

Free Volume Theory

Temperature Dependence of Self Diffusion of Polystyrene and Polyethylene in the Melt An Interpretation in Terms of the Free Volume Theory

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Summary

The temperature dependence of the self diffusion coefficients of polystyrene and polyethylene in the melt was measured with the pulsed field gradient nmr technique. The temperature and molar mass dependences of the self diffusion coefficients can be described by the free volume model. Taking into account the matrix effect we detected the beginning of the break of the reptation process for polystyrene at low molar masses. The activation energies of the self diffusion process are comparable with those observed for viscosity.

Introduction

In a previous paper (1) we reported the molar mass dependence of the self diffusion coefficients of polystyrene and polyethylene in the melt. The results confirmed the reptation process of the chain molecules in the melt i.e. the relation $D \propto M^{-2}$ according to de Gennes' reptation concept (2) was fulfilled down to very low molar masses. This was also found by Bachus and Kimmich (3). As extensively discussed by Kimmich (4) and also by other authors there is a matrix effect which influences the mobility of the chain molecules, the mobility of the chain is determined by the topological constraints (entanglements) and the free volume in the system.

In this paper we interpret our measurements of the temperature dependence of the self diffusion of polystyrene and polyethylene in the melt with the free volume theory in the form of Doolittle (5) and Fujita (6) to get more precise information about the microdynamics of the chain and the effect of the matrix on the diffusion process.

Theory and Parameter Evaluation

We consider the chain confined in a tube by the neighbouring chains, i.e. we use the tube picture in the same sense as Kimmich (4) and not the tube like regions of Doi and Edwards (7). One segment of the length l has the mobility μ_1 , thus the diffusion coefficient of the chain of N segments in the tube is

$$D_t = \frac{kT\mu_1}{N} = \frac{D_1}{N} \quad (1)$$

In the reptation time T_r the chain diffuses along its own length L , thus

$$T_r = \frac{L^2}{6D_t} = N^3 \cdot \tau_1 \quad (2)$$

with $L = Nl$ and $\tau_1 = l^2/6D_1$. τ_1 is a microscopic time constant for the diffusion of a segment.

During the time T_r the centre of mass of the chain is displaced by the end-to-end-distance $\langle R^2 \rangle^{1/2}$ of the chain, and for the self diffusion coefficient we obtain, with $\langle R^2 \rangle = Nl^2$,

$$D_s = \frac{\langle R^2 \rangle}{6 T_r} = D_1 \cdot N^{-2} \quad (3)$$

In the free volume model one can write

$$D_s = A_1 \exp\left(-\frac{B}{f(M,T)}\right) \cdot N^{-2} \quad (4)$$

The first term describes the influence of the free volume in the system on the mobility μ_1 or the diffusion coefficient D_1 of one segment. Here f is the fractional free volume dependent on the molar mass and the temperature, B is a constant characterizing the hole size needed for a jump of a segment which should be in the order of unity.

The fractional free volumes of the polystyrenes are given by

$$f = f_g + \Delta\alpha(T - T_g(M)) \quad (5)$$

with $f_g = 0.025$ and $\Delta\alpha = 3.0 \cdot 10^{-4} K^{-1}$ according to Fox and Flory (8) with the exception of PS 600 for which we have used $\Delta\alpha = 4.1 \cdot 10^{-4} K^{-1}$. The glass temperatures $T_g(M)$ are from the literature (9,10). The fractional free volumes of the polyethylenes were calculated from the data of Doolittle (5) with the assumption of $f_g = 0.025$ at the glass temperature of $-36^\circ C$ (11).

The constants B were determined by fitting eq. (4) to the experimental values of D with the above mentioned fractional free volumes.

