4454 *Macromolecules* **1997,** *30,* 4454−4458

Large-Scale Heterogeneities in Entangled Polymer Solutions. Light-Scattering Study on Polystyrene in Toluene

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Received December 4, 1996; Revised Manuscript Received April 1, 1997[⊗]

ABSTRACT: Static and dynamic low-angle light-scattering experiments carried out on semidilute and moderately concentrated solutions of polystyrene in toluene provide evidence for the existence of heterogeneities in the entanglement network with correlation lengths of several hundred nanometers. The slow mode showing up in the correlograms in addition to the gel mode reflects the diffusive motion of these chain associations. The tendency to form associations increases with the solute concentration and with decreasing temperature. The observations indicate that the reptation time does not represent the longest relaxation time in the system; a complete reorganization of the entanglement network requires a much longer period.

1. Introduction

In dynamic light-scattering experiments on semidilute and moderately concentrated polymer solutions one often observes a decay of the intensity correlation function in two steps (see ref 1 and the references cited therein). The findings indicate that the concentration fluctuations which produce the scattering are composed of two different groups of relaxatory processes, briefly addressed as fast and slow modes. A seemingly good explanation was already offered after the first observation by Adam and Delsanti[2] in a treatment by Brochard and de Gennes.[3] Chains in semidilute and concentrated solutions set up a temporary network which exists up to the characteristic time necessary for the disentangling. Therefore, for times below this limit concentration fluctuations take place as a swelling and deswelling of a gel, and only for longer times do they include additionally the reorganization of the entanglement network. The fast and the slow modes were associated with these two steps and thus are understood as representing gel modes and network reorganization processes, respectively. On the basis of this picture, the relaxation time of the gel mode could be directly written down. It is determined by the retracting force of the temporary network, as given both by the osmotic modulus and the shear modulus of the network and by the solvent viscosity. As shown in the treatment, the dynamics may also be described as a diffusive motion of the chain parts between entanglements by applying the Stokes−Einstein relation, i.e. as

$$\tau_1^{-1} = D_c q^2 \quad \text{with} \quad D_c = \frac{kT}{6\pi\eta\xi} \tag{1}$$

(τ_1^{-1}, relaxation rate of the fast mode measured at wave vector q; η, solvent viscosity; ξ, mesh size given by the chain parts between entanglements). Experimental results for the fast mode fully agree with this view. Comparison of the mesh size ξ as derived from the collective diffusion coefficient D_c with that deduced from the static structure factor gives always similar values (the dynamic value being always somewhat larger than the static one 1), and the dependence of D_c on the concentration and the molecular weight of the solute mostly agrees with theoretical scaling predictions.

The slow modes represent in this view the additional fluctuations which result from the reorganization of the network. Hence, they should take place on the time scale of the disentangling time, as measured in mechanical shear experiments on solutions, and furthermore, one expects in light-scattering experiments q-independence. This was, indeed, observed in Adam and Delsantis experiments and later also in measurements on Θ solutions by Brown et al.[4,5]

Interestingly enough, other authors reported a quite different behavior. In the measurements of Amis et al.,[6,7] not only the fast mode but also the slow mode exhibited a diffusive character, as indicated by a q-dependent relaxation time τ_2

$$\tau_2^{-1} \sim q^2 \tag{2}$$

and a similar result came up in several other studies.[1] An explanation for this different behavior was presented by Burchard[8] and again by Brown.[1] They proposed that the dissolution process might result in a nonhomogenous network structure or, in other words, that associations between chains might occur. The translational motion of these associates then could produce the observed behavior.

Hence, for the slow mode we have varying experimental results and different assignments. Obviously not only one but at least two different mechanisms exist, and depending on the system under study, the preparation procedure, or the q-range, their relative weights vary. For further clarification, more experiments are certainly helpful.

