Investigation of the Chain Length Dependence of Self-Diffusion of Poly(dimethylsiloxane) and Poly(ethylene oxide) in the Melt with Pulsed Field Gradient NMR

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ABSTRACT: The chain length dependence of the self-diffusion coefficients of PDMS and PEO has been measured with pulsed field gradient NMR (PFG NMR). With PDMS the maximum molar mass region attainable with PFG NMR could be investigated. For molar masses larger than about $10M_e$ the proportionality $D \sim M^{-2}$ according to the strict reptation picture was observed; at small M Rouse-like diffusion is observed separated from the reptation part by a $D(M)$ dependence characterized by a strong slowing down of the self-diffusion coefficient. The monomeric friction coefficients for PDMS derived from diffusion with the Doi–Edwards theory agree satisfactorily with those obtained from viscosity and also neutron scattering. Quantitatively, a discrepancy remains between the high molar mass part of $D(M)$ where the monomeric friction coefficient is by a factor of about 0.5–0.6 smaller than that determined from the Rouse part of $D(M)$ at low molar masses. Within experimental accuracy, for PDMS the activation energy of diffusion is equal to the activation energy of viscosity. For PEO the activation energy decreases from 24 to 18 kJ/mol at a molar mass of about 20 000 g mol^{-1}.

Introduction

Long-range self-diffusion of polymer molecules in the melt has been investigated with several experimental methods, e.g. holographic grating technique,[1] neutron scattering,[2] IR–microdensitometry,[3] forward recoil spectroscopy,[4] fluorescence redistribution after pattern photobleaching,[5] and pulsed field gradient (PFG) NMR.[6] These methods observe self-diffusion in time scales long in comparison with the longest relaxation time of the polymer molecule in the entangled melt, the reptation time T_r or tube disengagement time T_d, or in other words, in space scales larger than the Flory radius of a chain. PFG NMR has the advantage of working without any chemical labeling of the chains. However, in comparison with the methods mentioned above, the time scale is rather short, i.e., from a few milliseconds up to the nuclear magnetic relaxation times of the spins which are, in favorable cases, of the order of 1 s. Therefore in PFG NMR experiments polymers of high molecular mobility should be used. Such polymers are in particular polyethylene (or hydrated poly(butadienes) or poly(isoprenes)), poly(dimethylsiloxane), and poly(ethylene oxide). With these polymers the long-range self-diffusion coefficient can be measured over a broad molar mass range which is important to verify the theoretical predictions for the dependence of D on M.

In polymer melts the tube picture of Doi and Edwards[7] and the reptation mechanism[8] are well established and verified especially in viscoelastic experiments. The situation is less clear in self-diffusion experiments. An excellent review about the theoretical and experimental situation is given in a paper by Lodge and co-workers.[9] In the last few years new theoretical models have been developed which for very long chain lengths predict the same molar mass dependence of the self-diffusion coefficient as the Doi–Edwards theory.[10,11] The crucial point is the transition from Rouse diffusion to the constraint diffusion in the "entangled melt", the dramatic slowing down of the self-diffusion when increasing the chain length beyond M_e, the entanglement molar mass. This molar mass region is not described by the Doi–Edwards theory, and deviations from this theory for not too large molar masses may be accounted for by additional dynamic processes of the polymer chains.

For a more quantitative comparison between the different theories better experimental data of self-diffusion are necessary. This includes the knowledge of the $D(M)$ dependence in the molar mass region from M_e up to M values many orders larger than M_e, the monomeric friction coefficients derived from the different molar mass regions, and the time dependent (apparent) self-diffusion of the chain segments in space scales smaller than the Flory radius.

