

Field-Cycling Nuclear Magnetic Resonance Relaxometry and Field-Gradient Nuclear Magnetic Resonance Diffusometry of Polymers Confined in Porous Glasses: Evidence for a Restricted-Geometry Effect

Siegfried Stapf and Rainer Kimmich*

Universität Ulm, Sektion Kernresonanzspektroskopie, 89069 Ulm, Germany

Received February 21, 1995; Revised Manuscript Received November 14, 1995[®]

ABSTRACT: The chain dynamics of oligomer and polymer melts confined in porous glasses (pore diameters 4 and 30 nm) was studied with the aid of proton field-cycling NMR relaxometry (total frequency range: $(2 \times 10^3) - (3 \times 10^8)$ Hz) and field-gradient NMR diffusometry. The frequency dependence of the spin–lattice relaxation time, T_1 , is discussed in terms of restrictions due to adsorption on the pore surfaces and to the geometry of the pore space. The behavior of polymers larger than the pores (strong adsorption as well as geometry effects) was compared with that of oligomers (strong adsorption but vanishing geometry effects). A tentative ansatz for the separation of the geometry dependent relaxation rate is proposed. The resulting frequency dependence of polymers exceeding the pore size is much steeper than in bulk melts and approaches the proportionality $T_1 \propto \nu^{0.75}$ above 5×10^5 Hz, in accordance with the reptation model. The molecular weight dependence of T_1 suggests a critical molecular weight which may be defined by the coincidence of the coil and pore diameters. Field-gradient NMR diffusometry indicated a dramatic slowing down of self-diffusion when the coil dimension approaches that of the pores.

Introduction

When de Gennes¹ originally suggested the reptation model for polymer segment displacements, he assumed a three-dimensional network of fixed obstacles in which the chains are trapped. Random coils are ideally connected with a Gaussian end-to-end distance distribution irrespective of the length of the considered chain part. In this case the frequency dependence of the spin–lattice relaxation time, T_1 , was predicted to follow a power law in the low-frequency limit according to

$$T_1 \propto \nu^{0.75} \quad (1)$$

In previous experimental studies of melts of entangled polymers,^{2–5} power laws of the T_1 dispersion were found indeed but the exponents were much less (0.25 or 0.50) than expected according to the original reptation model. Therefore the notion of fixed obstacles confining the polymer chains appears to be inappropriate for polymer melts in bulk. On the other hand, based on a memory-function formalism,^{5,6} a perfect description of the experimental T_1 dispersion behavior was established in accordance to Schweizer's renormalized Rouse model.⁷

Before the background of the existing T_1 dispersion studies of polymer melts in bulk, it is tempting to seek experimental conditions more closely representing the assumptions of the reptation concept. The fixed-obstacle situation appears to be given for polymers confined in the narrow pore network of porous glass.

The nature of chain dynamics also reveals itself in the self-diffusion behavior. In addition to field-cycling NMR relaxometry, we have therefore employed field-gradient NMR diffusometry for studies of the characteristics of polymer dynamics in pore networks.

Experimental Section

Proton field-cycling data were recorded with a homemade instrument. Spin–lattice relaxation times at higher frequencies were recorded with conventional NMR spectrometers. The total frequency range was $(2 \times 10^3) - (3 \times 10^8)$ Hz. All spin–

lattice relaxation curves were found to decay monoexponentially within the experimental error over at least 1 decade. Field-gradient NMR diffusometry measurements were carried out using the pulsed-gradient stimulated echo (PGSE) version⁹ as well as the supercon fringe field (SFF) method¹⁰ leading to identical results. The maximum field gradient was 32 T/m.

Vycor porous glass (VPG; no. 7930, 96% SiO₂) was purchased from Corning Inc., Corning, NY 14831. The average pore diameter was specified by the manufacturer as 4 nm (96% of the pore volume is within 4 ± 0.6 nm), the porosity as 28%, and the specific surface as 250 m²/g. Note, however, that literature values of the specific surface of this material are considerably smaller.¹¹ Vycor tends to adsorb organic vapors from the air. In order to remove such impurities and following the recommendations of the manufacturer, the samples were boiled in 30% H₂O₂ for 20 min before evacuating the material several days and filling it with the polymer liquids using the bulk-to-bulk method. Depending on the molecular weight, this procedure took up to 2 months at 100 °C.

