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Self Diffusion in Melts of Polystyrene and Polyethylene Measured by Pulsed Field Gradient NMR

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SUMMARY

The self diffusion coefficient of melts of four monodisperse molecular weight polystyrenes and nine fractions of linear and branched polyethylene was measured by pulsed field gradient nmr. The relation $D \sim N^{-2}$ holds in the range of N (number of monomeric units) from about 20 up to 1500, i.e. the diffusion goes via reptation. No break was observed at the critical molecular weight M_c. Due to long chain branches in polyethylene the self diffusion coefficient is lowered considerably.

INTRODUCTION

In polymer dynamics the self diffusion coefficient is a well defined and interpretable quantity which can be measured by a number of methods, e.g. radioactive tracer technique (BUECHE 1968), IR microdensitometry (KLEIN 1978), forced rayleigh scattering (HERVET et al. 1979) and field gradient nmr (McCALL et al. 1959). While there are some results for self diffusion in polymer solutions the results for polymer melts are rather limited, above all due to the slow diffusion process.

Self diffusion in polymer melts (and solutions) can be described by the theory of BUECHE (1962) and the reptation model of DE GENNES (1971, 1979). The latter considers the diffusion process of a molecule of N monomeric units as the wiggling through a tube confined by the neighbouring molecules which

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for linear molecules gives

$$D \sim N^{-2} \quad . \qquad (1)$$

For long chain branched macromolecules the reptation process is strongly hindered (DE GENNES 1975, 1979). The prerequisite for the reptation process is the entangled behaviour of the melt or the condition that the time taken by a tube to renew its configuration is greater than the reptation time, the time the molecule diffuses along its length L in the confining tube (KLEIN 1978, DAOUD and DE GENNES 1979). While in viscosity the onset of entangled behaviour is attributed to the break in the logη -log M diagram the situation in self diffusion is less clear.

In 1959 self diffusion investigations in the melt were made by McCALL et al. (1959) who measured two fractions of polyethylene (M = 4100 and 5800) besides higher alkanes; they found $D \sim M^{-5/3}$. Detailled investigations by KLEIN (1978) of the self diffusion of melts of polyethylene fractions from M = 3600 up to 23000 in matrices of comparable and higher molecular weight polyethylenes confirmed the reptation model down to the lowest molecular weight. ZUPANČIČ et al. (1981) measured the self diffusion coefficient of three fractions of polyethylene in the melt. They observed a strong dependence of the self diffusion coefficient on the diffusion time which they explained by hindered diffusion. In a nearly classical work BUECHE (1968) measured the diffusion of ^{14}C-labelled polystyrene (M = 80000) in polystyrene matrices of higher molecular weight. The self diffusion coefficient was found to be independend of the matrix molecular weight which is in accordance with the reptation model.

In the present work we report the investigations of the self diffusion coefficients of four polystyrene standards and of nine fractions of linear and branched polyethylene. Our aim is to compare the self diffusion coefficients for these polymers, to confirm the reptation model in a broader range of molecular weights for these polymers and to look for the onset of entangled behaviour in self diffusion (in comparison with viscosity).

The temperature dependence and the variation of the self diffusion coefficient with the diffusion time will be reported in a subsequent paper.

EXPERIMENTAL

The measured samples are characterized in the table 1. Because of the strong dependence of the diffusion coefficient on the molecular weight (eq. (1)) narrow fractions are very important. For better comparison the self diffusion coefficients are related to the number N of monomeric units.

TABLE 1: Sample characteristics

sample	M_w	M_w/M_n	N	n	
PS 2100	2100	1.06	20		
4000	4000	1.1	38		
12000	12200	1.1	115		
19000	19400	1.03	182		
PE 2300	2740	1.39	83		fractions of LDPE (branched)
5700	6210	1.23	203		
20000	22400	1.19	733	3	
35000	38500	1.23	1240	2.5	
7800	8720	1.26	277		fractions of HDPE (linear)
12000	13500	1.21	440		
18000	20000	1.22	650		
37000	42400	1.34	1310		
45000	52700	1.36			

N: number of monomeric units computed from the geometric mean of M_w and M_n
n: number of long chain branches per molecule

The following pulse programme was used in pulsed field gradient nmr (PFG-NMR):

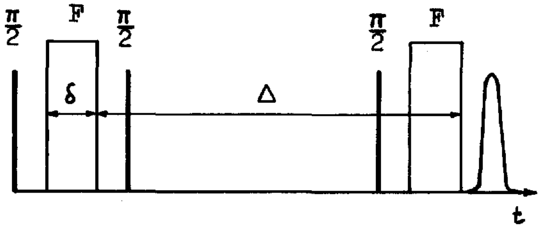

Fig. 1 Pulse programme

$\frac{\pi}{2}$: 90° radio frequency pulses

F: field gradient pulses

In such experiments the spin echo is damped due to the diffusion of the species in addition to the transverse relaxation if one applies two field gradient pulses F of magnitude g, duration δ and distance Δ :

$$\Psi = \Psi_0 \exp(-\gamma^2 \delta^2 g^2 D \Delta) \qquad (2)$$

(γ = gyromagnetic ratio, $\delta \ll \Delta$).

The self diffusion coefficient was derived from the echo attenuation plot $\ln \Psi/\Psi_0$ vs. δ^2. The diffusion times Δ were about 200 ms for polystyrene and about 700 ms for polyethylene. A typical spin echo attenuation plot is given in fig. 2.