In the present work we will report on long-range self-diffusion measurements of PDMS and PEO. Measurements of time dependent (apparent) self-diffusion coefficients are presented in a forthcoming paper.[12] PDMS is a very mobile polymer with a static glass transition temperature of $T_g = -125$ °C. Though it is available in rather monodisperse samples, no exact data about self-diffusion in a broad molar mass region are reported in the literature. The first study has been carried out by McCall et al.[13] More recent results suffer from the fact that samples with a rather broad polydispersity were used.[14–16] The recent investigation of Cosgrove et al.[17] is limited to a molar mass range up to 35 000 g mol^{-1} where reptation or a well established tube is not yet expected. We have also measured self-diffusion of the mobile polymer poly(ethylene oxide) in the melt with a set of nearly monodisperse samples. In the literature self-diffusion results were reported from Sevreugin et al.[18] and Cheng et al.[19] The first results, measured over a broad molar mass region, are obtained with commercial samples not very well characterized. PEO shows two features which may lead to complications in the interpretation of the measurements: PEO crystallizes at low temperatures from the melt, and the OH groups at the chain ends form hydrogen bonds with the chain oxygens and may complicate the diffusion mechanism especially at low molar masses. Sevreugin et al.[18] have interpreted their measurements of PFG NMR with cluster formation in the melt of PEO, i.e. by assuming that the chains form aggregates with a distinct

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Table I. Molecular Parameters, Maximum Molar Masses M_{max}, and Their Self-Diffusion Coefficient $D(M_{max})$ for PDMS, PEO, and PE

	$10^{20}K_1/m^2$	$K_2/m^2\ s^{-1}$	$M_e/g\ mol^{-1}$	$M_{max}/g\ mol^{-1}$	M_{max}/M_e	$10^{16}D(M_{max})/m^2\ s^{-1}$
PDMS	0.54[a]	7.7×10^{-4} [d]	12000	930 000	78	9.0
PEO	1.01[b]	4.3×10^{-5} [d]	2200	295 000	134	5.0
PE	0.9[a]	1.25×10^{-4} [c]	1750	440 000	250	6.5

[a] Reference 21. [b] Reference 22. [c] Reference 23. [d] This work. K_2 and $D(M_{max})$ are given for T = 200 °C (PE), 60 °C (PDMS), and 100 °C (PEO), respectively.

lifetime which increases with increasing molar mass. Up to now this was not reproduced by other authors.

The aim of our work is precisely to measure the long-range self-diffusion coefficient of PEO and PDMS with pulsed field gradient NMR in a molar mass range as large as possible and to compare the results with theoretical predictions for the dependence of D on M, under special consideration of the slowing down from Rouse diffusion to constraint diffusion in the so-called entangled melt. This includes the comparison of the monomeric friction coefficients and activation energies of diffusion with results of other measurements (viscosity, neutron scattering).

Experimental Section

In principle, PFG NMR is a scattering experiment.[20] The measured quantity, the spin echo attenuation ψ, is identical with the scattering function $S(q, t)$ in quasielastic incoherent neutron and light scattering:

$$\psi = \exp(-q^2Dt) \tag{1}$$

q, the "scattering vector", is equal to $\gamma\delta g$. γ is the gyromagnetic ratio of the proton; δ and g are the width and magnitude of the field gradient pulses, respectively.

ψ is the signal amplitude A of the primary or stimulated echo with applied field gradients divided by that without field gradients A_0. In the case of the stimulated echo experiment used by us A_0 is given by

$$A_0 = A_{00} \exp(-2\tau/T_2 - t/T_1) \tag{2}$$

where τ is the time between the first and second rf $\pi/2$ pulses and t is the diffusion time, i.e. the time between the second and third of these pulses (in our experiments $\tau \ll t$). A_{00} is the signal intensity in the limit of vanishing τ and t, and T_1 and T_2 are the longitudinal and transverse nuclear magnetic relaxation times of the polymer under investigation, respectively. Since the signal intensity A_0 decreases with increasing diffusion time t, it is in particular important to have a polymer with long T_1 if small diffusion coefficients are to be measured.

The long-range self-diffusion can only be determined for chains whose reptation time T_r is shorter than the longest in the experiment accessible diffusion time t. For polymers with long T_1 the diffusion time can be extended to about 1 s. Using the relations $R_F^2 = K_1M$ and $D = K_2M^{-2}$, with

$$T_r = R_F^2/6D \tag{3}$$

and $T_r = t \approx 1$ s, we obtain for the maximum molar mass M_{max} of chains which can be investigated with respect to long-range diffusion

$$M_{max} \approx (6sK_2/K_1)^{1/3} \tag{4}$$

The data for PDMS, PEO, and for comparison PE are given in Table I.

