876 *Macromolecules* 1980, *13*, 876–880

Segmental Diffusion of Polymer Molecules in Solution As Studied by Means of Quasi-Elastic Neutron Scattering

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Received July 23, 1979

ABSTRACT: The segmental diffusion of polymers in dilute solution was investigated by coherent quasi-elastic neutron scattering. The dependence of the line width $\Delta\omega$ as a function of the ratio of the temperature T to the solvent viscosity η was studied. Measurements were performed on protonated poly(dimethylsiloxane) dissolved in deuterated benzene or chlorobenzene in a temperature range between −12 and +74 °C. Thus, T/η was varied by a factor of about 5. It is shown that the line widths of the spectra are all proportional to $(T/\eta)Q^3$, as predicted for the Zimm model under Θ conditions. No experimental indications were found for a different behavior of segmental diffusion in Θ and good solvents.

The dynamic behavior of polymer molecules in solution on the scale of segmental diffusion (Flory radius $R_F > r >$ segment length l) and its effects on quasi-elastic neutron scattering have been treated extensively from a theoretical point of view.[1-9] These theories, commonly restricted to Θ conditions, are based on a hydrodynamic description where entropic restoring forces and, in the case of the Zimm model,[10] additional hydrodynamic interactions between the chain segments are taken into account. In the limit of $Ql \rightarrow 0$ and infinite long chains the correlation functions and the corresponding coherent and incoherent scattering laws have been calculated explicitly for dilute solutions.[1,2] On the basis of the Zimm model the line width $\Delta\omega$ of the quasi-elastic spectra was predicted to scale with the cube of the momentum transfer $\hbar Q$ and to be proportional to T/η, where T is the temperature of the solution and η the viscosity of the pure solvent.[2,3] No special polymer properties enter the equations for line width and line shape.

Near the transition from Θ to good solvent conditions an additional influence of the temperature is expected. The proportionality factor between $\Delta\omega$ and $(T/\eta)Q^3$ has been calculated to increase by approximately 30% when passing from a Θ solvent to a good solvent.[7] On the Q scale this crossover occurs at $Q \sim 1/\xi_\tau$, ξ_τ being a temperature-dependent correlation length which describes the size of Gaussian chain sections within the overall swollen polymer coil near the Θ temperature.

The experimental verification of these predictions has been difficult up to now because high resolution is required at momentum transfers small compared with the reciprocal value of the segment length, which is of the order of 0.2 Å^{-1}. Since only the upper part of the Q regime was available a short time ago, earlier measurements[4,11,12] suffered from this instrumental limitation. However, by extending the Q range in conventional neutron backscattering spectroscopy[13] to smaller values and, especially, by employing a neutron spin echo spectrometer,[14,15] it became possible to reach the Q regime suitable for studying the segmental motion of polymer molecules, and confirmation of the scaling predictions of the Zimm model ($\Delta\omega \sim Q^3$) was made for the first time[16] by a spin echo technique in the case of a dilute solution. Moreover, a line-shape analysis revealed severe deviations from a simple exponential decay in the time regime.

After the theoretically predicted scaling law ($\Delta\omega \sim Q^3$) for dilute solutions was established, the dependence of $\Delta\omega$ on temperature and viscosity was investigated. For this purpose high-resolution quasi-elastic neutron scattering experiments, using a back-scattering spectrometer, were performed on dilute solutions of poly(dimethylsiloxane) (PDMS), a polymer where the absolute values of the line width were found to be close to the theoretically expected values.[16]

Theory

In the so-called "Gaussian approximation" the intermediate scattering laws for the quasi-elastic coherent and incoherent neutron scattering due to the segmental motion of a polymer chain in solution are given by[1]

$$I_{\mathrm{coh}}(Q,t) = \frac{1}{N}\sum_{n,m}\exp\left[-\frac{1}{6}Q^2\langle|r_n(t) - r_m(0)|^2\rangle\right] \quad (1)$$

and

$$I_{\mathrm{inc}}(Q,t) = \frac{1}{N}\sum_{n}\exp\left[-\frac{1}{6}Q^2\langle|r_n(t) - r_n(0)|^2\rangle\right] \quad (2)$$

The magnitude of the momentum transfer $\hbar Q$ is related to the scattering angle 2θ and the neutron wavelength λ by $Q = (4\pi/\lambda)\sin\theta$. Also, $r_n(t)$ and $r_m(0)$ denote the locations of the nth and mth segment at time t and time zero, respective.