Recently, we constructed a light-scattering apparatus which yields both the static structure factor in absolute values, i.e. the Rayleigh ratio, and the intensity correlation function down to low angles. Primarily the equipment was built up for studies of the long-range density fluctuations found in polymer melts, but it could also be used for investigations of polymer solutions. We chose the system polystyrene in toluene, with concentrations in the semidilute and moderately concentrated range, and obtained results which provide additional insight into the nature of the slow modes. In fact, the results speak in favor of the existence of large scale heterogeneities in the entanglement network and provide a more precise characterization in quantitative terms.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

S0024-9297(96)01781-0 CCC: $14.00

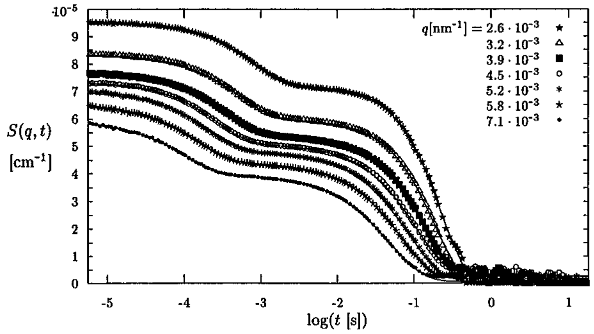

Figure 1. Intermediate scattering functions of 12.5% PS (M_w = 78 000) in toluene at 45 °C derived from static and dynamic light scattering experiments.

2. Experimental Section

Experiments were carried out for a fraction of polystyrene (PS) purchased from Polymer Standard Service (Mainz, Germany) with

$$M_w = 78\,000 \text{ g·mol}^{-1} \qquad M_w/M_n = 1.02 \tag{3}$$

and a second fraction with nearly identical properties

$$M_w = 80\,000 \text{ g·mol}^{-1} \qquad M_w/M_n = 1.03 \tag{4}$$

which was synthesized in the group of Prof. Mülhaupt at the Institute of Macromolecular Chemistry of our university. Three solutions were prepared, with weight fractions of polystyrene of 12.5%, 20%, and 25%. To prepare the solution, the predetermined amount of polystyrene was put into a flask filled with toluene and kept there under gentle agitation for several hours. Then, solutions were filtered through a 0.2 μm Millipore filter directly into the dust-free scattering cell. All three solutions showed a slow mode, in contrast to solutions with PS weight fractions below 10%, where it was absent.

For light scattering experiments in the low-angle range, the number of optical components should be chosen as small as possible to keep the reflections on the lowest possible level. We therefore simply used a helium–neon laser with a wavelength of 633 nm (output: 20 mW) together with a lense which focused the beam to a diameter of 50 μm. Five percent of the primary beam intensity was extracted with the aid of a splitting mirror and directed onto a photodiode, enabling a continuous monotoring of the primary beam intensity. The sample cell had a rectangular shape and was placed into a holder which allowed a controlled heating up to temperatures of 200 °C. The scattered light was registered with the aid of a monomode fiber of Spindler and Hoyer (type SM-633-FC-2m). The photons picked up by the fiber were registered by a photomultiplier (EMI D9797). Intensity correlation functions were then obtained with the help of an ALV-5000 correlator, which was also used for a registration of the average scattering intensity. Using this simple set-up, we could register the light scattering down to a Bragg angle of 3°, corresponding to $q \approx 1 \times 10^{-3}$ nm^{-1}.

3. Results

Figures 1–5 give the results obtained in static and dynamic light-scattering experiments on solutions with 12.5% polystyrene, which is within the semidilute range (the critical concentration at the overlap limit is 3.2%). Figure 1 shows the intermediate structure factors

$$S(q,t) = S(q)g_1(q,t) \tag{5}$$

obtained at the indicated q's at 45 °C. We derived the normalized field correlation function, g_1, from the normalized intensity correlation function, g_2, by applying the Siegert relation

