Notes

Chain Length and Temperature Dependence of the Self-Diffusion of Polyisoprene and Polybutadiene in the Melt

Gerald Fleischer* and Matthias Appel

Fakultät für Physik und Geowissenschaften, Institut für Experimentelle Physik I, Abteilung Polymerphysik, Universität Leipzig, Linnestrassse 5, D-04103 Leipzig, Germany

Received August 22, 1994
Revised Manuscript Received April 25, 1995

Introduction

The self-diffusion coefficient of polymer molecules has often been investigated because it is a fundamental quantity in polymer dynamics.[1–3] However, the measurement of low self-diffusion coefficients by pulsed field gradient NMR (PFG-NMR) is not easy. Therefore, the slowing down of self-diffusion for chain lengths beyond M_e, the entanglement chain length, could often not be reliably detected in earlier work. Recently, two papers were published where, in a very broad molar mass range, the self-diffusion coefficients of mobile chains, hydrogenated polybutadienes, poly(dimethylsiloxane)s and poly(ethylene oxide)s were investigated with PFG-NMR[2,3] and in which the slowing down of self-diffusion in the molar mass region above M_e was clearly observed. In this paper we present additional results of self-diffusion measurements on (mainly) polyisoprene and polybutadiene with PFG-NMR. In the literature there are only limited data on the self-diffusion of these polymers.[4,5]

Experimental Section

The *cis*-1,4-polyisoprene samples were purchased from Polymer Standards Service, Mainz, Germany. They were synthesized by standard anionic polymerization with *sec*-butyllithium as initiator. The 1,4 content was about 78%. The polybutadienes were purchased from Polymer Labs. Inc., Shropshire, GB. The PFG-NMR self-diffusion measurements were carried out as described in refs 3 and 6.

Results and Discussion

In Figure 1 and Tables 1 and 2 the self-diffusion coefficients of both polymers, polyisoprene and polybutadiene, are shown as a function of molar mass at the temperature of 100 °C. For molar masses much larger than the entanglement molar mass M_e, the dependence $D \sim M^{-2}$ is well fulfilled. This dependence has often been verified in experimental investigation (see, e.g., ref 1) and is generally taken as a proof for reptation. At the low molar mass end of the curves we expect $D \sim M^{-1}$ if free volume effects are absent. The dependence is predicted from the Rouse model. Here, we cannot precisely determine the relation between D and M because of a lack of samples below M_e. However, Rouse dynamics at $M < M_e$ is well established by many experimental investigations. For polyisoprene self-diffusion, von Meerwall et al.[5] have reported data in the molar mass range from 411 up to 22 000 Da. After a free volume correction with the Vrentas–Duda theory,[7] they very precisely found $D \sim M^{-1}$ up to $M \approx 10\,000$ Da. However, their data are not completely in agreement with our data (the reasons are unknown). The free volume theory need not always be applicable, we come back to this point below.

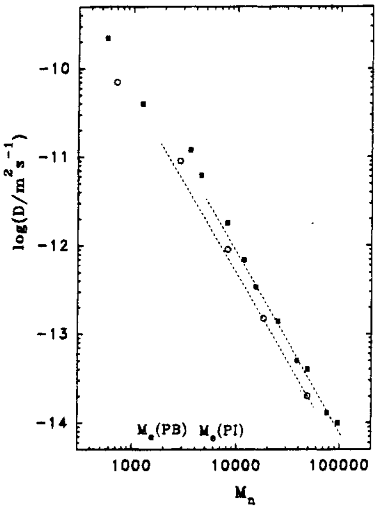

Figure 1. log–log plot of the self-diffusion coefficients of polyisoprene (■) and polybutadiene (○) at $T = 100$ °C as a function of the molar mass. The dashed lines are drawn with slope −2 through the high molar mass part of *D(M)* and extrapolated up to the entanglement chain length M_e.

Table 1. Self-Diffusion Coefficients of Polyisoprene at $T = 100$ °C

M_n	M_w/M_n	D/(m^2 s^{-1})
560	1.16	2.2×10^{-10}
1230	1.11	4.0×10^{-11}
3540	1.08	1.2×10^{-11}
4500	1.04	6.2×10^{-12}
8160	1.03	1.8×10^{-12}
11800	1.03	6.9×10^{-13}
15300	1.02	3.4×10^{-13}
25300	1.02	1.4×10^{-13}
39000	1.03	5.0×10^{-14}
50300	1.04	4.0×10^{-14}
75400	1.01	1.3×10^{-14}
98200	1.02	1.0×10^{-14}

Table 2. Self-Diffusion Coefficients of Polybutadiene at $T = 100$ °C

M_n	M_w/M_n	D/(m^2 s^{-1})
690	1.09	7.0×10^{-11}
2820	1.04	9.0×10^{-12}
8210	1.03	9.0×10^{-13}
18260	1.03	1.5×10^{-13}
49900	1.02	2.0×10^{-14}

The slowing down of the self-diffusion process above M_e in the constraint release region between Rouse and reptation is clearly observed. This confirms the earlier measurements of Pearson et al.[2] and Appel and Fleischer.[3] As already observed in our preceding paper,[3] this slowing down is weaker than predicted by the strict reptation picture according Doi and Edwards[8] in connection with the Rouse model.