The corresponding scattering laws $S_{\mathrm{coh}}(Q,\omega)$, where $\hbar\omega$ is the energy transfer, are obtained from (1) and (2) by a Fourier transformation in time.

For the Zimm model under Θ conditions the explicit evaluation of the correlation functions $\langle|r_n(t) - r_m(0)|^2\rangle$ and $\langle|r_n(t) - r_n(0)|^2\rangle$ and the corresponding scattering laws (1) and (2) was performed by Dubois-Violette and de Gennes in a straightforward manner.[2] The model leads to hydrodynamic equations in which deviations from equilibrium are counterbalanced by entropic restoring forces. In addition, the hydrodynamic interaction between different chain segments described by the preaveraged Oseen tensor is taken into account. The half-width at half-maximum of the quasi-elastic neutron scattering spectra was found to be

$$\Delta\omega_{\mathrm{coh}} = 0.28(T/\eta)Q^3 \quad (3)$$

$$\Delta\omega_{\mathrm{inc}} = 0.38(T/\eta)Q^3 \quad (4)$$

Without preaveraging of the Oseen tensor, a 15% larger line width results.[3,23]

Equations 3 and 4 are limited to the range of segmental diffusion ($R_F Q >> 1 >> Ql$). The prefactor is of a universal nature, being independent of polymer properties or

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polymer–solvent interactions. The calculated line shape exhibits considerable deviations from a Lorentzian. The most pronounced discrepancies appear in the wings of the curve at higher energy transfers.[12]

Another access to the line width of the quasi-elastic neutron spectrum was given by Akcasu and Gurol.[3] Employing Kirkwood's generalized diffusion equation, these authors calculated the initial slope $\Omega(Q) = \lim_{t\to 0}\,[-\mathrm{d}\ln I(Q,t)/\mathrm{d}t]$ of the intermediate scattering law 1. For dilute solutions under Θ conditions the results are, apart from a constant factor, identical with those from eq 3. Because only the equilibrium properties of the polymer were used, this approach is applicable to good solvents and in Q regions where the properties of the entire coil or the monomers determine the relaxation behavior. In particular, the extent of critical fluctuations near the transition from Θ to good solvent conditions is described by a temperature-dependent correlation length[7]

$$\xi_\tau \sim l\Theta/(T-\Theta) \qquad (5)$$

where Θ is the Θ temperature. ξ_τ is a measure of distance, beyond which excluded-volume interactions between the monomers become important. For $Q > Q^* = 6^{1/2}/\xi_\tau$, the statistics are Gaussian and a Θ-like behavior is expected, whereas for $Q < Q^*$ the excluded-volume interaction comes into play and the line width is predicted to increase by about 30% compared to a Θ solution with the same viscosity and at the same temperature. In addition the calculations were extended to smaller and larger Q regions.[3] In both regimes the line width was found to be proportional to Q^2. For $R_F Q << 1$ the diffusion of the coil as a whole is observed, whereas for $Ql >> 1$ the diffusion of the monomers dominates. The advantage of this approach is due to the fact that the initial slope $\Omega(Q)$ does not depend on memory effects, which generally have to be incorporated in explicit line-shape calculations. However, from the experimental point of view it is difficult to determine the initial slope with sufficient accuracy if the shape function is not known in addition.

Experimental Section

For these investigations protonated PDMS, dissolved in deuterated benzene and chlorobenzene, respectively, was used. The polymer concentration was 0.05 g/cm^3 in both cases.