With polyethylene the broadest molar mass range at $M > M_e$ can be investigated. Older data, e.g., from our group[23] exist, and new experiments are in progress. More recent data are of Pearson et al.[24] With PDMS a broad molar mass range at $M < M_e$ can be investigated since it has a rather large M_e. Due to its high molecular mobility and long T_1 it can be measured up to the theoretical limit M_{max} where $t \approx T_r$ is reached. (T_1 has a value of 0.7 s nearly independent of chain length, and T_2 for the highest M has a value of about 8 ms.) The diffusivity of PEO is slower, T_1 is shorter than those of PDMS, and the experimentally accessible molar mass range is limited.

In our PFG NMR experiments (see also, e.g., refs 6 and 25) g was generally kept constant and δ was varied between 0 and 2.1 ms. g values up to 23 T/m were realized. The diffusion time t was chosen in the interval between 13 ms and 3 s. The echo attenuations were measured with special caution to equalize precisely the area of the field gradient pulses. Since we always observe to a good approximation an exponential echo attenuation although the samples have a small polydispersity, we have evaluated the self-diffusion coefficients from this single exponential echo attenuation. The thus determined self-diffusion coefficient was attributed to the so-called diffusion average

$$M_D = (\int w(M)M^{-n}\,dM)^{-1/n} \tag{5}$$

of the molar mass distribution.[26] $w(M)$ is the normalized mass distribution of M. n is the exponent of the relation $D \sim M^{-n}$. For $w(M)$ a log-normal distribution was assumed which is for most of the samples well fulfilled (suppliers data). It is not a priori evident to which average of the molar mass distribution the self-diffusion coefficients must be related. This point will be discussed below. For the high molar mass samples of PDMS the diffusion time t was chosen sufficiently long ($t > T_r$) to avoid the measurement of an apparent self-diffusion coefficient. In a special experiment the apparent diffusion coefficient D_{app} was explicitly determined for the PDMS 716 000.

The investigated samples were purchased from Polymer Standards Service in Mainz, FRG, and used as received. Four PDMS samples were synthesized at the Max-Planck-Institut für Polymerforschung, Mainz. The data are given in Table II. The polymers were sealed under vacuum in NMR sample tubes of 7.5-mm o.d.

Results

In Figure 1 two typical examples of the echo attenuation plots are shown. No dependence of the diffusion coefficient on the diffusion time is observed. Cluster formation in these polymers in the melt must be ruled out. The clusters in PEO melts as observed by Sevreugin et al.[18] may have their origin in chemical impurities of the commercial samples used in these experiments. Within experimental accuracy in the measured range of $\psi = 1$ down to $\psi \approx 0.1$ no deviation from single exponential behavior of ψ for all of our samples is observed (apart from occasionally observed small fast diffusing traces.) This is somewhat surprising since at least in the reptation regime a superposition of the diffusion of the individual chains differing in their N should be observed. Reptation implies individual diffusion of the chains independent of the matrix molar mass. With our experimental accuracy it should be possible to detect the distribution of self-diffusion coefficients in a sample of M_w/M_n as low as 1.03 with $D \sim M^{-2}$. Careful inspection of Figure 1a shows that a description of ψ with the superposition of exponentials is not possible. There seems to be an averaging process not compatible with the strict reptation picture. In the literature such an effect is already described,[27,28] but the exact mechanism is not yet explained.

An open question is to which molar mass average the self-diffusion coefficients are to be related. If all the samples have equal polydispersity the molar mass exponent of the self-diffusion coefficient is independent of the chosen average, but the prefactor depends on the polydispersity.[29] We have preferred the diffusion average M_D, eq 5, since the initial slope of the echo attenuation must be related to M_D[6,26] and this slope is constant over the whole measured echo attenuation plot. When M_D is used, the prefactor (or the absolute value of the self-diffusion coefficients) agrees best with measurements of other

Table II. Molar Masses M and Self-Diffusion Coefficients D for PDMS at 60 °C and PEO at 100 °C