$$g_2(q,t) = 1 + f|g_1(q,t)|^2 \tag{6}$$

The factor $f(0<f<1)$ accounts for the integrating effect of the finite area of entrance into the optical fiber. It was at first determined by a scattering experiment on a latex suspension, where we obtained $f = 0.8$. We measured the same value for the solutions, which implies that we had no elastic component in the scattering and thus a complete decay of the correlation function. We observe in Figure 1 two processes. As a check showed, both possess a nearly single-exponential shape, i.e. g_1 (q,t) could be represented as

$$g_1(q,t) = \alpha \exp -(t/\tau_1)^{\beta_1} + (1 - \alpha) \exp -(t/\tau_2)^{\beta_2} \tag{7}$$

with

$$0.9 \le \beta_1, \quad \beta_2 \le 1$$

The fast process represents the gel mode. As expected, its intensity is q-independent and, as indicated in Figure 2, the relaxation rate obeys a quadratic law

$$\tau_1^{-1} \sim q^2 \tag{8}$$

The slope yields the collective diffusion coefficient associated with the gel mode.

The slow mode exhibits a pronounced q-dependence in both the intensity and the relaxation rate. As indicated by Figure 3, the relaxation rate, τ_2^{-1}, shows a quadratic dependence on q. Hence, for this sample, the slow mode is of the diffusive type. Figure 4 depicts the effect of temperature on the intensity correlation functions g_2 measured at $q = 5.85 \times 10^{-3}$ nm^{-1}. One observes a drastic change in the relative weights of the two contributions. Additional measurements showed us that, as expected, the intensity of the gel mode is essentially temperature-independent. The observed changes in the relative weights therefore are due to changes in the intensity of the slow mode; a decrease in temperature leads to a strong increase in their intensities. The temperature changes are fully reversible, as shown by the perfect agreement of the two measurements carried out at 288 K at the begin and the end of the series. Finally, Figure 5 depicts the temperature-dependencies of τ_1 and τ_2 in an Arrhenius representation. We found similar although not exactly equal activation energies for the two processes, with values

$$E_1/k = 2070 \pm 50 \text{ K}$$

$$E_2/k = 1600 \pm 200 \text{ K}$$

Some results obtained for solutions with 20% polystyrene are collected in Figures 6–8. At these higher concentrations only the slow mode is observed; the intensity of the fast mode is too low to show up in the plots. Figure 6 gives the static scattering intensity $I(q)$ (in arbitrary units) measured at 293 K. As indicated by the inserted plot, a satisfactory fit is achieved by the Debye–Bueche function

$$S(q) = \frac{8\pi^3(\Delta\epsilon)^2\phi(1-\phi)}{\lambda_0^4}\frac{a^3}{(1+q^2a^2)^2} \tag{9}$$

This function has often been successfully used for a representation of scattering curves measured for ran-

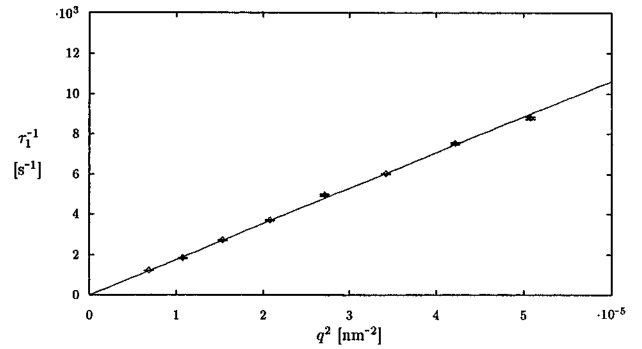

Figure 2. q-dependence of the relaxation rate of the fast mode derived from the curves in Figure 1.

