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Light-Scattering Study of Fluctuations in Concentration, Density, and Local Anisotropy in Polystyrene–Dioxane Mixtures

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ABSTRACT: Static and dynamic light scattering was applied in a comprehensive study of the different modes of relaxatory motion in polystyrene–dioxane mixtures, comprising the whole range of different compositions from dilute solution to plasticized melts. For the analysis of data measured in the presence of the nearly elastic anomalous excess scattering usually encountered in concentrated solutions and the melt, a generalized Siegert relation was used. Analysis of depolarized dynamic scattering data obtained for the PS-rich mixtures indicates a simple Vogel–Fulcher temperature dependence for the relaxation rates of the anisotropy fluctuations with T_g as the only relevant parameter. The dynamics observed in polarized scattering continuously changes its character, being dominated at low temperatures and high concentrations by density fluctuations and in the limit of high temperatures and low concentrations by concentration fluctuations. Density and anisotropy fluctuations show identical relaxation rates.

Introduction

Light-scattering experiments have been widely applied in intense studies of the structure and dynamics of polymer solutions. For dilute and semidilute solutions they led to a thorough understanding, in good agreement with the predictions of scaling and renormalization group theories.[1,2] The cases of concentrated solutions, plastized melts, and the pure polymer melt have been much less investigated. One reason might be the lower stage of the theoretical development, another one the experimental difficulty, that samples due to their high viscosity frequently do not reach a thermal equilibrium state.[3] Nonequilibrium structures, which are kinetically determined by the previous thermal treatment, may occur, which vanish only slowly and lead to an ultraslow or practically elastic additional scattering.[4–6] First, this has been considered as a problem which has to be eliminated before measurements can start; however, as shown recently by Pusey and van Megen,[7] one can also deal properly with this situation. It is now in fact possible to conduct a light-scattering experiment for a solvent–polymer mixture over the full range of concentrations. In this contribution we report on a comprehensive investigation on the dioxane–polystyrene system.

Our special interest concerns the dynamics in polystyrene-rich mixtures. Here in general the motion is set up by three components, by fluctuations in (i) the local concentration, (ii) the density, and (iii) the local anisotropy, i.e. the segment orientation. Segment reorientations can be directly studied by depolarized dynamic light scattering; the density and concentration fluctuations become detectable in the correlation function of the amplitude of the polarized scattered light. The three components differ in their basic properties. Concentration fluctuations decay by a diffusive process, with a relaxation rate $\Gamma = Dq^2$, being determined by the cooperative diffusion coefficient. On the other hand, the fluctuations in density and segment orientation are based on local processes and therefore exhibit a relaxation rate, which is q-independent within the angular range of the light-scattering experiments. As shown in recent work by Fytas, Floudas, and Ngai,[8] concentration and density fluctuations also differ in their temperature dependence. The density fluctuations are coupled to the glass transition. As indicated by Wang and Fischer[9] on the basis of the fluctuation–dissipation theorem, the spectrum of the density fluctuations can be directly related to the time-dependent longitudinal compliance. For polymer melts the α-process constitutes the dominant dispersion and therefore shows up in the light-scattering spectrum with a WLF-like temperature dependence.[10] The temperature dependence of the concentration fluctuations is much weaker. It appears that they are coupled to local processes rather than the glass transition. In fact, the diffusion of small molecules through a polymer matrix does not stop at T_g and continues down to lower temperatures. We are not aware of any systematic study of the anisotropy fluctuations in polymer-rich polymer–solvent mixtures. There are reports on depolarized dynamic light-scattering experiments on pure polystyrene melts.[11] A broad nonexponential decay is observed.

In the following we shall first describe the procedure for a data evaluation in the case of presence of an elastic scattering component and then give the single-chain properties derived from a conventional analysis of the dilute solution data and discuss the static and dynamic properties in the semidilute regime. The main chapter deals with the fluctuations in the polystyrene-rich region with PS concentrations between 0.4 and 0.8 g/cm^3. The different properties of the three components enable a discrimination and comparison.

Experimental Part

Samples. Measurements were conducted on two polystyrene fractions with nominal molecular weights $M_w = 23\,000$ and 48 000 ($1 < M_w/M_n < 1.05$). Samples were first purified by filtration of a dioxane solution through 0.2-μm Millipore filters, followed by freeze drying. Solutions for the measurement were then prepared using freshly distilled dioxane. They were transferred into a dust-free ampule which was sealed. Samples with higher polymer concentrations were obtained by evaporation of the dioxane, the polymer fraction being derived from the change in weight. It is possible that this procedure also contributes to the formation of density fluctuations, if the distribution of the solvent becomes inhomogeneous after a partial evaporation. In order to avoid time-dependent effects, we always waited with the measurement until the scattering intensity was constant within the measuring time.

Light-Scattering Experiments. Static and dynamic light-scattering experiments were conducted using a commercially available goniometer equipped with a photon correlator (manufactured by ALV, Langen, Germany; Model 3000). The light

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source was an Ar ion laser (Coherent, Model Innova 90-3). The ampule with the sample was placed into a bath of silicon oil which was index-matched with regard to the quartz glass of the basin. Temperature variation between room temperature and 150 °C was accomplished by heating the bath fluid, achieving a precision of ±0.1 °C.

