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Self-Diffusion in Concentrated Solutions of Polystyrene in Toluene: No Evidence for Large-Scale Heterogeneities

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In a recent paper, Strobl and co-workers have reported static (SLS) and dynamic (DLS) light scattering experiments of semidilute and moderately concentrated solutions of polystyrene in toluene.[1] They found two modes of concentration relaxations, the well-known and well-understood fast mode of the cooperative diffusion of the overlapped chains and a slow mode. This slow mode is an often observed phenomenon in dynamic light scattering experiments in polymer solutions, but until now no conclusive explanation could be given.[2] The slow mode was attributed to the reorganization of the temporary network of overlapping chains,[3] a process which should be determined by self-diffusion and the tube disengagement of the chains. The observed concentration dependence of the relaxation rate of the slow mode, which is similar to that of the self-diffusion coefficient, supports this view. Burchard[4] and Brown et al.[2] have proposed another explanation: the dynamics of the formation of associations between chains should be responsible for the arising of a slow mode.

In this note, we present self-diffusion experiments on solutions of polystyrene in toluene with similar concentrations and molar masses as used in the investigations of Strobl et al.[1] We like to answer the question: are there characteristics in the self-diffusion having the same origin as the slow mode detected by DLS?

To discuss polymer solutions, one has to rely on three characteristic concentrations: $c_e(M)$, the concentration at which entanglements start to form, $c^*(M)$, the overlap concentration, and c^{**}, the concentration at which the semidilute concentration region ends. $c_e(M)$ was determined from viscoelastic data of ref 5. $c^*(M)$ was taken from ref 6, and c^{**} has a value of about 20% for flexible chains.[6]

Strobl et al. investigated solutions of polystyrene with $M = 80\ 000$ g/mol and three concentrations, 12.5%, 20%, and 25% (w/w), in toluene at different temperatures.[1] These concentrations are smaller than and about equal to c_e ($\approx$25% for $M = 80\ 000$ g/mol); entangled behavior is not expected. For the 25% solution, the fast mode was almost completely masked by the high relative amplitude of the slow mode. A correlation length of concentration fluctuations of 400 nm was found in SLS, and a hydrodynamic radius of 293 nm was obtained from the relaxation rate of the slow mode in DLS using the Stokes−Einstein relation and the viscosity of the solution. The cluster diffusion coefficient derived from the relaxation rate of the slow mode is by a factor of 50 smaller that the self-diffusion coefficient (taken from ref 7). Strobl et al. excluded that the slow mode is related to the decay of a temporary network. They also excluded a reversible association−dissociation process of chains with kinetics within the time window of the experiment or shorter. The results indicate that the slow mode is related to the dynamics of existing objects (clusters?). The volume content of these objects was estimated to be very small. The heterogeneities in the polystyrene solutions have been compared with the large-scale heterogeneities found in low-molar-mass glass-forming liquids. They seem to be a common feature in glass-forming liquids which up to now are not fully understood.[8] Are long-living clusters visible in self-diffusion experiments for the polystyrene homopolymer solutions in the good solvent toluene?

Whereas DLS measures the intermediate coherent scattering function, in self-diffusion experiments the intermediate incoherent scattering function $S_{\mathrm{inc}}(q,t)$ of the positions of the chain segments is monitored from which the single-particle correlation function is obtained. Pulsed-field-gradient NMR as a method to measure self-diffusion works at a space scale $1/q$ from about 100 nm up to a few micrometers. This is similar, or slightly larger, to DLS which covers ca. 30 nm up to 0.5 μm. The time scale of PFG-NMR is, however, limited to 3 decades from 1 ms to 1 s. We have performed pulsed-field-gradient NMR experiments on solutions similar to those used in the experiments of Strobl et al.[1] The polystyrene has a molar mass $M_w = 125\ 000$ g/mol and a polydispersity $P = 1.02$. It was purchased from Polymer Standards Service, Mainz, Germany. As solvent, fully deuterated toluene (Deuchem, Leipzig, Germany) was used. Seven concentrations between 9.7% and 39.9% have been investigated at room temperature (22 °C). The concentrations are given in % (w/w). Our polymer has an unperturbed chain end-to-end-distance $\langle r^2 \rangle_0^{0.5}$ of 24 nm, and the overlap concentration c^* was estimated to 6.5% and c_e to be 16%; i.e., the solutions studied are well overlapped and cover the concentration range $0.5c_e \lesssim c \lesssim 2c_e$.

If species with only one self-diffusion coefficient D_s are present in the sample under study, the $S_{\mathrm{inc}}(q,t)$ shows single-exponential behavior with respect to q^2t: $S_{\mathrm{inc}}(q,t) = \exp(-q^2D_st)$ with the generalized scattering vector q. q is proportional to the area of the field gradient pulses (for details of PFG-NMR cf. refs 9 or 10). t denotes the diffusion or observation time. Data for different observation times t and scattering vectors q merge to one master curve in an $S_{\mathrm{inc}}(q,t)$ vs q^2t representation in the case of such ordinary self-diffusion. If clusters and/or a distribution of self-diffusivities are present, $S_{\mathrm{inc}}(q,t)$ deviates from single-exponential behavior. The influence of cluster formation on $S_{\mathrm{inc}}(q,t)$ was recently demonstrated in solutions of a random copolymer of styrene and methyl methacrylate dissolved in acetone, a bad solvent for styrene.[11]

