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Self Diffusion of Alkanes in Low Density Polyethylene as Measured by Pulsed Field Gradient NMR

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SUMMARY

With pulsed field gradient NMR the self diffusion of five alkanes in low density polyethylene was measured. The results are interpreted in terms of the Fractional Free Volume Theory. The spherulite boundaries do not act as diffusion barriers. The measured self diffusion coefficients are greater than the mutual diffusion coefficients measured by conventional techniques, which is caused by the absence of any nonstationary process in our systems.

INTRODUCTION

The diffusion process of gases and vapours dissolved in semicrystalline polymers is more complicated than in amorphous polymers, and there are many difficulties in interpreting the measurements (PETERLIN 1975, KREITUSS & FRISCH 1981). The diffusion of gases and vapours takes place only in the amorphous regions of these polymers because the crystallites act as impermeable and nonswellable fillers.

The method of pulsed field gradient NMR (PFG-NMR) (STEJSKAL & TANNER 1965) permits us to measure self diffusion processes. The self diffusion coefficient D and the mutual diffusion coefficient D_m are related by the equation

$$D_m = D \frac{d \ln a}{d \ln c} \qquad (1)$$

with the activity a of the diffusant and the concentration

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c in the polymer. The PFG-NMR method in principle measures the mean square translation $\langle z^2 \rangle$ of a diffusing molecule in the z-direction during the diffusion time Δ; and Δ, $\langle z^2 \rangle$ and D are connected by the equation

$$D = \frac{\langle z^2 \rangle}{2\,\Delta} \quad . \tag{2}$$

An advantage of this method is the existence of fixed concentrations of the diffusant in the samples with no time dependence and no concentration gradient. Another advantage is the fact that one has a well defined diffusion time in this method which can be varied depending on the nmr-parameters of the system. So in our study we were able to observe the diffusion process within one spherulite and also across the spherulite boundary.

The diffusion of vapours above the glass transition temperature T_g can be successfully described by the Fractional Free Volume Theory (FUJITA 1961). For low concentrations of the diffusant this theory gives (PETERLIN 1975)

$$D = D_o \exp(\gamma c) \tag{3}$$

with
$$D_o = A \exp(-\frac{B}{f_2}) \tag{4}$$

and
$$\gamma = \frac{B(f_1 - f_2)}{f_2^2} \quad .$$

A and B are constants, B reflecting the size of the diffusing molecule. f_1 and f_2 are the fractional free volumes of the pure diffusant and the pure polymer, resp.

ZUPANČIČ et al. (1978) measured the pressure dependence of the self diffusion coefficient of butane in one linear polyethylene with the PFG-NMR method and they could interpret their results with the FFV theory. In our work we investigated the concentration dependence and diffusion time dependence of the self diffusion coefficients of five alkanes in three low density polyethylenes.

EXPERIMENTAL

The self diffusion coefficients were measured by the PFG-NMR method with the home-built FEGRIS 80 spectrometer. The stimulated echo was used (KÄRGER & HEINK 1971). The diffusion time Δ was varied from a few milliseconds up to about 300 ms. The diffusion of n-butane, n-pentane, n-hexane, n-octane and cyclohexane was investigated in the concentration range from about 10 % up to the saturation concentration. The concentrations are given as the mass concentration in the amorphous parts: $c_a=c/1-\alpha_m$. The mass crystallinities α_m were determined from the densities and the concentrations c in the whole polymer gravimetrically. The spherulite radii were measured by small angle light scattering according to STEIN and RHODES (1960). Within the experimental error the spherulite radii do not alter during the uptake of the alkanes. The polyethylenes were either rapidly cooled (r) or slowly cooled (s) with 2 K/h from the melt. All measurements were performed at room temperature. The data of the polyethylenes are given in TABLE 1.