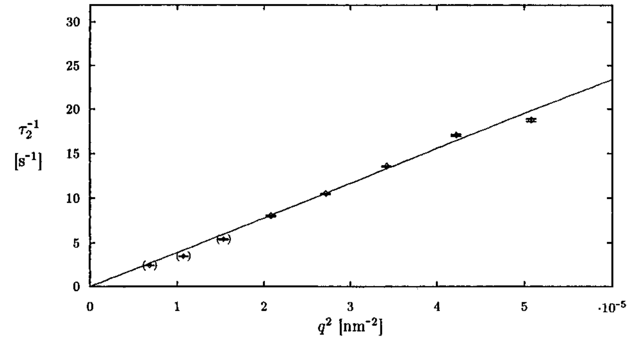

Figure 3. q-dependence of the relaxation rate of the slow mode derived from the curves in Figure 1.

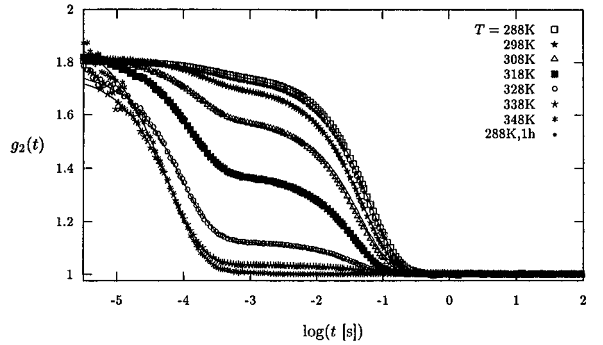

Figure 4. Normalized intensity correlation functions of 12.5% PS ($M_w = 78\,000$) in toluene obtained at $q = 5.95 \times 10^{-3}$ nm^{-1} for various temperatures.

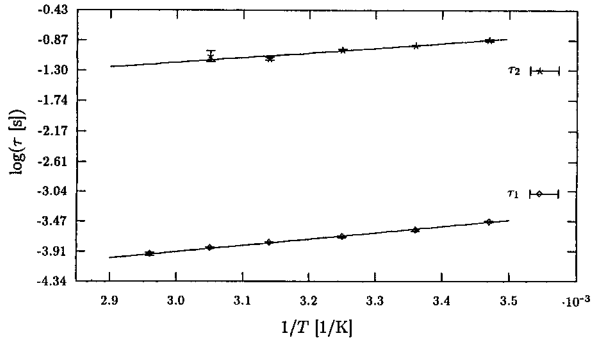

Figure 5. Arrhenius plot of the relaxation rates of the fast and the slow modes derived from the curves in Figure 4.

dom two-phase systems. It just represents the Fourier transform of an exponentially decaying correlation function

$$\langle \delta\epsilon(0)\, \delta\epsilon(\vec{r})\rangle \sim \exp -\frac{r}{a} \qquad (10)$$

The characteristic parameter of the Debye–Bueche

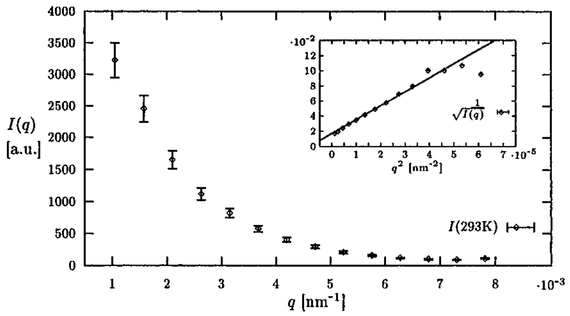

Figure 6. Static scattering intensity of 20% PS ($M_w = 80\,000$) in toluene at 20 °C. The plot in the insert demonstrates that the scattering curve may be represented by the Debye–Bueche function.