Bioran B30 porous glass was purchased from Schott Glaswerke, Mainz, Germany. The mean pore diameter was specified by the manufacturer as 30 nm with a narrow pore size distribution (90% within $\pm 5\%$). The porosity was specified in the range 0.67–0.69.

Alkane, poly(dimethylsiloxane) (PDMS), and poly(ethylene glycol) (PEG) samples were purchased from Fluka, Polysciences, and Sigma, respectively.

Results

Figure 1 shows the T_1 dispersions of alkanes in porous glasses in comparison to bulk data. Molecular dynamics computer simulations^{13,14} predict a flat, relatively ordered arrangement of alkane chains adsorbed on surfaces. The NMR relaxation data certainly suggest an influence of the surfaces on the alkane reorientation dynamics. It is, however, much less pronounced than with polar adsorbates.^{15,8}

Much stronger frequency dependences were found with PDMS and PEG confined in porous glasses. Figure 2 shows typical data sets for oligo- and poly(dimethylsiloxane)s in bulk melts, confined in Bioran B30, and confined in Vycor, respectively. The highest molecular weight investigated is 115 000.

The shortest species, the dimer (or hexamethyldisiloxane; $M_w = 162$) and the oligomer with $M_w = 340$,

[®] Abstract published in *Advance ACS Abstracts*, February 1, 1996.

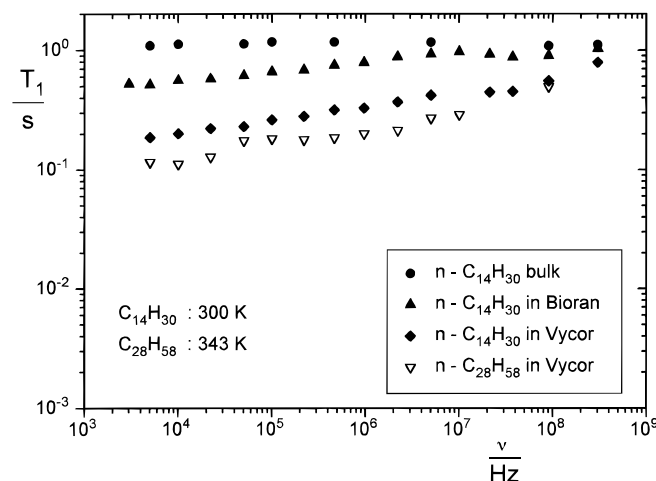


Figure 1. ^1H T_1 dispersion of liquid alkanes confined in porous glasses. Data of $n\text{-C}_{14}\text{H}_{30}$ measured in bulk are given for comparison.

show extremely weak frequency dependences in bulk (Figure 2a) which gradually increase when filled into Bioran B30 (Figure 2b) and Vycor (Figure 2c). The reason for this finding must be sought in the interaction with the pore surface ("adsorption effect"). In fact, the slope is intermediate in the range spanned by "polar" and "nonpolar" solvents in porous glass.^{15,8} The stronger dispersion in Vycor results from the larger surface-to-volume ratio compared with Bioran B30. Similar adsorption effects have also been observed with other NMR techniques.^{16–18}

The T_1 dispersion of PDMS in bulk³ (Figure 2a) depends on the molecular weight almost in the whole range referred to. Filling the oligomers/polymers into the pore space of Bioran B30 reduces the absolute T_1 values as well as the dependence on the molecular weight (see Figure 2b). The fact that the data of PDMS 17 000 in bulk and in Bioran B30 almost coincide indicates that there is no perceptible influence of the pore space geometry on the chain dynamics of this polymer.