The correlator was operated in the linear τ and the multiple τ mode, encompassing a time range between 10^{-6} and 10^2 s. Absolute intensities, expressed by the Rayleigh ratio

$$R = \frac{1}{V}\frac{d\sigma}{d\Omega}\ (\mathrm{cm}^{-1}) \tag{1}$$

where $d\sigma/d\Omega$ denotes the differential cross section and V gives the scattering volume, were obtained by a comparison with the scattering intensity of toluene in an identical situation. The Rayleigh ratio of toluene dependent on the wavelength is given by the equation

$$R = 1.0194 \times 10^{-5} - \frac{7.4507}{\lambda^2} + \frac{3.4224 \times 10^6}{\lambda^4}$$

The equation refers to a polarized scattering experiment at 20 °C.

The field correlation function $g_q(t)$ for the scattering at the wave vector q $(=4\pi (\sin\theta)/\lambda)$

$$g_q(t) \equiv \langle A_q(0)A_q{}^*(t)\rangle/\langle|A_q|^2\rangle \tag{2}$$

in normal cases can be derived from the intensity autocorrelation function

$$G_q(t) \equiv \langle I_q(0)I_q(t)\rangle/\langle|I_q|^2\rangle \tag{3}$$

by use of the Siegert relation

$$G_q(t) = 1 + f|g_q|^2(t) \tag{4}$$

Equation 4 holds for a Gaussian distribution of the field amplitude. The factor f $(0 < f < 1)$ accounts for the integrating effect of the finite detector area. If the detector area is small compared to the size of one speckle, f becomes equal to unity and the fluctuations show their full theoretical value $(G_q(0)/|g_q(0)|^2 = 2)$. The parameter f depends on the scattering volume in the sample and the detector area. In principle it can be determined by one calibration measurement, for example using a dilute polymer solution.

Equation 4 is usually applied in dynamic light-scattering experiments. However, it is only correct, if all fluctuating modes in the sample completely decay within the measuring time. For the system under study this was not always the case. For polymer concentrations above $c = 0.2$ g/cm^3 usually an excess scattering with very long or even unmeasurable relaxation times showed up. As explained in the next chapter, it is possible to deal with this situation and derive $g_q(t)$ for the fluctuating components, using a generalization of eq 4. The reason for the occurrence of the ultraslow modes so far has not been clarified. Here we describe a way which eliminates their effect on the fluctuating part of the spectrum.

Generalized Siegert Relation

Pusey and van Megen discussed in detail the scattering properties of amorphous "nonergodic media", that are systems where the density fluctuations are partly frozen.[7] We shall follow their treatment but will make use of the results in a slightly different way.

For a system with partly frozen density fluctuations the scattering amplitude at wavevector q, A_q, is set up as a superposition of a constant, "elastic" part, $A_{q,c}$ and a fluctuating, completely decaying component, $A_{q,f}$:

$$A_q(t) = A_{q,c} + A_{q,f}(t) \tag{5}$$

In normal cases $A_{q,f}$ can be described as a Gaussian statistical variable with zero mean

$$\langle A_{q,f}(t)\rangle = 0 \tag{6}$$

The brackets here denote a time average.

In the treatment of Pusey and van Megen the nonergodic system is modeled as a glass, where the particles perform confined motions about fixed average positions. $A_{q,c}$ is then related to the average positions; $A_{q,f}$ reflects the confined motions. In a more general case, which is given for the mixture under study, $A_{q,c}$ and $A_{q,f}$ can also be associated with different degrees of freedom of the system. As an example, $A_{q,c}$ could be associated with frozen or ultraslow density fluctuations, $A_{q,f}$ with concentration fluctuations. The consequences are the same as for the glass model.

Starting from eqs 5 and 6 the field correlation function and the intensity autocorrelation function can be directly calculated. One obtains (compare eqs 3.8 and 3.9 in ref 7):

$$\langle A_q(0)A_q{}^*(t)\rangle = \langle A_{q,f}(0)A_{q,f}{}^*(t)\rangle + I_{q,c} \tag{7}$$

with

$$I_{q,c} = \langle|A_{q,c}|^2\rangle$$

and

$$\langle I_q(0)I_q(t)\rangle = \langle I_{q,f}\rangle^2|g_{q,f}|^2(t) + 2I_{q,c}\langle I_{q,f}\rangle Re g_{q,f}(t) + \langle I_q\rangle^2 \tag{8}$$

with

$$I_q = |A_{q,c}|^2$$

$$I_{q,f} = |A_{q,f}|^2$$

$$g_{q,f} = \langle A_{q,f}(0)A_{q,f}{}^*(t)\rangle/\langle|A_{q,f}|^2\rangle$$

The meaning of eq 8 becomes clear by writing it in a form similar to the Siegert relation

$$\frac{\langle I_q(0)I_q(t)\rangle}{\langle I_q\rangle^2} = 1 + \frac{\langle I_{q,f}\rangle^2}{\langle I_q\rangle^2}|g_{q,f}|^2 + 2\frac{I_{q,c}\langle I_{q,f}\rangle}{\langle I_q\rangle^2}Re g_{q,f} \tag{9}$$

Equation 9 represents a form which interpolates between the homodyne case, given by the second term, and the heterodyne case, described by the third term.[12] In fact, the elastic scattering component acts like a local oscillator. For $I_{q,c} \gg I_{q,f}$ the third term becomes dominant and one is dealing with the pure heterodyne case.

