) \tau$, Γ being the gamma function, and this relation is confirmed by our data within experimental error.

We see from table 1 that α is a decreasing function of both polymer length and ionic strength of the solution. We find that α is about 1 for the shortest polymer at very low ionic strengths and saturates to 0.44 ± 0.02 for the longest polymer at an ionic strength of around 2 mM.

The non-exponential dynamics of flexible chains are usually discussed in terms of a discrete set of relaxation modes [18, 19]. Although the experimental relaxation function can be fitted very well by a superposition of three or four exponentials, it is not easy to understand the meaning of the fitting parameters and to make a connection with theory. We propose instead the following interpretation. Following [20], we note that the amplitude of the electric birefringence response of a single chain is a function of its end-to-end distance R . In considering a dilute solution, we may imagine writing the relaxation

Table 1. The time constants and the stretch exponent obtained with different molecular weights of NaPSS at various ionic strengths and polymer concentrations.

10^{-3} M	I (mM)	c (mg cm $^{-3}$)	τ (μ s)	$\langle \tau \rangle$ (μ s)	α
100	0.05	0.05	6.5	6.5	1.00
100	4.00	0.10	2.5	2.8	0.80
200	0.20	0.01	27.0	29.0	0.86
200	0.40	0.02	22.0	23.0	0.82
200	0.70	0.04	14.8	16	0.80
200	1.20	0.06	11.0	13	0.76
200	2.00	0.10	7.5	9	0.70
400	0.2	0.005	99	128	0.80
400	0.4	0.01	56	80	0.70
400	0.7	0.02	48	66	0.68
400	1.2	0.03	32	46	0.64
400	2	0.04	31	45	0.62
780	0.2	0.005	137	221	0.56
780	0.4	0.01	76	127	0.52
780	0.7	0.02	57	111	0.51
780	1.2	0.03	61	124	0.47
780	2	0.05	52	110	0.47
1200	0.2	0.005	176	367	0.48
1200	0.4	0.01	132	279	0.47
1200	0.7	0.02	90	231	0.45
1200	0.2	0.03	88	217	0.44
1200	2	0.05	65	150	0.44

of birefringence $B(t)$ as a sum of individual-chain responses, weighted by the probability density $P(R)$ of the fluctuating quantity R :

$$B(t) = \int dR S(R)P(R) \exp\left(-\frac{t}{\tau(R)}\right) \quad (8)$$

where $S(R)$ is some signal function and $\tau(R)$ is the relaxation time appropriate to a chain with end-to-end distance R .

Since the shape of $P(R)$ is known only the limit case in which the extended polymer length L is much larger than the persistence length L_p , we first discuss the situation $L/L_p \gg 1$. For a non-self-avoiding polymer, $P(R)$ is Gaussian, $P(R) \approx \exp[-(R/R_g)^2]$, where R_g scales as $L^{0.5}$. For real polymers in good solvents, where excluded-volume constraints swell the chains from their Gaussian size, it has been demonstrated that $P(R)$ also decays as the exponential of a power of R ,

$$P(R) \approx f(R) \exp[-(R/R_g)^\delta] \quad (9)$$

where now $\delta = 1/(1 - \nu)$ is given in terms of the universal exponent $\nu = 0.59$ appropriate to a self-avoiding walk, and the prefactor $f(R)$ varies as some power of R . From our data and other studies [17] we estimate a power-law dependence of $S(R)$ on R , $S(R) \approx R^r$, with $r \approx 1$. Finally, we treat $\tau(R)$ as a rotational relaxation time: $\tau(R) \approx R^q$, with $q = 3$. By using equation (5), we can express α as $\alpha = 1/[1 + q(1 - \nu)]$. Thus, in

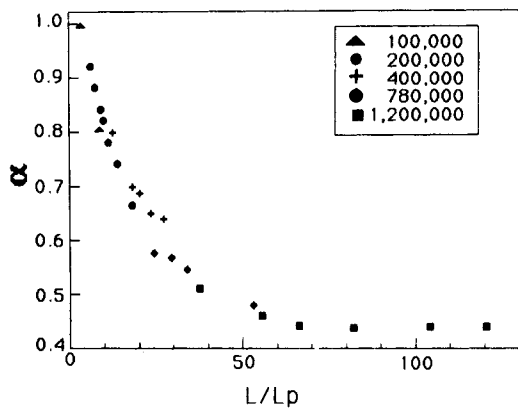


Figure 4. Experimental stretch exponent α as a function of the ratio of polymer length to persistence length, for various molecular weights of polymer and ionic strengths.