In two earlier works of Maklakov et al.[12] and Fleischer et al.,[7] a nonexponential $S_{\mathrm{inc}}(q,t)$ was measured in two semidilute solutions of polystyrene ($M = 380\ 000$ g/mol, $c = 13.5\%$ and $M = 230\ 000$ g/mol, $c = 10\%$, both concentrations slightly above c_e) which furthermore splitted for different observation times in the log $S_{\mathrm{inc}}(q,t)$ vs q^2t representation. Such a behavior can be explained by cluster dynamics, and the authors have taken this behavior as a proof for cluster formation and exchange of chains between the free state and the cluster state. Our measurements are presented in Figure 1. Opposite to the above-mentioned results, the

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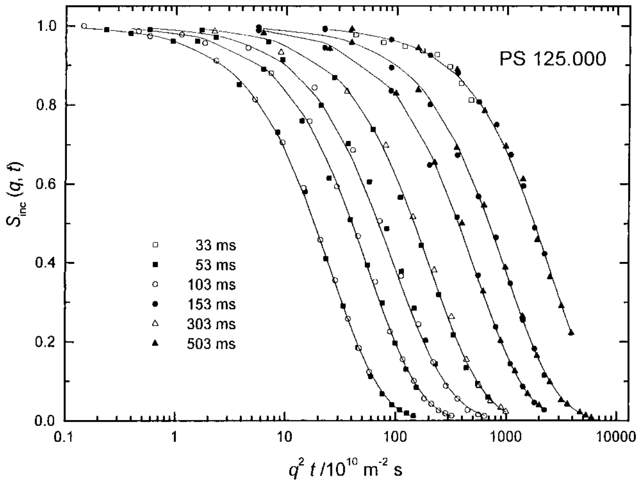

Figure 1. $S_{inc}(q,t)$ vs q^2t for polystyrene ($M = 125\ 000$ g/mol) in toluene at the concentrations 9.7%, 14.6%, 19.4%, 24.2%, 29.7%, 33.9%, and 39.3% (from left to right). The different observation times are given in the figure. The lines are fits with a log-normal distribution of self-diffusion coefficents. No dependence of the self-diffusivity on the observation time is observed.

Table 1. Median Self-Diffusion Coefficients $D_{s,0}$ ($m^2\ s^{-1}$) and Widths ln σ of the Distributions of Self-Diffusivities

c/%	$D_{s,0}{}^a/10^{-13}$	ln σ	c/%	$D_{s,0}{}^a/10^{-13}$	ln σ
9.7	37	0.30	29.7	1.85	0.33
14.6	17	0.34	33.9	0.98	0.31
19.4	8.9	0.31	39.3	0.39	[b]
24.2	4.6	0.37			

[a] Experimental error ±5%. [b] No determination possible.

$S_{inc}(q,t)$ are found to be very well single exponential. The weak curvature is caused by the polydispersity alone. The lines are fits of a log-normal distribution of self-diffusivities: $w(D_s) \sim \exp(-(\ln^2(D_s/D_{s,o})/2\ \ln^2\ \sigma))$. The self-diffusivities $D_{s,0}$ (the median value of the distribution) and the ln σ values are given in Table 1 for the seven measured concentrations. When approximating the distribution of the molar masses with a log-normal distribution, which is sufficiently good for the small polydispersity, then $\ln \sigma = \alpha(\ln P)^{0.5}$ using the relation $D_s \sim M^{-\alpha}$. From the fitted ln σ values we get $\alpha \approx 2$ for all concentrations. ($D \sim M^{-2}$, characteristic for reptation, was found for self-diffusion in solutions of linear chains for all concentrations $c \gtrsim c^*$; cf. ref 6.) We have no indications of a second, slow process in the self-diffusion experiments! Additionally, no dependence of D_s on t could be found in the investigated time interval. The observed cluster diffusion reported in refs 7 and 12 must be questioned; it is possibly caused by experimental artifacts and could not be confirmed with our spectrometer. We do not detect cluster diffusion in the PFG-NMR experiments, not even in solutions where DLS detects only slow mode diffusion! The concentration of clusters must be well below 1%; otherwise, they could be detected in our experiments as a deviation of $S_{inc}(q,t)$ from exponentiality (a decreasing slope of $S_{inc}(q,t)$) at the high q^2t end of the curves). This upper limit of concentration is in accord with the light-scattering results. In polyelectrolyte solutions no indications of cluster formation in self-diffusion experiments was detected as well, [13] whereas in QELS experiments a slow mode is always present.[14] The values of the self-diffusion coefficients measured in this work (cf. Table 1) are in accord with earlier data.[6,7,15]

In conclusion, PFG NMR self-diffusion measurements cannot detect cluster diffusion in solutions of polystyrene in toluene; also in solutions in those QELS detects almost only a slow mode. The concentration of clusters must be well below 1%. We still like to stress that the broadly accepted blob picture and the reptation mechanism in a tube of blobs[16,17] seem to be sufficient for the description of the concentration dependence of the self-diffusion coefficients of linear chains in semidilute solutions.[6] No additional dynamic process is needed. However, there are also many features of polymer dynamics that are not properly accounted for by the above-mentioned theoretical model, mainly the dependence on the molar mass. Further experimental and theoretical effort in this field is highly desirable.

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