PDMS				PEO			
M_w/g mol^{-1}	M_w/M_n	M_D/g mol^{-1}	$D(M_D)$/m^2 s^{-1}	M_w/g mol^{-1}	M_w/M_n	M_D/g mol^{-1}	$D(M_D)$/m^2 s^{-1}
3 610	1.50	2 407	5.0×10^{-11}	330	1.08	302	2.1×10^{-10}
5 900[a]			1.65×10^{-11}	580	1.06	542	1.3×10^{-10}
15 900[a]	1.09	14 590	7.2×10^{-12}	940	1.05	890	4.85×10^{-11}
18 070	1.05	17 210	5.5×10^{-12}	1470	1.03	1420	3.2×10^{-11}
22 530[a]	1.035	21 400	3.6×10^{-12}	1960	1.03	1890	1.7×10^{-11}
33 000	1.07	29 815	1.25×10^{-12}	3060	1.03	2960	1.1×10^{-11}
44 260	1.03	42 340	7.6×10^{-13}	4240	1.03	4100	5.5×10^{-12}
53 340	1.14	43 820	4.3×10^{-13}	6000	1.03	5730	2.5×10^{-12}
71 000	1.08	63 260	2.2×10^{-13}	7000	1.03	6680	1.6×10^{-12}
89 800	1.05	83 460	1.1×10^{-13}	10900	1.19	8290	1.2×10^{-12}
118 300	1.05	110 000	6.5×10^{-14}	12300	1.04	11560	4.7×10^{-13}
160 200	1.05	149 000	2.8×10^{-14}	21100	1.15	16930	1.25×10^{-13}
344 300	1.08	306 800	8.1×10^{-15}	41500	1.14	33760	4.3×10^{-14}
716 000[a]	1.40	432 000	4.5×10^{-15}				

[a] From MPI für Polymerforschung, Mainz.

methods.[26] When D is related to M_w the self-diffusion coefficients from PFG NMR are considerably higher than those determined by other methods. The other methods mentioned in the Introduction work in larger space and time scales than PFG NMR so that, probably, the tube and, hence, the distribution of self-diffusion coefficients is well developed whereas in the short time scale of PFG NMR the different modes of motion for $t < T_r$ an $t > T_r$ still have some influence and average the self-diffusion process.

In Figures 2 and 3 the measured dependence of D on M_D for PEO and PDMS is shown. We consider this as the exact relation of D on M (within experimental accuracy). The four PDMS samples from the MPI für Polymerforschung and the PSS samples fit very well into one curve. Only the PDMS 53 340 sample seems to deviate to lower D. This sample has the largest $M_w/M_n = 1.14$; however, ψ is exponential with only a slight curvature upward concave near the ordinate. For PDMS, the literature data of McCall et al.[13] and Vasiljev et al.[15] are more or less consistent with our data; the latter, however, show a large scattering probably due to a rather high polydispersity of the samples. The data of refs 14 and 16 which have been obtained at $T = 20.5$ and 26 °C, respectively after a temperature shift to 60 °C are lower than our data. The reasons for this deviation are unknown. There is good agreement of our PEO results with those of refs 18 and 19.

The most widely accepted model for polymer dynamics is the tube concept of Doi and Edwards.[7] We use it as a starting point of the discussion of our results. For our purpose, the main ideas of the Doi–Edwards theory are summarized as follows.

For a chain of N monomeric units and N smaller than the entanglement chain length N_e the monomeric units of the polymer molecules in the melt are topologically constrained only by the chemical bonds between them; the coils move freely over distances larger than the Flory radius R_F with a diffusion coefficient (Rouse diffusion)

$$D = kT/N\zeta_0 \tag{6}$$

ζ_0 is the monomeric friction coefficient and kT has the usual meaning. Increasing the chain length above the critical chain length $N_c \approx 2N_e$, the chain becomes hindered in its lateral mobility. For $N \gg N_c$ it behaves as being confined to a tube: reptation. In this strict reptation picture we obtain for D[7]

$$D = kTN_e/3\zeta_0N^2 \tag{7}$$

At $N = N_e$ the self-diffusion coefficient discontinuously drops by a factor of 3 because the diffusion becomes one-dimensional along the tube. In reality there is, however, no sharp drop; we have a smooth crossover (often called constraint release[30]).

Equations 6 and 7 contain the topological properties of the melt (N and N_e) and the monomeric friction coefficient ζ_0 characterizing the mobility of the monomers. ζ_0 depends, apart from the chemical constitution of the monomer, only on temperature. However, for low molar masses it becomes molar mass dependent due to the increasing contribution of the large fractional free volume of the chain ends to the total fractional free volume f in the system. This may be described by the simple free volume theory[31,32]

$$\zeta_0 \sim \exp(B/f) \tag{8}$$

B is an empirical constant of the order of 1.