As in the Siegert relation, eq 4, the finite size of the detector area may lead to a decrease in the fluctuation signal. For the limiting cases of a pure homodyne or a pure heterodyne experiment the decrease can be described by the same factor f.[12] This suggests the introduction of the parameter also directly into eq 9, which leads to

$$G_q(t) = 1 + f\frac{\langle I_{q,f}\rangle^2}{\langle I_q\rangle^2}|g_{q,f}|^2 + 2f\frac{I_{q,f}\langle I_{q,f}\rangle}{\langle I_q\rangle^2}Re g_{q,f} \tag{10}$$

Since

$$\langle I_q\rangle = I_{q,c} + \langle I_{q,f}\rangle \tag{11}$$

with

$$\alpha = \frac{I_{q,c}}{\langle I_q\rangle} \tag{12}$$

one finally arrives at the following generalized form of the Siegert relation

$$G_q(t) = 1 + f(1-\alpha)^2|g_{q,f}|^2 + 2f\alpha(1-\alpha)Re g_{q,f} \tag{13}$$

Equation 13 enables a derivation of the field correlation function of the fluctuating component from the measured intensity correlation function $G_q(t)$, if $g_{q,f}$ is a real quantity (which is often the case) and f and α are known. The parameter f can be determined by a separate measurement on a sample suitable for this calibration. The parameter α, which specifies the elastic part of the scattering intensity, in principle can be derived from

$$G_q(t \rightarrow 0) = 1 + f(1 - \alpha^2) \tag{14}$$

Equation 14 can be applied, if the extrapolation ($t \rightarrow 0$) is possible and if the fluctuations of all modes which contribute to $\langle I_{q,f} \rangle$ are included. There should be no rapid modes with relaxation times shorter than the time resolution of the correlator. Judgement of the latter requirement can be difficult. It requires a general knowledge about the relaxation processes in the system and their relative weights. If α is known, the intensity of the fluctuating part follows as

$$\langle I_{q,f} \rangle = (1 - \alpha)\langle I_q \rangle \tag{15}$$

For a nonergodic system the elastic scattering intensity $I_{q,c}$ varies between different locations in the sample. The individual values have no significance. The analysis shows that the interesting field correlation function $g_{q,f}(t)$ can be determined without any knowledge of the statistical properties of $I_{q,c}$. Here our approach differs from that presented by Pusey and van Megen. These authors explicitly assume Gaussian statistics also for the elastic component, $A_{q,c}$, and then give expressions for the ensemble-averaged correlation function $\langle G_q(t) \rangle_E$ and $\langle g_q(t) \rangle_E$. The proposed procedure necessitates a determination of the ensemble-averaged intensity, $\langle I_q \rangle_E$, which can be done by an additional measurement on a moved sample. Our discussion shows that, if one is only interested in $g_{q,f}(t)$, the additional step can be omitted.

Equation 13 allows one to judge qualitatively the effect of the presence of an elastic component. Obviously, the errors introduced in $g_{q,f}(t)$, when the normal eq 4 rather the correct generalized form eq 13 is used, are not too serious. The possible shift of the relaxation time away from the correct value is less than a factor 2, which is small on logarithmic scales, and also the change in the shape, say the β-parameter of a stretched exponential decay (eq 28), will remain small. On the other hand, the presence of an elastic component has to be properly accounted for, if one is interested in the intensity $I_{q,f}$, i.e. the structure factor, of a fluctuating mode. A determination of $I_{q,f}$ is possible using eqs 14 and 15.

Single-Chain Properties

The properties of single chains in the two samples followed from a conventional analysis of the light-scattering data obtained in dilute solution. The molecular weight M and the second virial coefficient A_2, defined by the osmotic pressure equation

$$\Pi = RT\left(\frac{c}{M_n} + A_2c^2 + ...\right) \tag{16}$$

followed from the Zimm equation

$$\frac{Kc}{R(q \rightarrow 0)} = \frac{1}{M_w} + 2A_2c \tag{17}$$

where K denotes the contrast factor

$$K = \frac{4\pi^2 n^2 \left(\frac{dn}{dc}\right)^2}{N_A \lambda_0^4} \tag{18}$$

(n, index of refraction of the solution; λ_0, wavelength in vacuo). The self-diffusion coefficient D_0 was derived as usual from the relaxation rate Γ at short delay times observed in a dynamic light-scattering experiment in the limit $c \rightarrow 0$

Table I
Single-Chain Properties of the Two Polystyrene Fractions, As Derived from Light-Scattering Experiments on Dilute Dioxane Solutions

sample	M_w	10^3A_2 [(mol cm^3)/g^2]	10^6D_0 (cm^2/s)	10^7R_H (cm)	k_D (cm^3/g)
PS1	22 800	0.9	0.45	3.87	10.5
PS2	48 600	0.8	0.31	5.56	11.0

$$\Gamma = D_0q^2 \tag{19}$$

For dilute solutions in general the collective diffusion coefficient D is obtained

$$\Gamma/q^2 = D(c) = D_0(1 + K_Dc) \tag{20}$$

D_0 is related to the hydrodynamic radius R_H by the Stokes–Einstein equation

$$D_0 = \frac{kT}{6\pi\eta_s R_H} \tag{21}$$

(η_s, viscosity of the solvent).