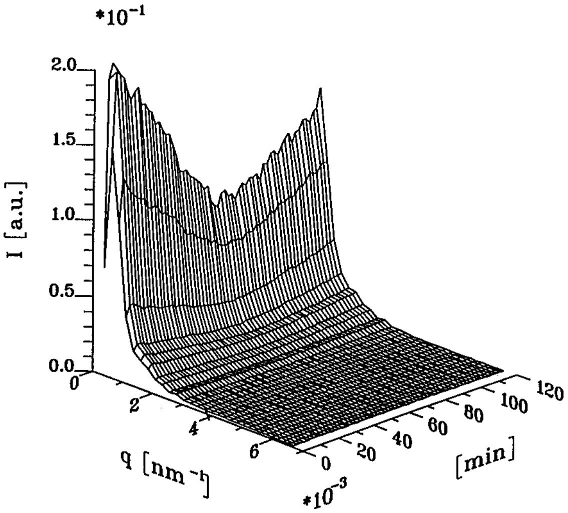

Figure 7. Static scattering curves of 20% PS ($M_w = 80\,000$) in toluene at 20 °C measured for various temperatures during heating from 20 to 80 °C (first hour) and successive cooling back to 20 °C (second hour).

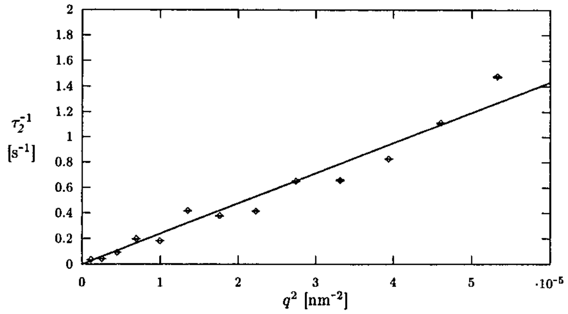

Figure 8. q-dependence of the relaxation rate of the slow mode of 20% PS ($M_w = 80\,000$) in toluene at 20 °C.

function is the correlation length a. The equation includes in addition the volume fractions ϕ and $1 - \phi$ of the two phases, the difference in the dielectric constant $\Delta\epsilon$, and the wavelength of the light in vacuum λ_0.

In comparison to the sample with the lower polystyrene concentration, the temperature dependence of the intensity is diminished. The behavior is shown in Figure 7, which gives the change of the static structure factor registered with the aid of a multidiode array during a heating with constant heating rate, from 20 to 80 °C within 1 h, followed by a successive cooling back to 20 °C, again within 1 h. As it appears, the shape of the scattering function is unchanged, which implies that the changes may originate from a temperature dependence of the contrast between the two phases, i.e. $\Delta\epsilon$, solely. Again the slow mode is of the diffusive type, as

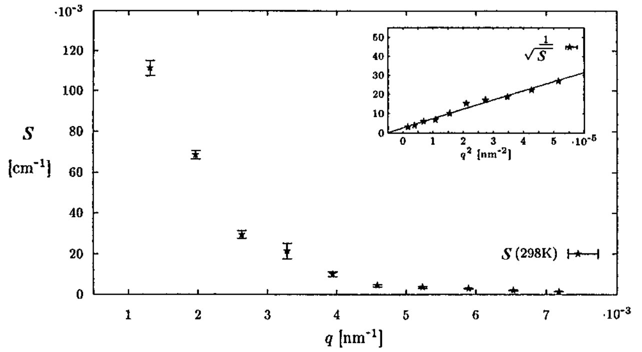

Figure 9. Static structure factor at 25 °C of 25% PS (M_w = 78 000) in toluene. The plot in the insert demonstrates that the scattering curve may be represented by the Debye–Bueche function.

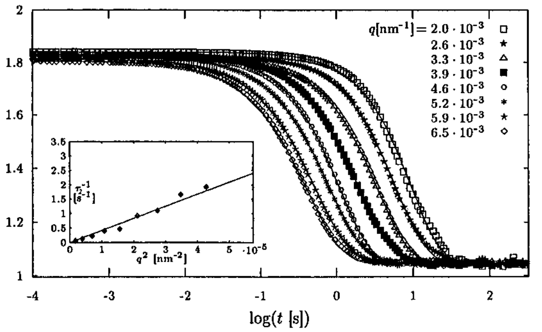

Figure 10. Intensity correlation functions obtained at 25 °C for 25% PS (M_w = 78 000) in toluene. The insert shows the q-dependence indicative for a diffusive process description.

indicated by the q-dependence of the relaxation rate obtained at ambient temperature, shown in Figure 8.