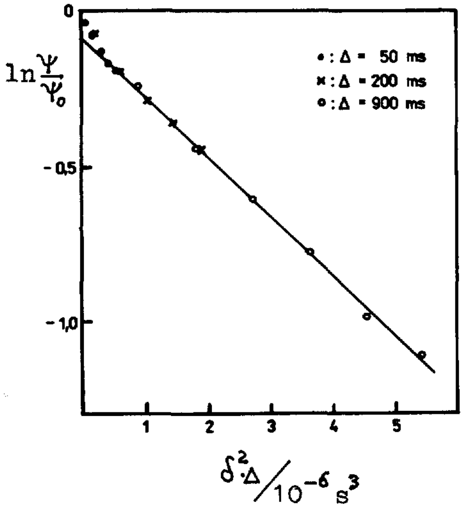

Fig. 2 Typical spin echo attenuation plot (PE 20000, 190°C) for three diffusion times Δ. For $\Delta \gtrsim 100$ ms the self diffusion coefficient is independend of the diffusion time

The rapid decay for short times is attributed to low molecular traces. Due to the decrease of the nuclear relaxation times with the molecular weight especially for polystyrene it was impossible to measure samples with higher molecular weights.

The measuring temperatures were 225°C for polystyrene and 200°C for polyethylene. We used the home-built spectrometer FEGRIS 80.

RESULTS and DISCUSSION

Since in our measurements the distances covered in the diffusion time are much greater than the radii of gyration and since for long diffusion times we observed a constant diffusion coefficient the measured self diffusion coefficient is the translational diffusion coefficient of the centre of mass. For short times PFG-NMR is able to measure rapid processes, e.g. gel-like fluctuations which were reported by CALLAGHAN and PINDER (1980) for semidilute polystyrene solutions. We also observed an increase of the self diffusion coefficient

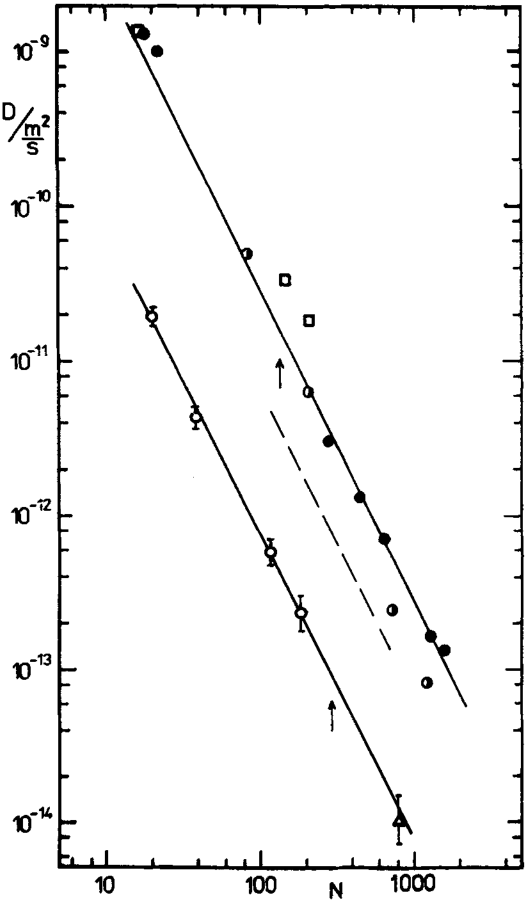

Fig. 3 Self diffusion coefficient D versus number of monomeric units N

○: PS, 225°C
●: HDPE, 200°C
◐: LDPE, 200°C
▲: PS after BUECHE (1968), corrected for 225°C with E_a= 90 kJ/mol
□: PE after McCALL et al. (1959), 200°C

dashed line: PE measured by KLEIN (1978), corrected for 200°C with E_a= 20 kJ/mol

The straight lines are drawn with the slope -2.0, the critical molecular weights M_c are indicated by arrows for short diffusion times for the higher molecular weights but not as much as measured by ZUPANČIČ et al. (1981).

In fig. 3 the dependence of the self diffusion coefficient on the number N of monomeric units is shown. The relation $D \sim N^{-2}$ holds very well for polystyrene and linear polyethylene which confirms the reptation model or the assumption of the weakness of the tube renewal process in the measured melts. This is also valid for molecular weights less than the critical molecular weight M_c observed in the melt viscosity, at least down to $N = 20$. In contrast to this result are the observations of VON MEERWALL et al. (1982) who for melts of cis-polyisoprene ($400 \leq M \leq 20000$) measured an exponent between -1 and -2 in eq. (1). They explained this exponent by nonentangled diffusion and free volume effects of the chain ends. Also in monte carlo calculations there is no evidence for reptation in the melts of relatively short chains (BISHOP et al. 1982). Obviously there is a need for further experimental material to clarify the dynamics in polymer melts.

The influence of long chain branches in the self diffusion of polyethylene melts is clearly seen: the self diffusion coefficient is lowered by a factor of about three for the two long chain branched polyethylenes. This effect is predicted theoretically (DE GENNES 1975), but there is no theory of the numerical value. With our method we see a possibility to detect long chain branches in macromolecules.

The activation energies of the self diffusion process were determined to be about 20 kJ/mol for polyethylene and 90 kJ/mol for polystyrene.

In fig 3. some data from the literature are also shown. The value from BUECHE (1968) corrected from 237°C to 225°C with the above given activation energy fits well in our diagram. The values from McCALL et al. (1959) for the two polyethylene fractions are higher by a factor of three than our values from which the somewhat smaller observed exponent in eq. (1) follows. This is possibly caused by the method which tends to overestimate the diffusion coefficients if one measures at the lower limit of the instrument. The excellent curve of KLEIN (1978) corrected from 176°C to 200°C with the above given activation energy is lower by a factor of about three than that measured by us. The reasons are not known.

We found that the self diffusion coefficient or the mobility of the polystyrene chains is lower by about one order than that of polyethylene of the same chain length. This means that the relatively bulky and rigid phenyl groups hinder the reptation process considerably.

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