Table 1: Densities, crystallinities and spherulite radii of PE's

Polyethylene	density g/cm^3	mass crystallinity %	spherulite radius µm
PE 1 r	0.915	45.9	2.3
PE 1 s	0.921	50.1	7.0
PE 2 r	0.919	48.7	2.1
PE 2 s	0.928	54.9	8.0
PE 3 r	0.929	55.6	2.6

RESULTS and DISCUSSION

In Figs.1 and 2 the concentration dependence of the self diffusion coefficient of the alkanes in PE 1 (rapidly and slowly cooled) is shown. Equation (3) holds well. With increasing size of the diffusant D decreases, the bulky cyclohexane having the smallest values of D.

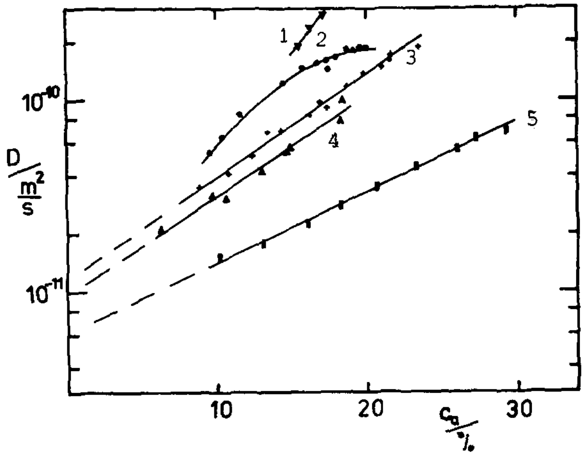

Fig. 1. Concentration dependence of D of various alkanes in rapidly cooled PE 1.

1 ▼ butane
2 ● pentane
3 + hexane
4 ▲ octane
5 I cyclohexane

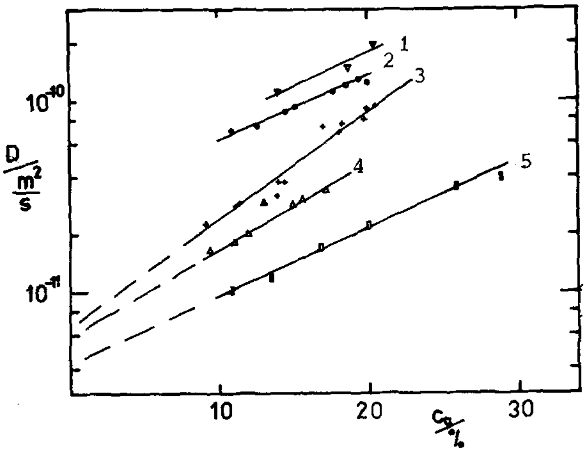

Fig. 2. Concentration dependence of D of various alkanes in slowly cooled PE 1.

1 ▽ butane
2 o pentane
3 + hexane
4 △ octane
5 II cyclohexane

In Fig. 3 the diffusion coefficients in different polyethylenes are shown. Here and also from Figs. 1 and 2 it is seen that the diffusion (under otherwise the same conditions) in rapidly cooled polyethylenes proceeds more quickly than in slowly cooled polyethylenes. This may be caused by the thinner amorphous layers in the slowly cooled polyethylenes which offers a greater geometrical resistance to the diffusion, by the lower chain mobility in the amorphous layers

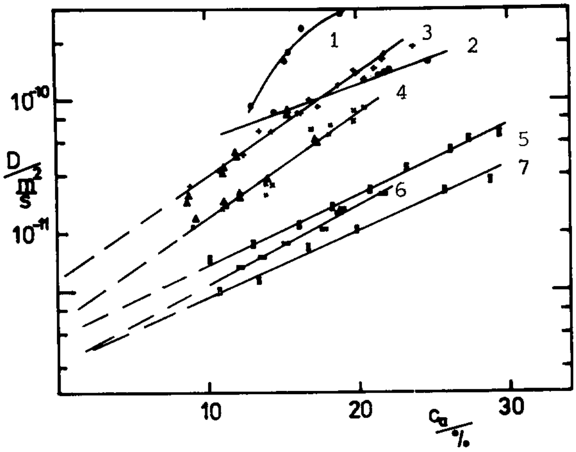

Fig. 3. Concentration dependence of D of various alkanes in different polyethylenes