The PDMS was prepared by anionic polymerization of hexamethylcyclotrisiloxane, using a modified break-seal polymerization technique.[17] With $(CH_3)_2Si(OLi)_2$ as initiator and $(CH_3)_3SiCl$ as terminating agent, polymers with only methyl side groups were obtained. Purification of the polymerization product was achieved by repeated precipitations from THF solutions, with purity checked by IR, UV, and NMR spectroscopy. The molecular weight, as determined by light scattering, was 30 000. The deuterated solvents, obtained from Sharp & Dohme GmbH, München, had a deuterium content of >99%. The temperature of the samples was varied between −12 and +74 °C for the chlorobenzene solution and between 6 and 70 °C for the benzene solution. The viscosities η of the pure solvents were determined in the range between 25 and 65 °C with the aid of an Ubbelohde viscosimeter,[18] using protonated benzene at 25 °C for calibration. Viscosity values outside this temperature range were obtained by extrapolation, assuming a temperature dependence similar to that for the corresponding protonated solvent. The scattering experiments were performed at the IN10 high-resolution back-scattering spectrometer in Grenoble.[13] At an incident energy of 2.074 meV (λ 6.28 Å) it provided an energy resolution (fwhm)—as measured with a vanadium standard—between 1.3 and 1.6 μeV, depending on the scattering angle. The detectors were set to Q values of 0.07, 0.11, 0.15, 0.19, 0.23 and 0.30 Å^{-1}. The energy window of the instrument was chosen to be ±12.7 μeV. As an example, Figure 1 shows the quasi-elastic spectra obtained from PDMS in benzene at 70 °C for $0.07 \le Q \le 0.3$ Å^{-1}.

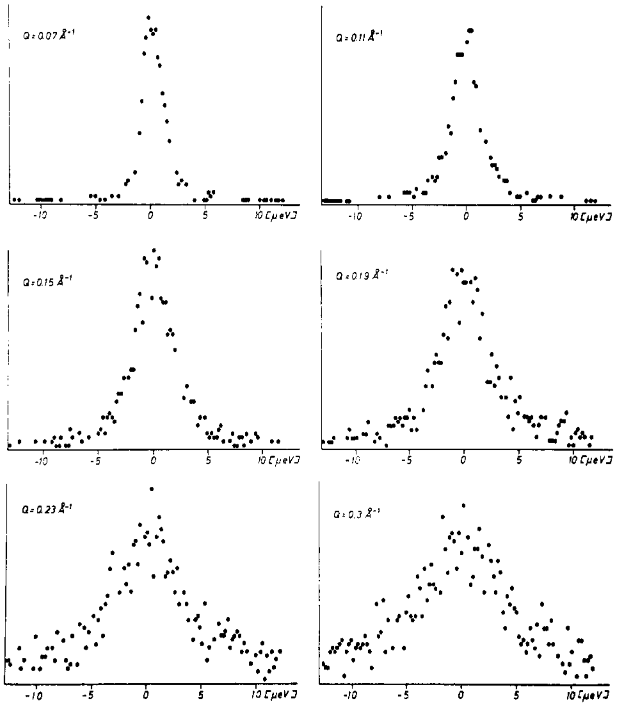

Figure 1. Quasi-elastic neutron scattering spectra of PDMS in benzene at 70 °C.

Results

Assuming an incompressible mixture, the total quasi-elastic scattering law $S(Q, \omega)$ of dilute polymer solutions includes three main contributions[19]

$$S(Q,\omega) = cK^2 S_{\mathrm{coh}}^{\mathrm{poly}}(Q,\omega) + c\frac{\sigma_{\mathrm{inc}}^{\mathrm{poly}}}{4\pi}S_{\mathrm{inc}}^{\mathrm{poly}}(Q,\omega) + (1-c)\frac{\sigma_{\mathrm{inc}}^{\mathrm{sol}}}{4\pi}S_{\mathrm{inc}}^{\mathrm{sol}}(Q,\omega) \qquad (6)$$