If the diffusion process is monitored over space scales smaller than the Flory radius or, equivalently, for times smaller than the reptation time T_r, we measure restricted diffusion of the individual segments along the tube and observe an apparent diffusion coefficient D_{app}

$$D_{app} = (d/6)(2kT/N\zeta_0t)^{1/2} \tag{9}$$

with d denoting the tube diameter. It depends on time with the power law $D_{app} \sim t^{-1/2}$.[7]

In Figures 2 and 3 we can clearly distinguish Rouse diffusion ($D \sim M^{-1}$) from reptation ($D \sim M^{-2}$). Rouse diffusion for $M < M_c$ is well confirmed.[24,33] For PDMS free volume corrections of our experimental data are not necessary because of its very low glass transition temperature and the rather high value of M_c (large Rouse region). For PEO we observe a slope of −1.3 in the Rouse region. Because of difficulties due to increasing specific interactions of the OH-terminated chain ends with the chain oxygens at decreasing chain length, we did not correct the monomeric friction coefficients for infinite chain length.

With increasing M, in a small molar mass range, we observe a sharp slowing down of the self-diffusion coefficient, the exponent of the $D(M)$ power law being about −3. Increasing the chain length by a factor of 3, the self-diffusion coefficient is diminished by 1 order of magnitude. In many investigations this crossover was not observed (e.g. see refs 15, 17, 18, and 24), whereas in others it was reported (e.g. see refs 23 and 34). Its detection also depends somewhat on the choice of the molar mass average to which the measured diffusion coefficients are related. If the values measured by Pearson et al.[24] are related to the diffusion average of the samples (eq 5), an indication of this crossover is seen. At very large molar masses we