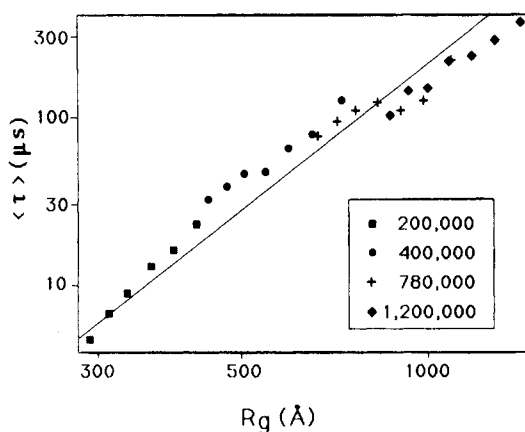


Figure 5. Relaxation time $\langle \tau \rangle$ as a function of the estimated radius of gyration of the polyelectrolyte. The line indicates a power-law fit with an exponent of 3.0 ± 0.2 .

the fully developed self-avoiding limit, the polymer relaxation is characterized by a stretched exponential form with a universal value of the stretch exponent α , itself expressed in terms of static and dynamic critical exponents. By using the numerical values of ν and q , we obtain $\alpha \approx 0.45$. The measured asymptotic value of the stretch exponent in the limit $L/L_p \gg 1$ is seen in table 1 (see also figure 4) to be in excellent agreement with this prediction.

The behaviour of the persistence length of polyelectrolytes as a function of the ionic strength is not clearly understood. The simple scaling formula proposed for very-low-ionic-strength solutions [21] does not seem adequate to describe the experimental results [22], although one should note that L_p is not measured directly but rather derived from the experimental data by using models which might also be questionable. We have estimated the persistence length for NaPSS by extrapolating to our conditions the data discussed by Tricot [22]. The behaviour of the exponent α as a function of L/L_p is shown in figure 4. Presented in this way, we see that the stretch exponent depends on polymer length and ionic strength only through the ratio L/L_p . Once L_p is given, the gyration radius can be estimated from the scaling law [21]: $R_g \approx L^{0.6}(L_p/\kappa)^{0.2}$, with κ the inverse screening length, which is rigorously applicable only in the limit $L/L_p \gg 1$, or by a slightly more complicated expression [21] valid for finite L/L_p . Figure 5 shows the experimental

Table 2. Calculated values of entanglement concentration c^* , persistence length L_p , and radius R_g of gyration of NaPSS solutions. The empirical formula used for L_p is $L_p^{-1} = 0.02 + 0.0258 I^{1/2}$, with L_p in nanometres.

10^{-3} M	I (mM)	c (mg cm $^{-3}$)	c^* (mg cm $^{-3}$)	L_p (nm)	R_g (nm)
100	0.05	0.05	2.4	38.8	124.5
100	4	0.10	3.9	14.0	20.8
200	0.2	0.01	0.7	31.4	47.4
200	0.4	0.02	1.0	27.2	42.3
200	0.7	0.04	1.3	23.7	39.1
200	0.2	0.06	1.7	20.4	35.9
200	2	0.10	2.2	17.4	33.0
400	0.2	0.005	0.4	31.4	72.6
400	0.4	0.01	0.5	27.2	65.5
400	0.7	0.02	0.7	23.7	60.1
400	0.2	0.03	0.9	20.4	55.2
400	2	0.04	1.2	17.4	50.8
780	0.2	0.005	0.2	31.4	109.4
780	0.4	0.01	0.3	27.2	98.8
780	0.7	0.02	0.4	23.7	90.6
780	0.2	0.03	0.5	20.4	83.2
780	2	0.05	0.6	17.4	76.7
1200	0.2	0.005	0.22	31.4	142.6
1200	0.4	0.01	0.34	27.2	128.8
1200	0.7	0.02	0.39	23.7	118.1
1200	1.2	0.03	0.43	20.4	108.5
1200	2	0.05	0.46	17.4	99.9

values of $\langle \tau \rangle$ plotted versus R_g . The data are consistent with the power law $\langle \tau \rangle \approx R_g^q$, with $q = 3.0 \pm 0.2$. We have computed from R_g the entanglement concentration c^* in order to verify that the condition $c \ll c^*$ was verified for all our data. The calculated c^* , together with L_p and R_g is reported in table 2.

As a conclusion, our model predicts a SE decay with the correct stretch exponent in the limit of a long flexible chain. In the opposite extreme (L/L_p of order unity), the macromolecule is rather stiff, with a narrow $P(R)$, and consequently $R(t)$ is an exponential ($\alpha = 1$). The fact that $R(t)$ appears to be a SE even at intermediate values of the ratio L/L_p might indicate that $P(R)$ presents a rapidly decaying tail of the type $\exp(-AR^p)$, with $p \geq \delta$. In order to derive the dependence of α on L/L_p , we would need to know the shape of $P(R)$ for a semiflexible chain.

7. Conclusions

We have studied three distinct systems:

- (i) critical binary mixtures,
- (ii) polydisperse micellar solutions,
- (iii) dilute polyelectrolyte solutions,

presenting as a common feature a wide distribution of characteristic sizes. We find in all cases a SE relaxation of electric birefringence. The results are explained by a simple model which is based on rather general assumptions. The stretch exponent α is related to the static exponent p , characterizing the size probability distribution, and to the dynamic exponent q , characterizing the power-law dependence of the relaxation time on size. In the case of TEB experiments, the technique probes rotational diffusion, i.e. $q = 3$. This means that the measurement of α gives direct information on the exponent p .

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