where c is the concentration and K the scattering length contrast between polymer and solvent. $S_{\mathrm{coh}}^{\mathrm{poly}}(Q,\omega)$, $S_{\mathrm{inc}}^{\mathrm{poly}}(Q,\omega)$, and $S_{\mathrm{inc}}^{\mathrm{sol}}(Q,\omega)$ are the coherent and incoherent scattering laws for the polymer and the solvent and $\sigma_{\mathrm{inc}}^{\mathrm{poly}}$ and $\sigma_{\mathrm{inc}}^{\mathrm{sol}}$ are the corresponding incoherent cross sections. The intensity contribution due to the instrumental background was negligibly small.

For both samples coherent scattering was predominant in the whole Q range used for these investigations. This is demonstrated in Figure 2, where the absolute intensities $\mathrm{d}\Sigma/\mathrm{d}\Omega$ are plotted as a function of Q for the PDMS/benzene system. While the incoherent scattering is independent of Q, the coherent scattering exhibits a Q^{-2} dependence characteristic for polymer molecules with a radius of gyration of about 60 Å in this range of Q.[20]

No corrections were, therefore, made for the incoherent scattering by the polymer. This approximation is justified further on, because the coherent and incoherent scattering contributions of the polymer result from the same dynamic process and the line widths of the related scattering laws show only a slight difference with respect to the prefactors (see eq 3 and 4).

The contribution of the solvent scattering was measured separately and subtracted from the total intensity measured on the sample. From the spectra, corrected for absorption and container and solvent scattering, integrated intensities $\mathrm{d}\Sigma/\mathrm{d}\Omega$ were determined and converted to an absolute scale by comparing them to the scattering intensity of a vanadium standard with known scattering power. There is always good agreement between experimental data and the corresponding values calculated for

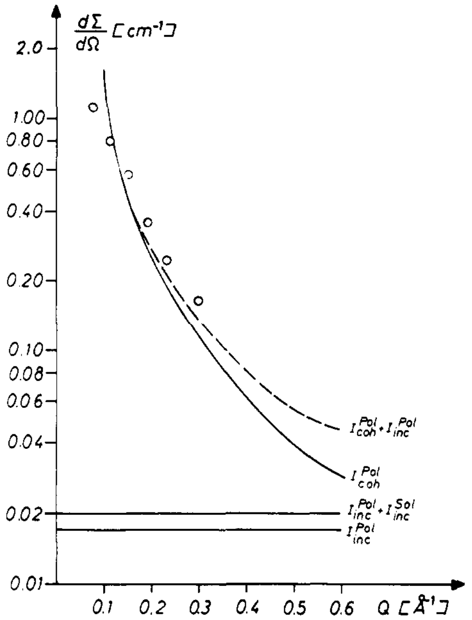

Figure 2. Calculated contributions of coherent and incoherent polymer and incoherent solvent scattering to the absolute neutron scattering intensity $d\Sigma/d\Omega$ of PDMS in benzene (0.05 g/cm^3) as a function of Q: (O) experimental values for the polymer scattering.