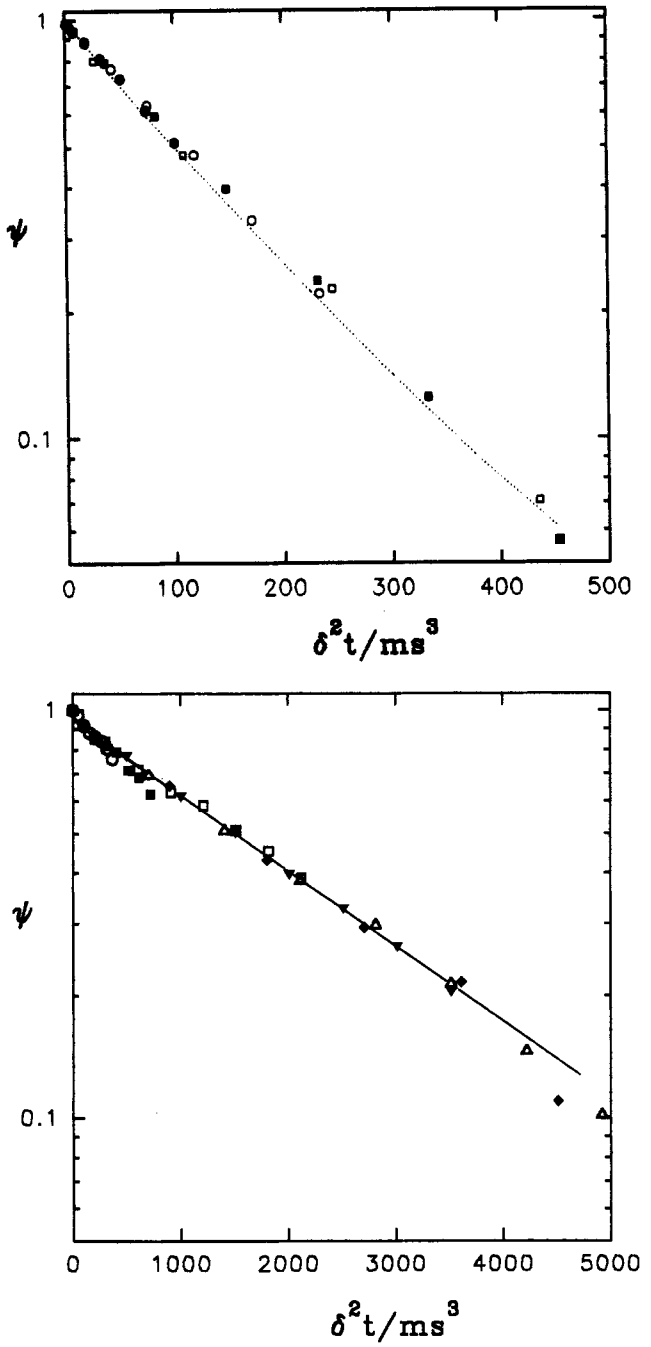

Figure 1. Echo attenuation plot (a, top) for the sample PDMS 44 260 at $T = 60$ °C and (b, bottom) for the sample PEO 21 100 at $T = 100$ °C. The diffusion times t are 23 ms (●), 53 ms (○), 103 ms (■), 303 ms (□), 503 ms (▼), 703 ms (△), and 903 ms (♦). The dashed curve is a superposition of self-diffusion coefficients of a sample with $M_w/M_n = 1.03$ and $D \sim M^{-2}$ (see text), the straight line is a guide for the eye.

observe the well-known exponent −2 of the power law of D on M, indicating diffusion within a tube.

A quantitative discussion of the dependencies shown in Figures 2 and 3 leads to some deviations from the Doi–Edwards theory. In the Doi–Edwards theory the ratio between Rouse diffusion and the extrapolated reptation part of $D(M)$ at $M = M_e$ (eqs 6 and 7) is equal to $^1/_3$. For both polymers, PDMS and PEO, we observe a somewhat higher value between 0.5 and 0.6. Two explanations may be discussed: (i) in the observed molar mass range a mechanism additional to reptation is active, or (ii) in diffusion experiments we have to use M_e values slightly larger than the M_e values from viscoelasticity.

The monomeric friction coefficient determined with eqs 6 and 7 from the Doi–Edwards theory can be quantitatively

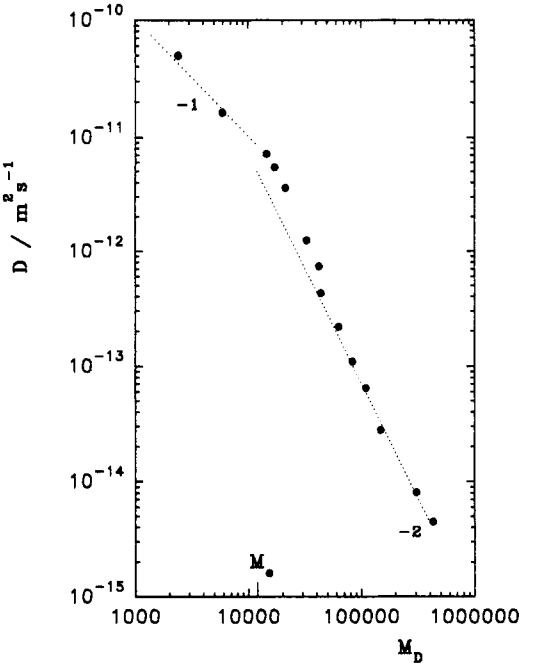

Figure 2. log–log plot of D vs M for PDMS at $T = 60$ °C. $D \sim M^{-2}$ is drawn through the high M values and extrapolated down to $M_e = M_c/2$.

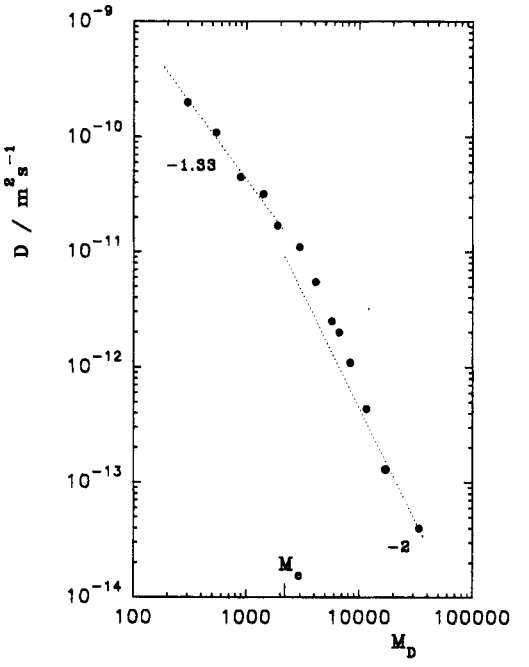

Figure 3. As for Figure 2 for PEO at $T = 100$ °C.