Finally, Figures 9 and 10 give the static structure factor and intensity correlation functions measured for a sample with 25% polystyrene. Again only the slow mode shows up. As in the previous case, the static structure factor may be represented with the aid of the Debye–Bueche function. A fit of the q-dependent Rayleigh ratio yielded a correlation length

$$a = 430 \text{ nm} \tag{11}$$

and the extrapolation to the origin gives

$$S(q{=}0) = 0.15 \text{ cm}^{-1} \tag{12}$$

From the absolute values additional information can be derived. Using

$$\Delta\epsilon = 2n\Delta n \tag{13}$$

we obtain

$$\Delta n^2\phi(1 - \phi) = 1.2 \times 10^{-8} \tag{14}$$

We also determined the diffusion coefficient, D_s, given by the slope of the line in the plot inserted in Figure 10. Its value is

$$D_s = 2.09 \times 10^{-14} \text{ m}^2 \text{ s}^{-1} \tag{15}$$

4. Discussion

The experimental results may be summarized as follows:

(i) In agreement with the observations of other authors on semidilute and concentrated polymer solutions, we found for solutions of polystyrene in toluene also a slow mode, in addition to the faster gel mode.

(ii) The slow mode represents the dynamics of a second component contributing to the concentration fluctuations in the solution.

(iii) The correlation length of the concentration fluctuations associated with this second component is on the order of several hundred nanometers.

(iv) The weight of the second component relative to that of the gel mode increases (a) with decreasing wave vector q, (b) with increasing concentration of polystyrene, and (c) with decreasing temperature.

(v) The decay rate changes with q according to the law τ_2^{-1}, characteristic for diffusive processes.

Which conclusions can be drawn from these observations? First, for the samples under study some of the explanations offered for the slow mode in the literature cannot be used. This holds for all explanations which associate the slow mode with the decay of the temporary network. Nearly all the points cited above contradict this picture, in particular the correlation length deduced from the static structure factor which is far above the mesh size. On the other hand, the results indeed agree with the suggestion that the slow mode might originate from heterogeneities existing in the entangled solution. This becomes particularly clear if we recall another case, namely the changes in the scattering resulting from the formation of micelles in a solution of surfactants at the cmc, the critical micelle concentration. The micelle formation leads to an increase in the static scattering intensities, and it introduces a new, larger spatial correlation length. In dynamic experiments one observes a decay of the correlation function due to the diffusive motion of the micelles. Our observations on polystyrene solutions obviously agree with all these behaviors. This strongly suggests that chains associate within the entanglement network and then move together as stable objects in the fluid background given by the solution.

Our experiments inform us about the size of these objects, as having typical values of several hundred nanometers. One has to be aware, however, that nothing can be deduced from the data about the form of the objects. These might be spherical clusters, classical fringed micelles, pieces of fibers or even a network of fibers which sets up another mesh, now with dimensions in the 100 nm range. Independent from the shape, it should be possible to apply the Stokes–Einstein relation, i.e. to write

$$D_s = \frac{kT}{6\pi\eta\xi} \tag{16}$$

and

$$\tau_2^{-1} = D_s q^2 \tag{17}$$

This requires a knowledge of the viscosity of the solution, η. We measured it with the aid of a capillary viscosimeter, obtaining η = 0.36 P. When combined with the value of D_s given above, we arrive for the solution with 25% polystyrene at

$$\xi = 293 \pm 10 \text{ nm} \tag{18}$$

This has the same order of magnitude as the static correlation length a in the Debye–Bueche function, as expected for a moving object.