1 ● pentane in PE 2 r
2 o pentane in PE 2 s
3 ▲ hexane in PE 2 r
4 Δ hexane in PE 2 s
3 + hexane in PE 1 r
4 x hexane in PE 1 s
5 I cy-hexane in PE 1 r
7 II cy-hexane in PE 1 s
6 ▬ cy-hexane in PE 3 r

of the slowly cooled polyethylenes (PETERLIN 1975) and by the higher order in these layers. From the parameter D_o of Eq. (3) it follows that the fractional free volume f_2 in the amorphous parts decreases with increasing crystallinity, and f_2 is smaller in the slowly cooled polyethylenes. The small D_o for the diffusion of cyclohexane arises from a high value of B caused by the greater cross sectional area of this molecule.

Deviations from Eq. (3) appear in the diffusion of pentane. After ESCOUBEZ et al. (1980) pentane tends to cluster in polyethylene at higher concentrations which gives an anomalous concentration dependence of the self diffusion coefficient. Due to the few measuring points for butane there is no evidence for the validity of Eq. (3) for this diffusant.

From Fig. 3 it follows that the amorphous parts of the three polyethylenes do not differ much with respect to their diffusion properties.

It is remarkable that our measured self diffusion coefficients are up to one order higher than the diffusion coefficients measured in analogous systems by conventional methods, e.g. permeation and/or sorption-desorption (KREITUSS & FRISCH 1981, RÖDICKER & ROLLIN 1980). According to Eq. (1)

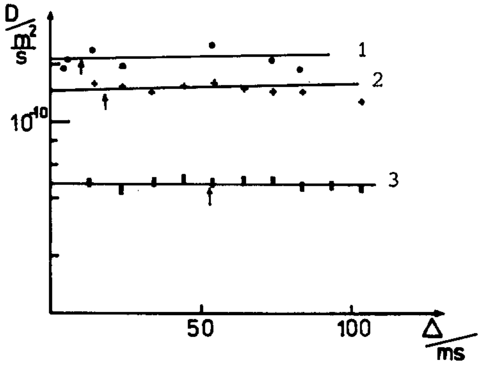

Fig. 4. Self diffusion coefficient D vs. diffusion time Δ for rapidly cooled PE 1.

1 ● 20.3 % pentane
2 + 17.2 % butane
3 I 29.3 % cyclohexane

At the times indicated by arrows the mean spherulite radius $\bar{R}$ = 2.3 µm is reached.

the mutual diffusion coefficient D_m is smaller than the self diffusion coefficient since the solution isotherms are upward concave for our systems with $T > T_g$ (cf. PETROPOULOS 1981), which gives dlna/dlnc < 1. From the sorption isotherms measured by ESCOUBEZ et al. (1980) for the system polyethylene-octane one can get a value for dlna/dlnc of about 0.75, which is too small to explain the observed large difference. Since in most of our measurements (and probably also in those of ZUPANČIČ et al. (1978) who also measured a high self diffusion coefficient) the spherulite boundaries are not crossed in the diffusion time Δ, the question arises whether the spherulite boundaries act as diffusion barriers as mentioned by VOROBEV et al. (1980). Our measurements shown in Fig. 4 demonstrate that the spherulite boundaries do not appreciately hinder the diffusion. We see the reason for our high diffusion coefficients in the fact that our systems are in equilibrium and without any concentration gradient and that no nonstationary stress effects due to swelling are present, which after BLACKADDER & KENIRY (1973) leads to an underestimation of the diffusion coefficients measured by conventional permeation experiments.

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