The values thus obtained for the two PS fractions are given in Table I.

Concentration Fluctuations in Dioxane-Rich Mixtures

The polarized scattering by solutions which are rich in dioxane is dominated by the concentration fluctuations. Density fluctuations and the fluctuations of the local anisotropy in this range give only a small, practically negligible contribution. Direct application of eqs 14 and 15 is therefore possible. Since the correlation length of the concentration fluctuations, $0 < \xi < R_G$ (R_G, radius of gyration) is small compared to the wavelength of light, i.e. $q\xi \ll 1$, one observes an angular independent scattering intensity $R = R(0)$. R is directly related to the reduced osmotic compressibility:

$$\frac{R(0)}{M_wKc} = \frac{RT}{M_w}\frac{dc}{d\Pi} \tag{22}$$

Figure 1 shows $R(0)$ dependent on the concentration c. The values were all obtained by use of eqs 14 and 15, which eliminates the effect of the elastic scattering

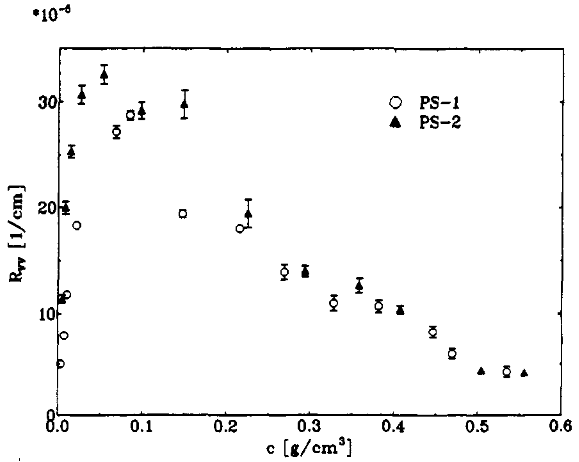

Figure 1. Intensity of polarized scattered light (R_{VV}: Rayleigh ratio for vertical directions of the polarizer and the analyzer) as a function of the PS concentration, obtained for two fractions (PS1, PS2).

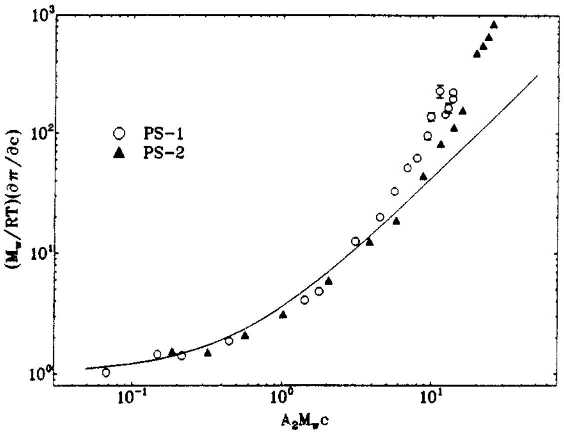

Figure 2. PS1 and PS2 dissolved in dioxane: dependence of the reduced osmotic modulus on the reduced concentration. Comparison is with theoretical curve.

superposed at polymer concentrations $c > 0.2$ g/cm^3. The difference in $R(0)$ for the two samples with different molecular weights, which is visible up to $c \simeq 0.15$ g/cm^3, disappears for the higher concentrations. Here an entanglement network with an M-independent correlation length is formed.

An explicit equation for the concentration dependence of the osmotic modulus dΠ/dc, valid in the dilute and semidilute regime for Gaussian chains, has been derived by Ohta and Oono[13] using a renormalization group treatment. The reduced osmotic modulus is given as a specific universal function F of a dimensionless scaling parameter

$$\frac{M_w}{RT}\frac{\mathrm{d}\Pi}{\mathrm{d}c} = F(X) \tag{23}$$

with

$$X = \frac{16}{9}A_2M_w \simeq c/c^* \tag{24}$$

Here c^* denotes the overlap concentration.

Figure 2 gives a presentation of the data in this scaled form, together with the theoretical curve $F(X)$. Up to $X \simeq 5$ the agreement is satisfactory. At higher concentrations the osmotic modulus deviates to higher values, in qualitative agreement with similar observations by Burchard[14] and Wiltzius et al.[15]

Concentration fluctuations generally decay with a rate

$$\Gamma = Dq^2(1-\phi) \tag{25}$$

where D denotes the cooperative diffusion coefficient (ϕ is the volume fraction of the polymer).[2] The dependence of D on the polymer concentration has been theoretically studied by different approaches, mean-field theories,[16] scaling analysis[1,17,2] and renormalization group treatments.[18] The scaling and renormalization group treatments are devised for dilute and semidilute solutions, the mean field theories are expected to be correct at higher concentrations. All theories predict an increase of D with increasing polymer concentration.