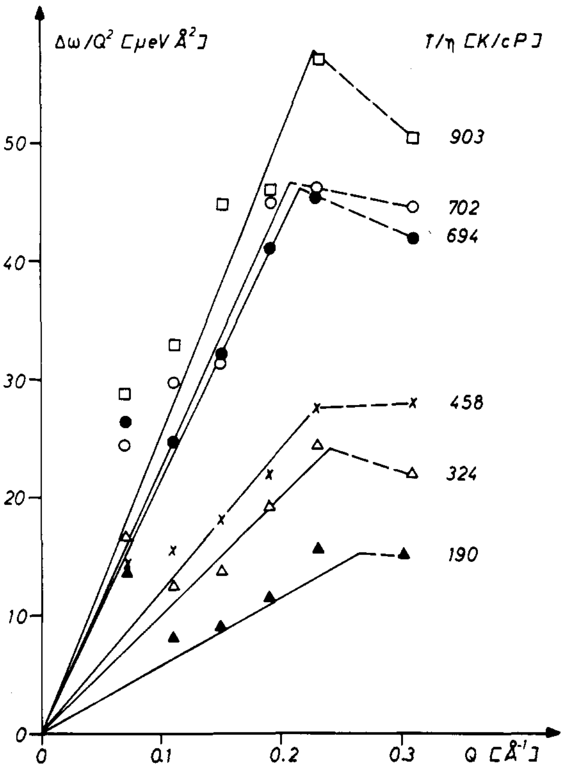

Figure 3. Line width $\Delta\omega/Q^2$ of the quasi-elastic neutron scattering spectra as a function of Q as obtained by fitting the scattering law $g_c(\tilde{\omega})$, calculated by Dubois-Violette and de Gennes, to the experimental data. Results of fitting the individual spectra: (▲, ●) PDMS in chlorobenzene; (△, ×, ○, □) PDMS in benzene. The solid line indicates results of fitting the spectra (T = constant; $Q < 0.2$ Å^{-1}) simultaneously, assuming a Q^3 power law. The dashed lines are guidelines for the eye.

the total scattering intensity of the polymer, as can be seen from Figure 2 in the case of PDMS in benzene.

The obtained quasi-elastic line widths at low Q values are of the order of magnitude or considerably smaller than the instrumental resolution. Therefore, a very careful data analysis was necessary in order to evaluate reliable line-width parameters. The procedure was the following: within a limited energy window, chosen 6 times the width of the corresponding spectrum, the measured spectra were fitted with a Lorentzian convoluted with the experimentally determined resolution function and with the resolution convoluted function $g_c(\tilde{\omega})$ ($\tilde{\omega} = 6\pi 2^{1/2}\omega/(kTQ^3/\eta)$, calculated by Dubois-Violette and de Gennes for the coherent scattering law.[2] Both scattering laws depend on two parameters, the line width and the intensity. The selection of an energy window equivalent for all the spectra turned out to be important in order to avoid the influence of large systematic errors in the outer wings of the measured spectra.

Besides these single-spectrum fits the whole set of spectra obtained at one temperature was fitted simultaneously by common variation of parameters. Fits assuming a Q^3 power law, as well as fits to determine the actual experimental value of the exponent of Q, were performed for both scattering laws.

In Figure 3 the line width $\Delta\omega/Q^2$ is plotted vs. Q for PDMS in benzene at T = 6, 25, 50, and 70 °C and for PDMS in chlorobenzene at −12 and +74 °C. The $\Delta\omega$ were obtained from fitting the individual spectra in a limited energy range ($\sim 6\Delta\omega$) with the function $g_c(\tilde{\omega})$.

In addition, the results of the common fits of the spectra, obtained for $0.07 \leq Q \leq 0.19$ Å^{-1}, are shown by solid lines. In these fits $\Delta\omega \sim Q^3$ was assumed. If the $\Delta\omega$ values are neglected at $Q = 0.07$ Å^{-1}, where, due to the very small line broadening, systematically large line widths are expected from the convolution procedure, it is evident that for all temperatures and both solvents the $\Delta\omega$ values of the individual spectra behave linearly with respect to Q^3, as predicted by eq 3 and just demonstrated by another neutron scattering method.[16] For higher Q values a deviation from this behavior to lower $\Delta\omega$ values can be observed. From examination of the T/η values, which are predicted to determine the line width as a characteristic parameter, a strong correlation between the increase of T/η and the increase of the slope of the Q^3-dependent section is observed. Fitting with a Lorentzian in general leads to higher values for $\Delta\omega$. As a typical example, the results of the single and common fits on the spectra of PDMS/benzene at 70 °C, using the two different scattering laws, are shown in Figure 4.