0024-9297/95/2228-7281$09.00/0

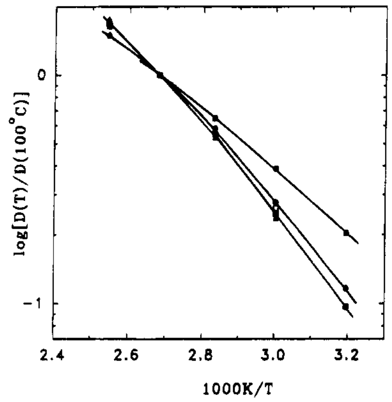

Figure 2. Arrhenius plot of the self-diffusion coefficients of polyisoprenes with M_n = 560 (■), 1230 (●), 3540 (□), 4500 (○), 8160 (▼), 11 800 (▲), 15 300 (▽), and 25 300 Da (△). The self-diffusion coefficients are divided by the value at T = 100 °C.

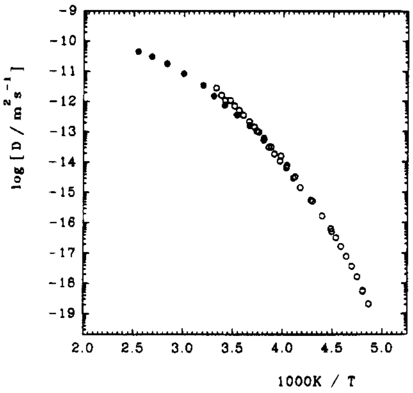

Figure 3. Arrhenius plot of the self-diffusion coefficient of polyisoprene 1230: (●) NMR measurements (for T < 30 °C the self-diffusion coefficients were measured in the stray field of a cryomagnet; cf. ref 6); (○) Calculated with eq 1 from dielectric data (see text).

For k_D in the relation $D = k_D M^{-2}$ we obtain 8.5 × 10^{-5} $m^2\ s^{-1}\ Da^2$ for polyisoprene and 5.0 10^{-5} $m^2\ s^{-1}\ Da^2$ for polybutadiene at 100 °C in our experiments. For polyisoprene Landry[4] reported 1.25 × 10^{-6} $m^2\ s^{-1}\ Da^2$ at 25 °C. If we extrapolate our data to this temperature (see below), we obtain 3.0 × 10^{-6} $m^2\ s^{-1}\ Da^2$. The polybutadiene self-diffusion coefficients are similar to the polyisoprene data. If the self-diffusion coefficients of both polymers are plotted against the number of chain carbons, the data coincide almost perfectly.

When discussing the molar mass dependence of dynamic quantities of polymer chains, the increasing effect of the chain end free volume to the total free volume with decreasing molar mass must be taken into account. The monomeric friction coefficient should be determined by the free volume in the system, but the evaluation of the free volume is still a matter of debate.[8] We have omitted a free volume correction of our data. Boese and Kremer[10] determined the WLF constants C_1 and C_2 and the VFT parameters B and T_∞ for polyisoprenes from the temperature dependence of the segmental and normal mode dielectric spectra. These parameters show a decrease of the monomeric friction coefficient for molar masses smaller than about 1000 Da, at best. We assume that at our measuring temperature of 100 °C free volume corrections must be taken into account only for molar masses smaller than about 1000 Da. This is, however, in contrast to the free volume correction of the data of von Meerwall et al.[3] which show a considerable free volume correction of the monomeric friction coefficient up to $M \approx 10\,000$ Da (at 100 °C). Recent dielectric investigations of the normal mode and segmental mode of polyisoprenes have shown a different temperature dependence of these two modes[10-12] in contradiction to the Rouse model in which both modes are controlled by the same monomeric friction coefficient. Certainly, further investigations on this topic are necessary.

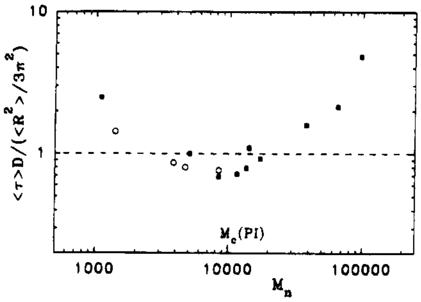

Figure 4. $\langle\tau\rangle D/(\langle R^2\rangle/3\pi^2)$ vs the molar mass for polyisoprenes at T = 50 °C: (■) $\langle\tau\rangle$-values from ref 10; (○) $\langle\tau\rangle$-values from ref 12. $\langle R^2\rangle$ was calculated according to ref 14.