Figure 3 shows the result of our measurements, for polymer concentrations up to $c = 0.50$ g/cm^3. The concentration fluctuations were clearly visible in the intensity correlation functions. The decay was exponential. Relaxation rates were proportional to q^2. One observes first the expected increase but, then, after passing over a maximum at $c \simeq 0.25$ g/cm^3, a drastic decrease in D. For the given samples with comparatively low molecular weight the semidilute regime with its characteristic scaling behavior ($D \sim c^{0.75}$, compare e.g. ref 19) is not reached before approaching the maximum.

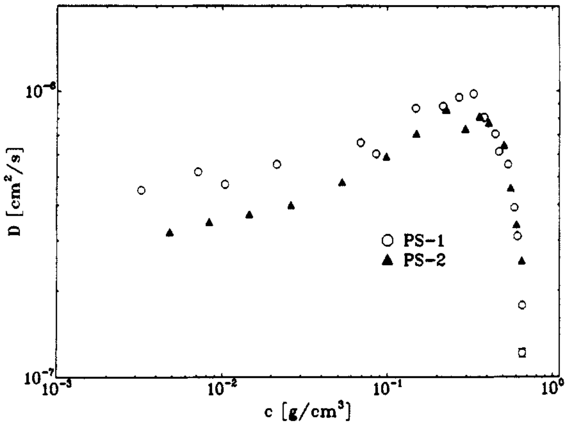

Figure 3. Dependence of the cooperative diffusion coefficient on the PS concentration, as derived from polarized light-scattering experiments for PS1 and PS2.

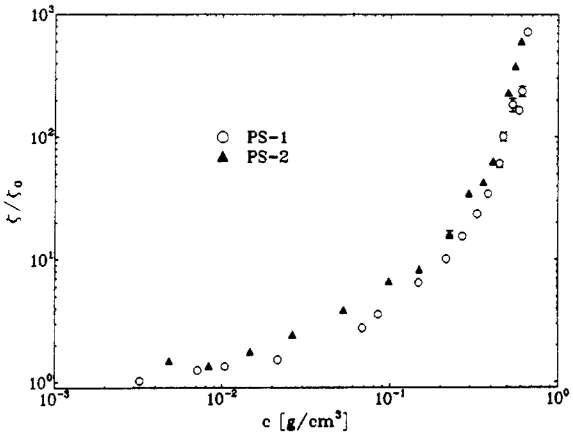

Figure 4. Friction coefficient as a function of the PS concentration.

The occurrence of a maximum in $D(c)$ indicates that at higher PS concentrations intersegmental friction contributes to the effective viscosity, which then becomes larger than η_s. The effect is well-known from other work (compare e.g. ref 19). It shows that the decrease in the correlation length ξ, with increasing concentration is overcompensated by the increase in the friction between the segments.

The friction coefficient (per chain), which is operative at a given concentration, can be derived from the general relation[20]

$$D = \frac{kT}{\zeta(c)}\left[\frac{M_w}{RT}\frac{\mathrm{d}\Pi}{\mathrm{d}c}\right](1-\phi) \tag{26}$$

In the limit $c \rightarrow 0$ ζ becomes identical with the friction coefficient of an isolated chain

$$\zeta(c \rightarrow 0) = 6\pi\eta_s R_H \tag{27}$$

Figure 4 shows the dependence of the reduced friction coefficient $\zeta(c)/\zeta(0)$ on the concentration. The slow increase at low concentrations is caused by the hydrodynamic interaction. The strong uprise, which follows at higher concentrations, is again indicative of an increase in the local viscosity due to intersegmental friction.

Fluctuations in Concentrations, Density, and Local Anisotropy in PS-Rich Mixtures

In mixtures rich in polystyrene the correlograms measured in dynamic light-scattering experiments include

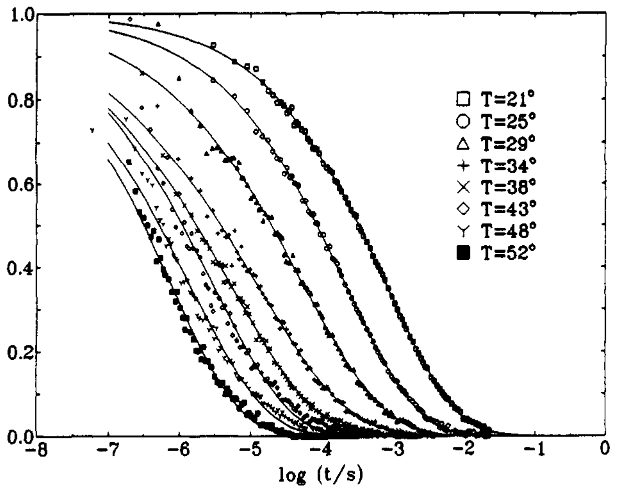

Figure 5. PS1 (0.7 g/cm^3)–dioxane mixture: field correlation functions derived from a depolarized scattering experiment, showing the dynamics of segment reorientations.