In Table I, the values of $\Delta\omega/Q^3$, based on the common fits, are compared with the corresponding theoretical values calculated from eq 3. There is satisfactory agreement in both cases. Only at small line widths (+6 and −12 °C) do deviations of more than 15% occur with the Lorentzian scattering law. As to the line shape, it was impossible to distinguish between a Lorentzian line and the Dubois-Violette–de Gennes function $g_c(\tilde{\omega})$. For example, for PDMS in chlorobenzene at 74 °C the following normalized χ^2 values (Lorentzian, $g_c(\tilde{\omega})$) are obtained: $Q = 0.07$ Å^{-1}, 1.85, 1.87; $Q = 0.11$ Å^{-1}, 1.50, 1.38; $Q = 0.15$ Å^{-1}, 1.31, 1.14; $Q = 0.19$ Å^{-1}, 1.57, 1.46. They do not allow any significant distinction between the two line shapes. On the other hand, however, the exponents resulting from the common-fit procedures deviate considerably. The exponents evaluated by a Lorentzian scattering law are systematically smaller (2.5–2.8) than the values determined by a fit with $g_c(\tilde{\omega})$ (see Table I).

Discussion

The line widths $\Delta\omega$, evaluated for $Q < 0.2$ Å^{-1}, follow quite accurately the Zimm-type Q^3 power law (eq 3) for PDMS in benzene at 6 and 25 °C and for PDMS in chlorobenzene. Deviations occur for PDMS in benzene at higher temperatures, which may be related to temperature

Table I
Quasi-Elastic Neutron Scattering on PDMS in Benzene and Chlorobenzene: Comparison between Experimental Results and Theoretical Predictions of the Zimm Model under Θ Conditions

			Q, Å^{-1}						fitted exponents[b]		$\Delta\omega/Q^3$, μeV Å^3		
			0.07	0.11	0.15	0.19	0.23	0.30				results of common fit procedure with exponent 3	
solvent	T, °C	T/η, K/cP	$\Delta\omega$,[a] μeV						A[c]	B[c]	theory (eq 1)	A	B
benzene	6	324	0.08	0.15	0.31	0.70	1.29	1.96	2.94	2.61	91	100	115
	25	458	0.07	0.19	0.41	0.80	1.46	2.52	3.03	2.63	128	120	140
	50	702	0.12	0.36	0.71	1.63	2.43	4.02	2.57	2.60	197	225	210
	70	903	0.14	0.40	1.01	1.66	3.03	4.54	2.56	2.26	253	255	280
chlorobenzene	−12	190	0.07	0.10	0.21	0.42	0.83	1.36	2.76	2.27	53	57	83
	74	694	0.13	0.30	0.72	1.49	2.42	3.77	2.92	2.45	194	215	227

[a] As determined from single-spectrum fits, using the scattering law $g_c(\tilde{\omega})$, as calculated by Dubois-Violette and de Gennes.[2] [b] Theory: 3. [c] (A) Scattering law $g_c(\tilde{\omega})$, as calculated by Dubois-Violette and de Gennes;[2] (B) Lorentzian-like scattering law.

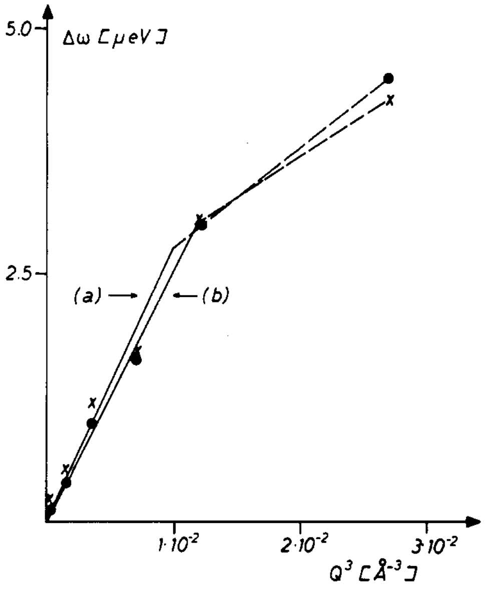

Figure 4. Line width $\Delta\omega$ (hwhm) of PDMS in benzene at 70 °C as a function of Q^3. Comparison between results from fitting a Lorentzian scattering law (×) and the scattering law $g_c(\tilde{\omega})$ (●) to the individual spectra. The solid line shows results of fitting the spectra ($Q < 0.2$ Å^{-1}) simultaneously: (a) Lorentzian scattering law; (b) $g_c(\tilde{\omega})$. The dashed lines are guidelines for the eye.