From eq. (4) follows for the Arrhenius activation energy

$$E = \frac{d \ln D}{d 1/T} = R \cdot B \cdot \frac{T^2}{f^2} \cdot \frac{df}{dT} \quad (6)$$

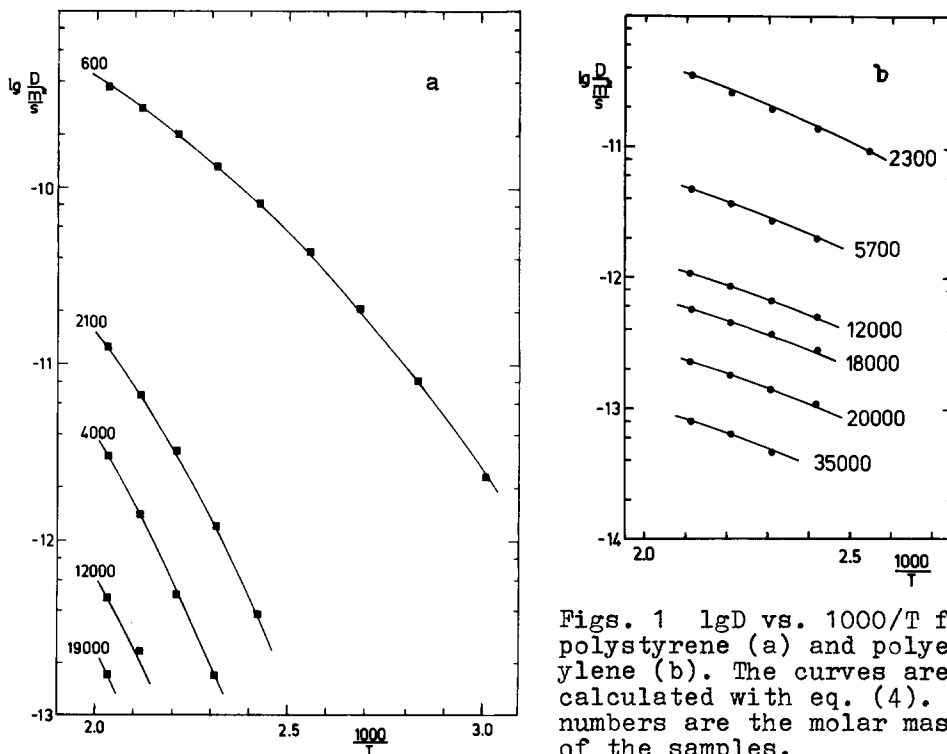
with the gas constant R .

Experimental

The measurements of the self diffusion coefficients were performed using the pulsed field gradient nmr technique. Details were described in the previous paper (1) where also the samples are characterized. We investigated polystyrene standards with molar masses from 600 to 19000 and fractions of linear polyethylenes with molar masses from 500 to 70000. Two fractions are from long chain branched polyethylene (PE 20000 and PE 35000). The highest measuring temperatures were 200°C (PE) and 225°C (PS).

Results and Discussion

The temperature dependence of the self diffusion coefficient of the polystyrene standards and some of the polyethylene fractions is shown in figs. 1 a and b. The curves are calculated using eq. (4). For the constants B we obtained 0.53 for



Figs. 1 $\lg D$ vs. $1000/T$ for polystyrene (a) and polyethylene (b). The curves are calculated with eq. (4). The numbers are the molar masses of the samples.

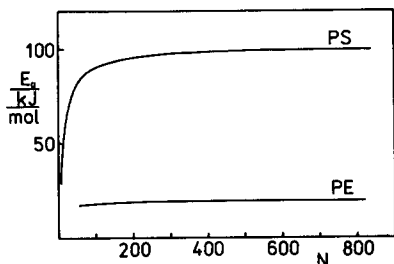
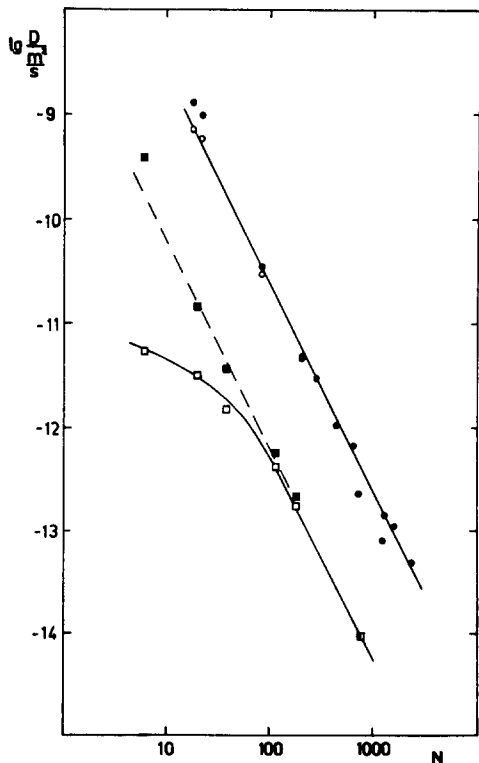