contributions from all types of fluctuations, fluctuations in the density, the concentration, and the local anisotropy. The anisotropy fluctuations are directly reflected in the depolarized scattered light; the density and concentration fluctuations show up in the polarized scattering. The intensity of the depolarized scattered light is much smaller than the polarized scattered light. A measurement in the melt of PS2 at 118 °C yielded

$$R_{VV} = 3.6 \times 10^{-5}\ \mathrm{cm}^{-1},\ R_{VH} = 0.9 \times 10^{-5}\ \mathrm{cm}^{-1}$$

For the mixtures the ratio R_{VH}/R_{VV} is even smaller. Contributions of the anisotropy fluctuations to the polarized scattering can therefore be neglected.

We begin with a discussion of the anisotropy fluctuations. Figure 5 presents as an example the result of a depolarized dynamic light-scattering experiment for a mixture with $c = 0.7$ g/cm^3. The field correlation functions derived from the data are much broader than a simple exponential decay. They can be described by the empirical Kohlrausch–Williams–Watts (KWW) relaxation function

$$g(t) = \exp - (t/\tau)^{\beta} \tag{28}$$

with $\beta = 0.4$. The shape of $g(t)$ does not change with temperature. Similar results were obtained for the other mixtures.

The analysis of the temperature dependence of the mean relaxation time

$$\langle \tau \rangle = \frac{\tau}{\beta}\Gamma\left(\frac{1}{\beta}\right) \tag{29}$$

for all investigated mixtures and the pure PS fractions led to a simple result. Figure 6 shows the data. They can be represented by Vogel–Fulcher curves

$$\frac{1}{\langle \tau \rangle} = A \exp - \frac{B}{T - T_0} \tag{30}$$

with common values for A and B

$$A = 8.77 \times 10^{11}\ \mathrm{s}^{-1}$$

$$B = 1625\ \mathrm{K}$$

The Vogel temperatures T_0 depend in a systematic manner on the glass transition temperatures T_g. Figure 7 shows T_0 and T_g (determined by DSC) for the mixtures and the pure PS fractions. T_0 and T_g are correlated by

$$T_0 = T_g - 55\ \mathrm{K}$$

Hence, the segment reorientation reflected in the depolarized quasielastic scattering is coupled to the glass transition.

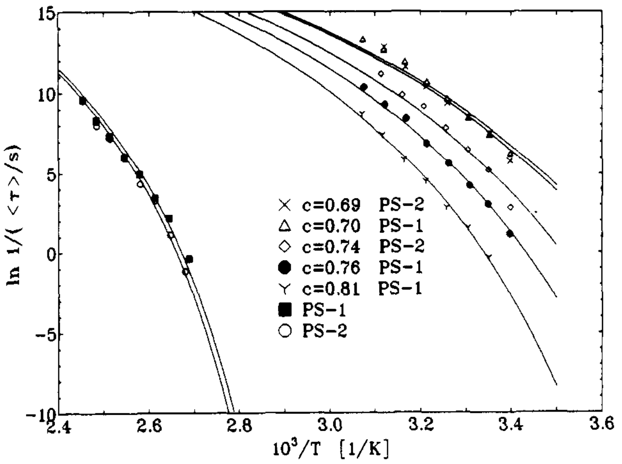

Figure 6. Temperature dependence of the mean reorientation time, obtained for various PS1–dioxane mixtures and the melts of PS1 and PS2. Data representation is by Vogel–Fulcher curves.

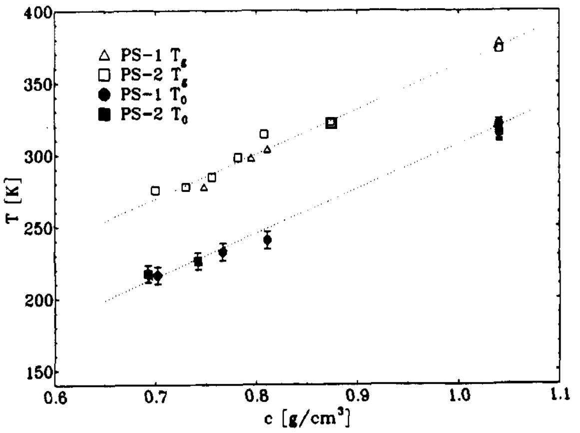

Figure 7. Comparison of Vogel temperatures T_0 and glass transition temperatures T_g for the PS1–dioxane mixtures and PS melts.

The nonexponential nature of the orientation relaxation can be due to different reasons. The motion of the phenyl groups, which give the main contribution to the optical anisotropy, is certainly coupled along the chain, so that cooperativity and a multimode structure results. There may exist additional intermolecular effects, like fluctuations in the free volume and the concentration, leading to varying segmental friction coefficients. All motions which change intersegmental distances and occur on time scales longer than $\langle \tau \rangle$ will contribute to a broadening. The phenyl groups probe these local variations.