cross-over effects (see below). The Q^3 dependence of line width ensures that the experiments have been performed in the regime of segmental diffusion, which is a necessary condition for a study of the predicted temperature dependence. For Q's larger than 0.2 Å^{-1} the observed line widths $\Delta\omega$ turn out to be smaller than expected from an extrapolation of the low-Q behavior. This indicates a change of the exponent.

According to the calculations of Akcasu and Gurol,[3] a Q^2 behavior of $\Delta\omega$ is expected at Q values which probe the spatial distances of monomer units ($Ql > 1$), and the Q^3 behavior should hold for $Ql < 1$. From this the segment length l of PDMS may be estimated at ~5 Å. Since similar l values are obtained for other polymers,[4] the upper Q range for observing segmental diffusion of polymers seems to be limited to ~0.2 Å^{-1}. Already Akcasu and Higgins have pointed out that the deviations from the Q^3 behavior of the line width, found in earlier experiments,[4] can be related to the Q range of these experiments, which was intermediate between the regimes of segmental and monomer diffusion. It should also be emphasized that the true coherent line width at $Q = 0.3$ Å^{-1} is even smaller than shown in Figures 3 and 4. The data were not corrected for incoherent polymer scattering (Figure 2), which becomes relatively more important at larger Q values and tends to increase the observed line width.

Comparison of the $\Delta\omega$ values, experimentally determined by the simultaneous-fit procedure and theoretically calculated for Θ conditions according to eq 3, shows a general good agreement (Table I). Thus, the relation between $\Delta\omega$ and $(T/\eta)Q^3$ as stated in eq 3 seems to be valid for all experimental data on PDMS which have been obtained with different solvents as well as with temperatures of the solutions in a range which corresponds to a change of T/η by a factor of about 5. In particular, no experimental indications are found for a different behavior of segmental diffusion in Θ and good solvents. This is in disagreement with the theoretical work presented by Benmouna and Akcasu.[7] According to their approach, the transition between both solvent conditions is characterized by a temperature-dependent correlation length ξ_τ (eq 5) which describes the size of Gaussian "blobs" within the swollen chains. For Q values smaller than $Q^* \sim 1/\xi_\tau$ the transition from the Θ- to the excluded-volume-type relaxation behavior, accompanied by an increase of the line width by about 30%, is predicted to occur.

Benzene and chlorobenzene are Θ solvents for PDMS,[21] benzene at −7 °C, and chlorobenzene at 68 °C. Assuming that the experimental values for ξ_τ found by Farnoux et al. for poly(tetrahydrofuran) (PTHF) in CS_2[22] also apply for this experiment, PDMS in benzene at 70 °C should behave in the whole Q range as a swollen chain ($Q^* = 0.46$ Å^{-1}), whereas PDMS in chlorobenzene at 74 °C should exhibit Θ behavior ($Q^* = 0.07$ Å^{-1}). Our experimental results, however, do not support this different behavior. In both cases the proportionality factor between $\Delta\omega$ and $(T/\eta)Q^3$ is the same. Also, the results on PDMS in benzene at different temperatures do not show any systematic deviations from the proportionality valid for Θ conditions, although the temperature dependence of ξ_τ shifts Q^* through the observation range of the experiment ($Q^*(70$ °C$) = 0.46$ Å^{-1}; $Q^*(6$ °C$) = 0.07$ Å^{-1}).