Fig. 2 Activation energy of the self diffusion coefficient E_a vs. chain length N for polystyrene and polyethylene ($T = 200^\circ\text{C}$). The curves are calculated with eq. (6) and the fractional free volume parameters given in table 1.

polystyrene and 0.45 for polyethylene which is less than those reported for viscosity (12), but it is reasonable that polystyrene has the greater value of B than polyethylene. As expected the activation energies of the self diffusion process increase with increasing chain length N as shown in fig. 2 (here N is the number of monomeric units in the chain). The activation energies are close to those obtained for viscosity but seem to be somewhat smaller. Long chain branched polymers have a higher activation energy of viscosity than their linear homologues (13). In our self diffusion investigations we do not detect such an effect either due to insufficient experimental accuracy or because the branches are not long enough. We see only a remarkable reduction of the self diffusion coefficient due to the long chain branches.



As did Bachus and Kimmich (3) we also observed a small irregularity in the temperature dependence of the self diffusion coefficient at the temperature T_u (see e.g. (14)) especially for the low molecular weight polyethylenes but a precise quantitative interpretation was not possible.

As is common in viscosity (12) we corrected the measured self diffusion coefficients for constant free volume (f_∞ for $M \rightarrow \infty$). These coefficients

Fig. 3 $\lg D$ versus $\lg N$

●, ■ measured values for polyethylene (200°C) and polystyrene (225°C) resp.

○, □ corrected for constant free volume f_∞

■ value of Bueche (16) corrected for 225°C with $E_a = 85 \text{ kJ/mol}$. The straight lines are drawn with the slope -2.0

are plotted as $\lg D$ versus $\lg N$ in fig 3. The relation $D \propto N^{-2}$ holds for polyethylene down to at least $N = 18$ whereas for polystyrene the reptation process begins to break at about $N = 50$. The tube-like region according to Doi and Edwards (7) or the distance between entanglements is 30 - 40 Å for polyethylene and 80 Å for polystyrene (15). So it is plausible that the reptation process for polystyrene breaks at higher N than for polyethylene.

Meerwall and Ferguson (17) which applied the fractional free volume theory in a similar manner to their measured self diffusion coefficients of rubbery polymers (M up to 22000) in the melt obtained $D \propto N^{-1}$ which is surprising in the light of our investigations. Bachus and Kimmich (3) found the self diffusion coefficient of polystyrene ($M = 3600$) in a matrix of deuterated polystyrene ($M = 31700$) at 230°C to be lower by a factor of 0.41 than in the pure state. With our version of the fractional free volume theory we calculate a factor of 0.51 which explains the decrease of the self diffusion coefficient as a matrix effect due to decreased free volume. The decrease of the self diffusion coefficient of polyethylene ($M = 2440$) in a matrix of deuterated polyethylene ($M = 430000$) at 200°C by a factor of 0.057 also measured by the above authors can not be explained by free volume effects alone.

Table 1

	polystyrene	polyethylene	comments
$\Delta\alpha$ (K^{-1})	$3.0 \cdot 10^{-4}$	$5.1 \cdot 10^{-4}$	Fox and Flory (8) Doolittle (5)
f_∞	0.0544	0.148	for $T=200^\circ\text{C}$ and $M \rightarrow \infty$
B	0.53	0.45	"
D_1 ($\frac{\text{m}^2}{\text{s}}$)	$1.7 \cdot 10^{-9}$	$2.5 \cdot 10^{-7}$	"
τ_1 (s)	$2 \cdot 10^{-11}$	$6 \cdot 10^{-14}$	"
E_a ($\frac{\text{kJ}}{\text{mol}}$)	100	19.5	"

From eq. (3) it is possible to calculate D_1 , the diffusion coefficient of one segment and the microscopic time constant τ_1 , the time the segments diffuse over its own length. The values are given in the table 1 for a temperature of 200°C and the molar mass $M \rightarrow \infty$. Due to the small fractional free volume compared with polyethylene and the bulky substituents polystyrene diffuses more than two orders slower than polyethylene.

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