As an alternative to this picture of diffusing objects one could also envisage the fluctuations as being caused by a reversible association–dissociation process. The findings, however, contradict this view. In such a case the relaxation time would be proportional to the static structure factor

$$\tau_2 \sim q^{-2} S(q) \qquad (19)$$

as is true, for example, for a binary polymer mixture near the point of unmixing, but this is not found. Hence, we clearly observe the dynamics of given objects rather than the kinetics of their formation and dissociation.

It would be of interest, of course, to know about the volume occupied by the heterogeneities. For principal reasons this cannot be deduced from the data. The fit by the Debye–Bueche function implies that we represent the system as a two-phase structure, and the parameter following from the Rayleigh ratio is only the product $\phi(1 - \phi)(\Delta n)^2$, which couples volume fraction and contrast factor. The value obtained for the sample with 25% polystyrene is $\Delta n^2 \phi(1 - \phi) = 1.2 \times 10^{-8}$. What we can do is just a guess. If we set, for example, $\Delta n \cong 10^{-2}$, we arrive at $\phi \cong 10^{-4}$. This tells us, at least, that the experiment is rather sensitive and that the volume content of the heterogeneities might be rather low.

Several important questions remain open. First of all, are we really dealing here with an equilibrium phenomenon? Since we observed the heterogeneities in all studied solutions, and there in a reproducible manner, we feel that this might be the case. In an earlier work[9] we found that the heterogeneity scattering vanished after months; however, the chemical stability cannot be insured over such a long time, and this might change the behavior. The samples used by Brown in his studies[4] obviously didn't show the heterogeneity scattering, thus enabling the observation of the q-independent network reorganization modes. However, these samples were prepared in a special manner, by carrying out the polymerization process in the solution, and experiments were conducted at higher q s. In any case, independent of whether we deal with an equilibrium phenomenon or only with a transient state, there remains the problem of understanding the occurence of the heterogeneities. According to the established view, the longest relaxation time in polymer solutions and melts is the disentangling time, as observed in dynamic mechanical spectra at the onset of flow. In recent times, however, there arosed increasing evidence that in polymer melts, or more generally, in complex fluids with enhanced viscosities, there might occur structural relaxations also on much longer time scales. Indeed, in polymer melts one observes in light scattering experiments an anomalous scattering with properties very much like those observed for the slow mode discussed here.[10] They are again indicative of heterogeneities in the 100 nm range, which means, for melts, long-living heterogeneities in the density. Evidence for the existence of long-time relaxation processes also follows from polymer crystallization studies. There it is observed that the time needed for a nucleation of polymer crystallites subsequent to a melting strongly depends on the time of annealing the melt, for times which are far above the disentangling time.[11] We therefore feel that the association processes detected here for polymer solutions could be an example of a more wide spread general phenomenon. When thinking about its origin, it is again instructive to consider the micellar case. Micelles are stabilized by many-particle interactions, and their dissolution requires a cooperative action of many molecules. Similar properties might hold for the associates in the solution. They form a many-sequence state with multiple interactions and therefore can remain stable for times which are large compared to the reptation time needed to remove or exchange a single chain sequence. The formation of micelles may be addressed as a microphase separation process. Processes of this kind exist in various forms in polymers and, therefore, why not in a peculiar way in an entangled system? Hypothetically, one could envisage a process which leads to a separation between mobile and less mobile but more closely packed regions. Cohen and Grest[12] developed this idea in a description of the glass transition, and Fischer[13] uses a similar picture in his discussions of the anomalous scattering of polymer melts and other complex fluids. If we accept this view, we have to think about the driving force for the separation, since this would be the basis for any calculation of the properties of the heterogeneities. At present, this is an open field; there are no concepts for an understanding. Hence in conclusion, the structural origin of the excess scattering and the associated diffusive slow mode in polymer solutions seems to be clear, as being due to large-scale heterogeneities; we lack, however, a concrete picture allowing a treatment of the phenomenon.

Acknowledgment. M.H. expresses his gratitude for the financial support of the Markel-Stiftung, Stuttgart.

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MA961781K