The molar mass dependent free volume is reflected in the apparent activation energies E_A of self-diffusion. In Figure 2 we have shown the temperature dependence of the self-diffusion coefficients of polyisoprenes for different molar masses. For molar masses larger than about 1000 Da, E_A becomes independent of M. At 100 °C E_A is determined to be 33 kJ/mol, in approximate accordance with the von Meerwall data[5] and the temperature dependence of the normal mode dielectric relaxation times.[10,12] The latter have a slightly larger temperature dependence than our self-diffusion coefficients. For comparison, in Figure 3 the self-diffusion coefficients calculated with

$$D = \langle R^2\rangle/3\pi^2 <\tau> \qquad (1)$$

from the dielectric normal mode relaxation time $\langle\tau\rangle$ and the mean square end-to-end distance of the chain $\langle R^2\rangle$ for PI 1200 are also shown. $\langle R^2\rangle$ was calculated according to ref 14. For polybutadiene, where fewer data exist, the apparent activation energy was determined to be 25 kJ/mol between 60 and 100 °C. Polybutadiene has a lower glass transition temperature and, hence, a smaller apparent activation energy than polyisoprene.

To eliminate the monomeric friction coefficient in the expression for the self-diffusion coefficient, it is convenient to combine diffusion data with another dynamic quantity, e.g., viscosity.[2] Unfortunately, we do not have any actual viscosity data of our samples. Measurements are in progress.[13] We have compared our measurements with existing data of dielectric spectroscopy. Schönhals[12] has measured four samples identical to ours, and Boese and Kremer[10] have measured an earlier series from the same supplier. The product of the longest relaxation time $\langle\tau\rangle$ times the self-diffusion coefficient D is equal to $\langle R^2\rangle/3\pi^2$; cf. eq 1. This equation holds for Rouse motion, where $\langle\tau\rangle$ is the first normal mode relaxation time, as well as for strict reptation, where $\langle\tau\rangle$ is the tube disengagement time.[8] In Figure 4 we have depicted the product $\langle\tau\rangle D$ divided by $\langle R^2\rangle/3\pi^2$ with $\langle\tau\rangle$ values from refs 10 and 12 and our self-diffusion data. Up to molar masses of 20 000 Da the relation (1) holds sufficiently well. Only the two samples with the lowest M deviate significantly from eq 1. For these very short chains the Rouse model or the $\langle R^2\rangle$ vs M relation used by us may be incorrect. The deviation from eq 1 for $M > 20\,000$ Da is caused by disentanglement processes which are not included in the strict reptation model. This was stated by Pearson et al.[2] from their self-diffusion measurements and also confirmed by recent investigations of anomalous segment diffusion in polymer melts.[15]

Acknowledgment. The authors thank Prof. F. Kremer from our Institute for helpful comments, Dr. A. Schönhals, Berlin, for the detailed dielectric data of the polyisoprenes, and Inyong Chang, Universität Mainz, for the NMR measurements at the cryomagnet. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References and Notes

(1) Lodge, T. P.; Rotstein, N. A.; Prager, S. *Adv. Chem. Phys.* **1990**, *79*, 1.
(2) Pearson, D. S.; Fetters, L. J.; Graessley, W. W.; Ver Strate, G.; von Meerwall, E. *Macromolecules* **1994**, *27*, 711.
(3) Appel, M.; Fleischer, G. *Macromolecules* **1993**, *26*, 5520.
(4) Landry, M. R. Ph.D. Thesis, University of Wisconsin, 1985.
(5) von Meerwall, E.; Grigsby, J.; Tomich, D.; van Antwerp, R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1037.
(6) Chang, I.; Fujara, F.; Geil, B.; Hinze, B.; Sillescu, H.; Tölle, A. *J. Noncryst. Solids* **1994**, *172–174*, 674.
(7) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 403.
(8) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, UK, 1986.
(9) Gisser, D. J.; Johnson, B. S.; Ediger, M. D.; von Meerwall, E. D. *Macromolecules* **1993**, *26*, 512.
(10) Boese, D.; Kremer, F. *Macromolecules* **1990**, *23*, 829.
(11) Adachi, K.; Kotaka, T. Prog. *Polym. Sci.* **1993**, *18*, 585.
(12) Schönhals, A. *Macromolecules* **1993**, *26*, 1309.
(13) Pakula, T., private communication.
(14) Hadjichristidis, N.; Zhongde, X.; Fetters, L. J.; Roovers, J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 743.
(15) Appel, M.; Fleischer, G.; Kärger, J.; Fujara, F.; Chang, I. *Macromolecules* **1994**, *27*, 4274.

MA946361E