The reason that the 30% increase of the line width was not detected when passing from Θ to good solvent conditions may be due to the fact either that the transition is completely obscured by a simultaneous change of line shape or that ξ_τ of PDMS in benzene is much larger than estimated from the results on PTHF in CS_2. If the last alternative is true, Gaussian "blob", showing Θ-like behavior, are observed by these experiments. The decrease of the fitted exponents with increasing temperature (Table

I) for PDMS in benzene might be a hint toward a relatively large ξ_τ which starts to cross the observation range of Q at higher temperatures and thereby lowers the effective exponent.

However, on the basis of the experimental data available up to now, the problem of the crossover from Θ to good solvent conditions and the related increase of the line width cannot be solved. Further experiments with higher accuracy spin echo technique[14,15] are planned to investigate this problem.

As already stated, measurements of the quasi-elastic spectra $S_{\mathrm{coh}}{}^{\mathrm{poly}}(Q, \omega)$ now allow a line-shape analysis which can distinguish between a Lorentzian-like scattering law and the scattering law $g_c(\tilde{\omega})$, given by Dubois-Violette and de Gennes, as it was possible[16] by measuring $S_{\mathrm{coh}}{}^{\mathrm{poly}}(Q, t)$ in Fourier space. This is not surprising because the line shapes of both scattering laws differ mainly at higher energy transfers,[12] where systematic errors are larger than in the central parts of the spectra. On the other hand, deviations from the initial slope of $S(Q, t)$ are easily observed with the spin echo technique, which has a high accuracy in this range.

Acknowledgment. We thank Professor Dr. E. W. Fischer and Professor Dr. T. Springer for their continuous interest in this work and for many stimulating discussions. We are also indebted to the Institut Laue-Langevin, Grenoble, for providing the experimental factilities. The assistance of Dr. A. Heidemann and J. Bauchat in performing these experiments is gratefully acknowledged.

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Polymer/Polymer Diffusion. 2. Effect of Temperature and Molecular Weight on Macromolecular Diffusion in Blends of Poly(vinyl chloride) and Poly(ϵ-caprolactone)

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ABSTRACT: The effect of molecular weight and temperature on the mutual diffusion coefficient for a miscible binary polymer system has been examined by using a technique combining scanning electron microscopy and energy-dispersive X-ray analysis. The system studied, poly(vinyl chloride)/poly(ϵ-caprolactone), has been shown to be compatible on the molecular level. The mutual diffusion coefficients for various molecular weights of the PVC/PCL system were determined to be on the order of 10^{-12}–10^{-13} cm^2/s at 90 °C with the diffusion coefficient roughly proportional to M^{-1}, the latter result not predicted by the few existing theories of diffusion of macromolecules in the melt. Measurement of the diffusion coefficient at several temperatures shows an activation energy for diffusion of 11.7 kcal/mol. Comparisons between these results and various other theoretical and experimental investigations of macromolecular diffusion present some interesting contrasts.

Macromolecular diffusion in the solid or melt state is a subject infrequently addressed in the literature. In the first paper in this series,[1] an experimental technique which allows the measurement of the concentration profile of an interdiffused binary polymer system was described. The technique is a combination of scanning electron microscopy and energy-dispersive analysis of X-ray fluorescence, permitting direct observations of the interface between the two polymeric components and measurement of the concentration gradient of one, or both, of the materials. This technique has been applied to the polymer pair poly(vinyl chloride)/poly(ϵ-caprolactone). Specifically, the effects of molecular weight and temperature on the mutual diffusion coefficient for the system have been observed, with the diffusion coefficient calculated from the data using a solution to the diffusion equation.

Various theoretical models have been used for describing motion of a polymer molecule in the melt, resulting in as many relationships between the diffusion coefficient and molecular weight. Few studies have been undertaken to actually clarify this dependence. Results presented here will be compared with those of previous investigators and theorists.

Experimental System

The experimental details are described in ref 1; a brief description is included here. Sheets of PVC, cast on glass from THF solution, are dried and placed in a vacuum oven at the specified

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