The situation changes for PDMS in Vycor (Figure 2c). Even the relaxation times of the longest chains having a molecular weight of 115 000 are shorter, and the T_1 dispersion slope is steeper than in bulk. A strong molecular weight dependence can only be stated below a pore critical value of $M_c^p \approx 3000$. The relaxation times of chains longer than the critical value do not depend on the molecular weight in our frequency range.²

The "pore critical molecular weight" is well below the bulk critical value of $M_c^b \approx 20\,000$. Interestingly, at the pore critical molecular weight, the radius of gyration as calculated on the basis of the known relationship for the bulk approaches the mean pore radius of Vycor (see Table 1). The additional constraint becoming effective above M_c^p is attributed to a (molecular weight independent) "pore space geometry effect", that is, the chain modes are altered by the confinement in the rigid pore network. Note that the geometry effect could not be observed with Bioran B30 because in this case the mean pore radius exceeds the radius of gyration, even for the longest polymer investigated.

The geometry effect was tentatively separated from the adsorption effect by assuming that adsorption primarily affects local chain modes, i.e., chain parts corresponding to Kuhn segments. The chain lengths closest to a Kuhn segment length within our choice of

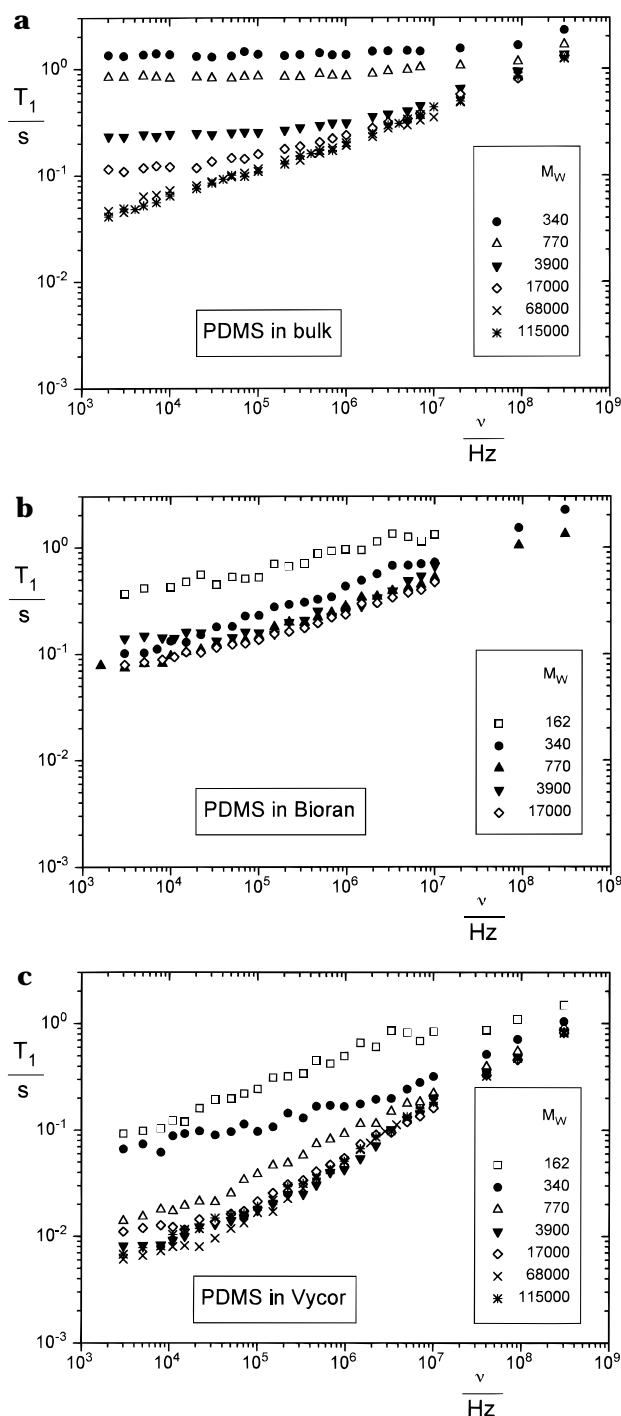


Figure 2. ^1H T_1 dispersion of PDMS melts at 293 K. The curve parameter is the weight-average molecular weight: (a) PDMS in bulk,³ (b) PDMS confined in Bioran B30, and (c) PDMS confined in Vycor.