compared with results from viscosity and neutron scattering. For PDMS at the temperature $T = 60$ °C we obtain from the Rouse region $\zeta_0 = 3.1 \times 10^{-12}$ kg/s and from the reptation region $\zeta_0 = 1.7 \times 10^{-12}$ kg/s using a value of 12 000 g mol^{-1} for M_e. From viscosity, $\zeta_0 = 4.5 \times 10^{-12}$ kg/s is determined.[35,36] Taking into account the stronger weighing of the longer chains of the molar mass distribution in the viscosity experiments, the agreement is satisfactory. The diffusion of PDMS in a space scale comparable with the tube diameter was measured by Richter et al.[37] using QENS. The experiment provides the quantity $W_0 = 3kT\sigma^2/\zeta_0$, with σ denoting the statistical segment length. The authors obtained a value of 0.9×10^{13} Å^4/s (recalculated from 100 to 60 °C with $E_A = 15$ kJ/mol). From our experiments in the Rouse region, with $\sigma = 6.1$ Å we obtain for this quantity 1.7×10^{13} Å^4/s. Taking into account the difference of about 6 orders of magnitude in

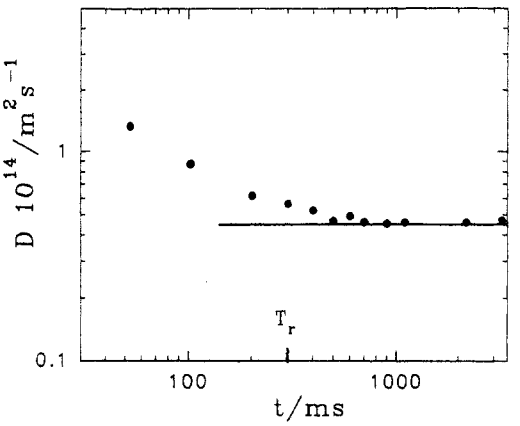

Figure 4. log–log plot of D_{app} vs diffusion time t for the sample PDMS 716 000 at T = 60 °C. The reptation time $T_r(M_w)$ is indicated. For long times a constant diffusion coefficient is observed.

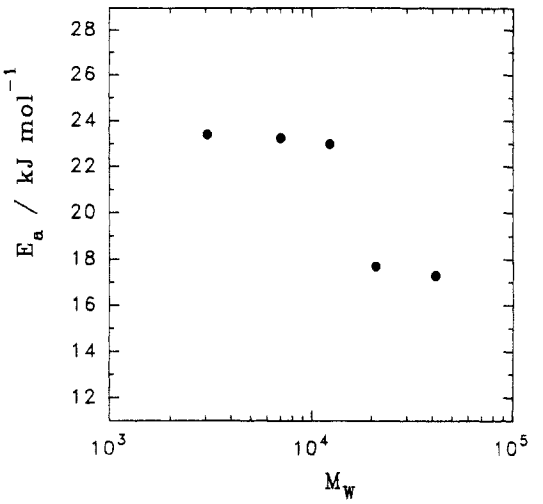

Figure 5. Apparent activation energy E_A for PEO dependent on molar mass M.

the time scales between both experiments, the agreement is rather good. The latter agreement may be taken as a proof of the Doi–Edwards theory; however, the difference between ζ_0 determined from the Rouse region and the reptation region again indicates remaining uncertainties in the diffusion mechanism at least in the investigated molar mass range.

Diffusion for $t < T_r$

A sensitive proof of the mechanism of motion of the polymer chain is the dependence of the mean square displacement of the chain segments in a space scale smaller than the Flory radius on time and molar mass. In the power law $\langle r^2 \rangle \sim t^{-a}M^{-b}$ the various theoretical models predict different values a and b. In the "classical" Doi–Edwards tube picture $a = b = 1/2$. More recent models that do not assume a priori a tube predict time exponents larger than $1/2$.[10,11,38] It is impossible to cover this space scale by the methods mentioned in the Introduction. It is only the field gradient NMR with very large field gradients by which this space scale becomes accessible in the experiments.[14,39,40] Experiments in this region are predominantly done up to now by field cycling NMR spectroscopy.[41]