The polarized dynamic light-scattering experiments indicate a peculiar behavior of the concentration and density fluctuations. Figure 8 shows the field correlation functions measured at different temperatures for a PS1–dioxane mixture with $c = 0.7$ g/cm^3 at $q = 1.21 \times 10^5$ cm^{-1}, in a comparison with those observed for a mixture with lower PS concentration, $c = 0.37$ g/cm^3. Decays are nonexponential for the high concentration and exponential for the lower concentrations. The nonexponential relaxation can be empirically described by the KWW function, eq 29. The width parameter β changes with temperature, from $\beta \simeq 0.6$ at 25 °C to $\beta \simeq 0.8$, as shown in Figure 9.

The complex relaxation behavior observed for $c = 0.7$ g/cm^3 is certainly due to the superposition of the density fluctuations on the concentration fluctuations. For $c = 0.37$ g/cm^3 only the concentration fluctuations show up, the density fluctuations here are too rapid to be observable.

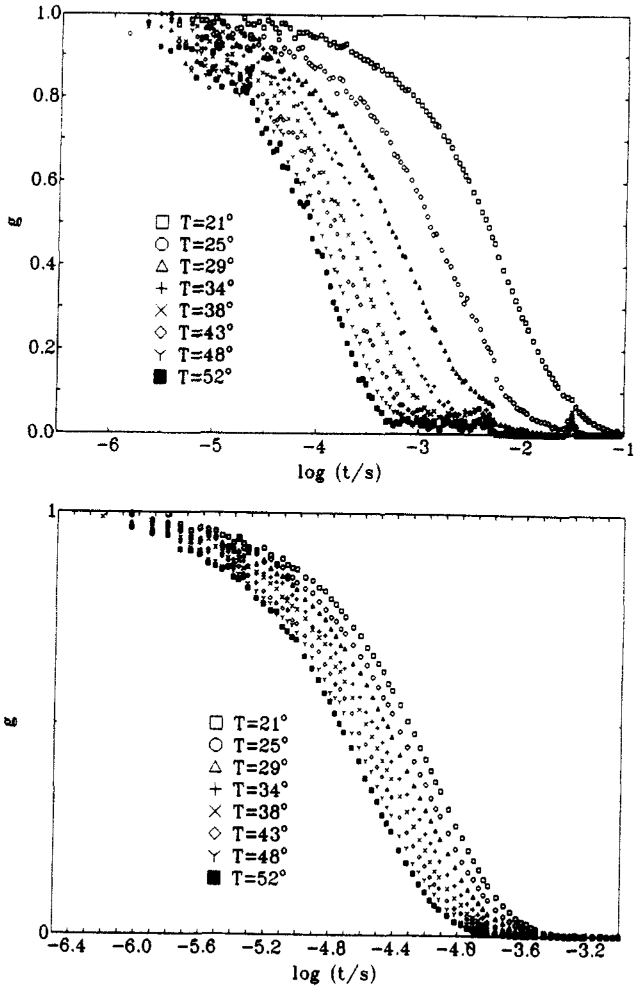

Figure 8. PS1–dioxane mixtures with $c = 0.7$ g/cm^3 (top) and $c = 0.37$ g/cm^3 (bottom): field correlation functions for different temperatures.

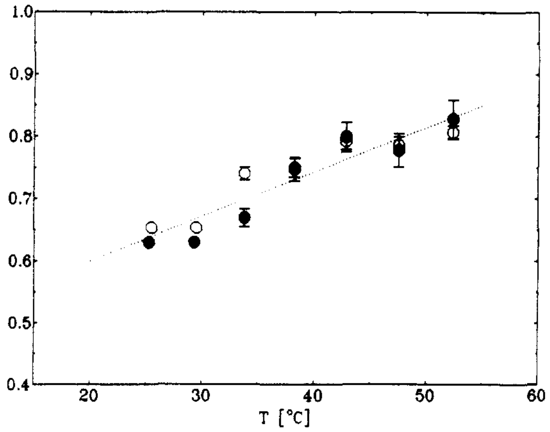

Figure 9. PS1 (0.7 g/cm^3)–dioxane mixture: temperature dependence of KWW width parameter β.

The fluctuations in density and in concentration can be in principle distinguished on the basis of the different q dependencies of the relaxation rates, being diffusive for the concentration fluctuations, $\Gamma \sim q^2$, and constant for the density fluctuations. For $c = 0.37$ g/cm^3 we found $\Gamma \sim q^2$. Figure 10 shows the check for $c = 0.7$ g/cm^3. The result is quite unusual: at low temperature the decay appears to be dominated by the density fluctuations (Γ = constant), and at high temperatures is dominated by the concentration fluctuations ($\Gamma \sim q^2$). The same tendency shows up in the temperature dependence of β (Figure 9). The value $\beta \simeq 0.8$ obtained at high temperatures indicates a dominance of the concentration fluctuations, the lower value observed at 25 °C points at an increasing weight of the density fluctuations. It is difficult to explain this behavior under the assumption of a superposition of independent density and concentration fluctuations. For independent motions the individual structure factors, i.e. the intensities associated with the two fluctuation modes, would only show a weak temperature dependence (as is demonstrated by measurements at lower concentrations and the pure melt). The obvious change in the weight of the two modes indicated by the change in the overall character of the relaxation suggests a coupling. This could be quite efficient, if the relaxation rates of the two modes are similar. Coupling results in a mixed mode, which could show a continuously changing character.