Table 1. Estimated Dimensions of the System PDMS/Vycor^{20,21}

	M_w		
	340	3900	115 000
chain diameter (nm)	0.7	0.7	0.7
chain length (nm)	1.3	15	450
radius of gyration in bulk (nm)	0.5	1.7	9
mean pore radius (nm)	2	2	2

samples are those of PDMS 340 and 770. The spin-lattice relaxation rates of these oligomers were assumed to essentially represent the adsorption effect on a polymer chain including the corresponding modification of the local modes within a Kuhn segment. The dynam-

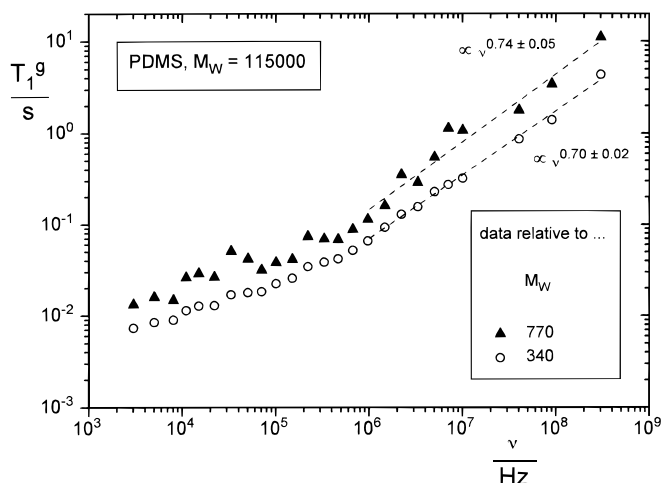


Figure 3. Tentative evaluation of the geometry effect of a typical long-chain data set according to eq 2. The “geometric” spin-lattice relaxation dispersion of PDMS 115 000, $T_1^g = T_1^g(\nu)$, was evaluated with the available reference samples with molecular weights close to that corresponding to a Kuhn segment, that is, $M_w = 340$ and 770 . The dashed lines indicate the power laws concluded from these evaluations.

ics of molecules with much lower molecular weights such as the dimer ($M_w = 162$) is also strongly affected by adsorption but does not represent the local modes in full. Therefore, they cannot be taken as a reference with respect to chain dynamics.

Chains having bulk radii of gyration larger than the pore radius should experience an additional spin-lattice relaxation rate due to the geometry effect. The net spin-lattice relaxation rates on this basis were estimated from the data of pairs of dimethylsiloxane polymer/oligomer samples with molecular weights close to that of a Kuhn segment, M_K , according to the tentative ansatz

$$\frac{1}{T_1^g} = \frac{1}{T_1(M_w \gg M_K)} - \frac{1}{T_1(M_w \approx M_K)} \quad (2)$$

Figure 3 shows the “geometry-induced” spin-lattice relaxation dispersions resulting from this analysis for PDMS 115 000. Similar dispersions were obtained for the molecular weights 3900, 17 000, and 68 000 using the same reference molecular weights.

The dispersion curves, $T_1^g = T_1^g(\nu)$, comprise slopes and absolute values in a relatively narrow range depending on the reference molecular weight. The slopes above about 10^5 Hz approach that given in eq 1. These evaluations are at variance to the bulk melt behavior where a power law,

$$T_1 \propto \nu^{0.25} \quad (3)$$

was found almost up to the highest frequencies of our range for the same polymer species at the same temperature.^{3,4}

PEG is of a more polar nature so that the adsorption effect is stronger than with PDMS (compare refs 8 and 15). The consequence is that in this case practically no geometry effect can be separated, although the longest polymers in our study have bulk radii exceeding the pore radius. Figure 4 shows T_1 dispersion data for molecular weights up to 10 000 in comparison to values measured in bulk melts.²²

Pronounced confinement effects have also been observed with self-diffusion experiments carried out with PDMS and PEG in Vycor. Figure 5 shows typical echo