With PDMS the maximum molar mass where the reptation time is not yet larger than the time window of our PFG NMR experiment could be reached with the sample PDMS 716 000. Using eq 3 and the data given in Table I, T_r can be estimated to be about 300 ms. At this time the crossover from restricted diffusion within the tube to free diffusion of the whole chain is clearly seen in Figure 4. For $t < T_r$ an apparent diffusion coefficient D_{app} is measured. The crossover is in accordance with the above estimated time. For a more precise determination of the time exponent of D_{app} and of the prefactor (see eq 9) more experiments, in particular with narrower distributed samples, are to be done. Such investigations are in progress.[12]

Activation Energies of Self-Diffusion

The temperature of the measurements is far above the glass transition temperatures for the investigated polymers, so that the temperature dependence of the self-diffusion process may be approximated by an Arrhenius equation

$$D = D_0 \exp(-E_A/kT) \qquad (10)$$

with E_A denoting an (apparent) activation energy. We have determined E_A for the self-diffusion of PDMS for molar masses from 15 900 to 89 800 g mol^{-1} in the temperature region between 40 and 100 °C and for the self-diffusion of PEO for molar masses from 7000 to 41 500 g mol^{-1} in the temperature region between 80 and 140 °C. For PDMS we observe Arrhenius-like behavior; for PEO there are small indications of a WLF-like behavior (very slightly upward convex curves), but E_A was determined assuming Arrhenius behavior. For PDMS we obtain E_A = 16 ± 1 kJ/mol. From viscosity measurements an activation energy of 15 kJ/mol is reported (cf., e.g., ref 32). From our experiment it cannot be decided whether this difference is physically relevant or not. Such a difference in the activation energy between diffusion and viscosity is predicted by the coupling model of Ngai et al.[38]

For PEO the activation energies dependent on molar mass are shown in Figure 5. There is a drop of E_A between the molar masses 10 000 and 20 000 g mol.$^{-1}$. E_A decreases from 23 to 18 kJ/mol. This drop was already observed by Cheng et al.,[19] the leveling off for M > 20 000 g mol^{-1}, however, was not reached in their experiments. The reason of this drop in E_A is the unusual molar mass dependence of the glass transition temperature T_g. It shows a maximum just at M = 10 000 g mol^{-1} with a T_g = −18 °C and decreases thereafter down to −53 °C.[42] For a comparison with the activation energy of viscosity it is recommended to measure the viscosity of the identical samples of the diffusion measurments. But this is beyond the scope of this investigation.

Summary and Conclusions

To confirm the theoretical expressions for the dependence of the center of mass or long-range self-diffusion coefficient of a polymer chain on the chain length, it is highly desirable to measure over molar mass ranges as large as possible. Since the time scale of the experiments must be limited to diffusion times larger than the reptation time there exists a maximum molar mass M_{max} up to which the molar mass region can be extended. The polymer must have long nuclear magnetic relaxation times (T_1 of the order of 1 s) and a high diffusivity if $D(M_{max})$ should be within the range of measurement of PFG NMR. PDMS is a polymer which fulfills these conditions whenever it has a rather large M_c, and M_{max}/M_e reaches the value of only 78. Polyethylene, e.g., allows one to measure still farther into the entangled region.

Three different diffusion regimes could be clearly distinguished, Rouse diffusion, reptation, and a crossover

between them characterized by a strong slowing down of the self-diffusion coefficient. The molar mass exponents predicted by the Doi–Edwards theory, $D \sim M^{-1}$ for Rouse diffusion and $D \sim M^{-2}$ for reptation, could be confirmed. Quantitatively, a difference in the Doi–Edwards theory remains between Rouse diffusion and reptation; the monomeric friction coefficients determined from the reptation part are about 30% smaller than those determined from the Rouse part. Motional mechanisms additional to strict reptation seem to work in the investigated molar mass region.

The monomeric friction coefficient for PDMS obtained from the diffusion data is roughly in agreement with data from different experiments (viscosity and quasielastic neutron scattering). The activation energy of diffusion is also found to be equal to that of viscosity within the limits of accuracy. PEO shows an interesting drop of the activation energy of molar masses of about 10 000 of mol^{-1} which must be referred to the anomaly of the glass transition temperature at these molar masses.

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