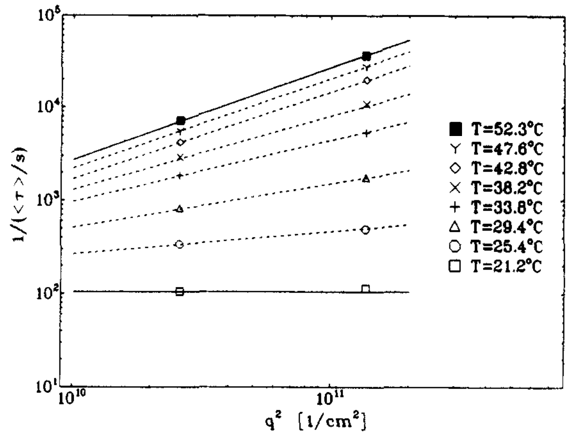

Figure 10. PS1 (0.7 g/cm^3)–dioxane mixture: q dependence of the relaxation rate for different temperatures (measurements at two scattering angles).

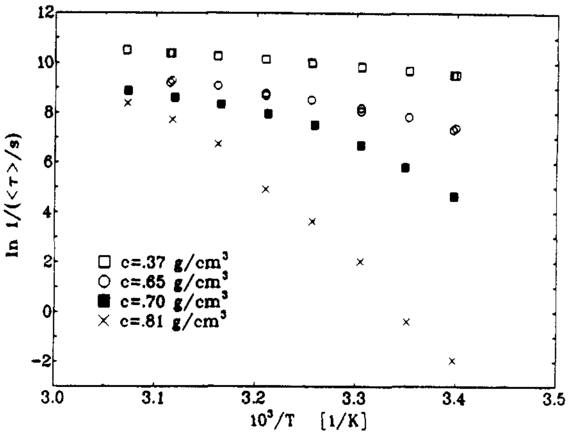

Figure 11. PS1–dioxane mixtures: temperature dependencies of the relaxation rates of the process showing up in polarized scattering experiments.

Work performed simultaneously by Brown et al.[21] on concentrated solutions of PS in toluene, which came to our knowledge after having completed the investigations, yielded analogous results. For a sample with a similar PS concentration it was also found that the decay rate was q-independent at low temperatures and diffusive, $\Gamma \sim q^2$, at the high-temperature end. Brown et al. continued the study to even higher PS concentrations. As it appears, density and concentration fluctuations then become separated again.

It has already been demonstrated by Fytas et al. in experiments on a plasticized poly(cyclohexyl methacrylate) that the relaxation rates of the density and the concentration fluctuations exhibit a different temperature dependence. This is confirmed in our studies. Figure 11 presents, for mixtures with different PS concentrations, the T dependencies of the relaxation rates for the process,

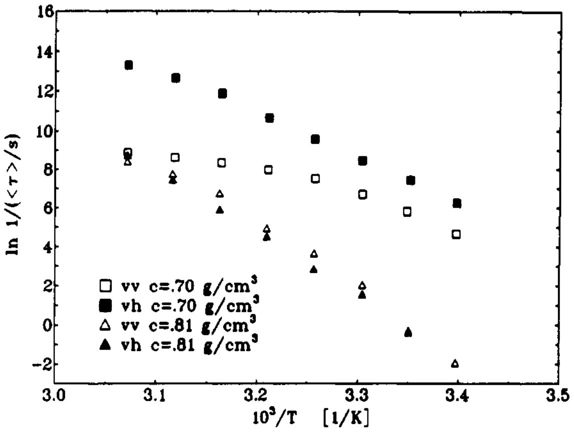

Figure 12. PS1 (c = 0.7/0.81 g/cm^3)–dioxane mixtures: comparison of relaxation rates of the processes showing up in polarized (VV) and depolarized (vh) dynamic light-scattering experiments.

which shows up in the polarized dynamic light-scattering experiment. As shown by the q dependence of $1/\tau$, one deals with pure concentration fluctuations for c = 0.37 g/cm^3, pure density fluctuations for c = 0.81 g/cm^3, and mixed modes for c = 0.65 and 0.70 g/cm^3. The T dependence is only weak for the concentration fluctuations and quite pronounced for the density fluctuations.

The sample with c = 0.70 g/cm^3 crosses over from one regime to the other. This is clearly demonstrated by a comparison with the relaxation rates of the anisotropy fluctuations, which are governed by the WLF equation, as discussed above. Figure 12 presents this comparison for two mixtures. For c = 0.81 g/cm^3 anisotropy and density fluctuations have identical relaxation rates. For c = 0.70 g/cm^3 they differ at high temperatures, when the concentration fluctuations dominate the mode, and approach each other at low temperatures.

It is interesting to note that the fluctuations in the density and the anisotropy modes possess identical relaxation rates. This points to the occurrence of a group of cooperative modes which cause rotations as well as translations of the chain segments.

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