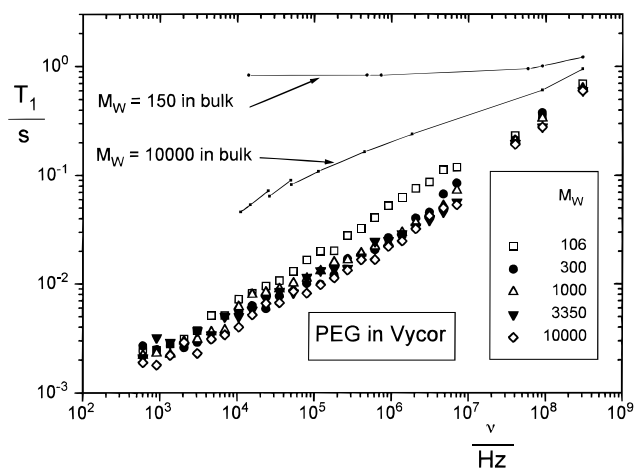


Figure 4. ^1H T_1 dispersion of PEG melts in Vycor at 348 K. The curve parameter is the weight-average molecular weight. The lines represent experimental data measured in bulk for comparison (from ref 22 supplemented by own high-frequency data points).

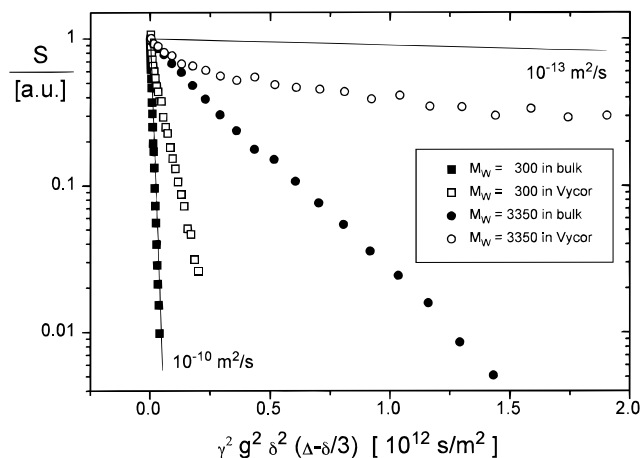


Figure 5. Field-gradient diffusometry echo attenuation curves of PEG melts measured in bulk and in Vycor at 353 K. The curve parameter is the weight-average molecular weight. The confinement leads to nonexponential decays. The slope of the solid lines indicate the range of diffusion coefficients covered in this experiment assuming regular diffusion. The quantities determining the abscissa scale are the gyromagnetic ratio (γ), the magnetic field gradient (g), and gradient pulse width (δ), and the gradient pulse separation from middle to middle (Δ).

attenuation curves measured with the aid of field-gradient diffusometry techniques. The diffusivities determining the slopes were reduced by factors of 6 (low molecular weights) up to 100 (high molecular weights above the pore critical value) relative to the bulk. Moreover pronounced deviations from monoexponential decays were found for confined oligomers or polymers. An evaluation adequate to the reptation model requires a special formalism.²³ Corresponding work is in progress.

Conclusions

The confinement of polymers in porous glass has a pronounced influence on chain dynamics, in particular if the bulk radius of gyration exceeds the pore radius. Otherwise the polymer behaves as an adsorbate interacting with the inner surfaces of the porous glass. The strength of this interaction depends on the polarity of the compounds.

The T_1 dispersion of polymers in narrow pore networks is of particular interest with respect to certain

features of chain dynamics predicted by polymer theories currently under discussion. Polymer theories often referred to are the so-called "tube/reptation" model^{1,19} and memory-function formalisms.⁷

In our previous work^{5,4} we have shown that the T_1 dispersion of polymer melts in bulk is compatible with the renormalized Rouse theory but contradicts the Doi/Edwards tube concept in the time scale of these experiments. Following de Gennes' reptation theory,¹ a proportionality, $T_1 \propto \nu^{0.75}$, is expected in the latter case. By contrast a $\nu^{0.25}$ law was observed in accordance with the renormalized Rouse theory.

The data for polymers in porous media suggest a proportionality of the geometric contribution $T_1^g \propto \nu^\alpha$ in an extended frequency interval where $\alpha \approx 0.70$ – 0.74 , that is, a tendency toward the behavior expected for the reptation model can be stated under these circumstances.

The pore diameter of Vycor exceeds the polymer chain diameter by far (see Table 1). Therefore we believe that concepts of global chain dynamics are still applicable. However, further tightening of the chain confinement leads to effects which cannot be discussed in terms of chain modes.^{24,25} The polymers are then permanently interacting with the pore walls. The intermittent segment desorption and free-dynamics intervals assumed in Vycor or Bioran B30 are then excluded.

Acknowledgment. We thank Professors A. Maklakov and V. Skirda for helpful discussions and A. Beier for assistance in the sample preparation. This work was supported by the Deutsche Forschungsgemeinschaft and the Volkswagen-Stiftung.

References and Notes

- (1) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.
- (2) Kimmich, R.; Bachus, R. *Colloid Polym. Sci.* **1982**, *260*, 911.
- (3) Weber, H. W.; Kimmich, R. *Macromolecules* **1993**, *26*, 2597.
- (4) Kimmich, R.; Fatkullin, N.; Weber, H. W.; Stapf, S. *J. Non-Cryst. Solids* **1994**, *172–174*, 689.
- (5) Fatkullin, N.; Kimmich, R. *J. Chem. Phys.* **1994**, *101*, 822.
- (6) Fatkullin, N.; Kimmich, R.; Weber, H. W. *Phys. Rev. E* **1993**, *47*, 4600.
- (7) Schweizer, K. S. *J. Chem. Phys.* **1989**, *91*, 5802.
- (8) Stapf, S.; Kimmich, R.; Seitter, R.-O. *Phys. Rev. Lett.* **1995**, *75*, 2855.
- (9) Tanner, J. E. *J. Chem. Phys.* **1970**, *52*, 2523.
- (10) Kimmich, R.; Fischer, E. *J. Magn. Reson. A* **1994**, *106*, 229.
- (11) Levitz, P.; Ehret, G.; Sinha, S. K.; Drake, J. M. *J. Chem. Phys.* **1992**, *95*, 6151.
- (12) Stapf, S.; Kimmich, R.; Niess, J. *J. Appl. Phys.* **1994**, *75*, 529.
- (13) Xia, T. K.; Ouyang, J.; Ribarsky, M. W.; Landman, U. *J. Chem. Phys.* **1992**, *69*, 1967.
- (14) Hentschke, R.; Winkler, R. G. *J. Chem. Phys.* **1993**, *99*, 5528.
- (15) Kimmich, R.; Stapf, S.; Seitter, R.-O.; Callaghan, P.; Khozina, E. *Mater. Res. Soc. Symp. Proc.* **1995**, *366*, 189.
- (16) Litvinov, V. M.; Spiess, H. W. *Makromol. Chem.* **1991**, *192*, 3005.
- (17) Litvinov, V. M.; Spiess, H. W. *Makromol. Chem.* **1992**, *193*, 1181.
- (18) Rethwisch, D. G.; Van Alsten, J.; Dybowski, C. R. *Macromol. Symp.* **1994**, *86*, 171.
- (19) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.
- (20) Elias, H.-G. *Makromoleküle*; Hüthig & Wepf: Basel, 1990.
- (21) Horn, R. G.; Israelachvili, J. N. *Macromolecules* **1988**, *21*, 2836.
- (22) Preissing, G.; Noack, F. *Prog. Colloid Polym. Sci.* **1975**, *57*, 216.
- (23) Fatkullin, N.; Kimmich, R. *Phys. Rev. E* **1995**, *52*, 3273.
- (24) Schilling, F. C.; Amundson, K. R.; Sozzani, P. *Macromolecules* **1994**, *27*, 6498.
- (25) Sozzani, P.; Bovey, F. A.; Schilling, F. C. *Macromolecules* **1991**, *24*, 6764.

MA9502112