Molecular weight and temperature dependence of self-diffusion coefficients in polyethylene and polystyrene melts investigated using a modified n.m.r. field-gradient technique

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Self-diffusion in polyethylene and polystyrene melts has been investigated using a modified n.m.r. field-gradient technique. In both polymer examples, self-diffusion coefficients were found to be proportional to $M_w^{-2.0\pm0.1}$ above and below the critical molecular weight M_c. The observation of undeuterated chains in deuterated matrices of varying chain length indicates only relatively weak matrix effects. The influence of internal field gradients, which have previously been reported for polyethylene melts, is demonstrated and discussed. Certain peculiarities have been observed in the temperature dependences of the diffusion coefficients.

Keywords Self-diffusion; polymer melts; reptation; n.m.r. field-gradient technique; internal field gradients; free volume

INTRODUCTION

The molecular weight dependence of self-diffusion coefficients in polymer melts is of special interest because it should reflect the type of translational motion of flexible macromolecules. As lateral displacements in an entangled chain structure are negligible compared with longitudinal diffusion or 'reptation' in the 'tube' formed by neighbouring molecules, the latter process is usually accepted as a suitable model[1-5]. The molecular weight dependence of the self-diffusion coefficient is then expected to obey:

$$D \sim M^{-2} \tag{1}$$

Though this power law has been verified by an infra-red microdensitometry technique[4,5], tritium tracer[6,7] and n.m.r. field-gradient[8-10] measurements led to quite different exponents. Thus we were prompted to reconsider the problem.

In the following we describe a new n.m.r. field-gradient apparatus permitting measurement of D at constant diffusion times by variation of the field-gradient amplitude. The constancy of the diffusion time will be shown to be important if chain length distributions play a role.

This method is also of interest if internal field gradients do not permit measurements at very short diffusion times. Using this technique we could confirm the validity of equation (1) both *above* and *below* the critical molecular weight M_c and for both *polyethylene* and *polystyrene*. Furthermore we have investigated matrix effects by observing undeuterated chains dissolved in deuterated matrices of different molecular weights. The results will be discussed in the light of our recent relaxation studies[11].

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MODIFIED FIELD-GRADIENT TECHNIQUE AND APPARATUS

Self-diffusion coefficients have been measured with a home-built apparatus using a temporally sinusoidal and spatially constant magnetic field gradient along the external magnetic field. The time dependence of the field gradient is given by:

$$g(t) = g_1 + g_2[1 - \cos(\omega_g t)] \tag{2}$$

Here g_1 is a small stationary gradient superimposed on a sinusoidal gradient which has an amplitude g_2 and an angular frequency ω_g. The parameters realized in our experiments were: $g_2 \leqslant 800\,\mathrm{G\,cm^{-1}}$, $\omega_g/2\pi = 100\,\mathrm{Hz}$, $g_1 < 40\ \mathrm{G\ cm^{-1}}$. The order of magnitude of g_1 ensured a high echo stability. On the other hand, the reduction of the echo amplitude as a consequence of the limited spectrometer bandwidth was minor.

The 90° and 180° r.f. pulses of the Hahn spin echo sequence[12] were irradiated at times $t_{90} = 0$ and $t_{180} = 2\pi/\omega_g$, respectively, so that the echo appeared at $t_E = 4\pi/\omega_g$. Measuring the echo amplitude E as a function of the field-gradient amplitude g_2 permits the evaluation of the self-diffusion coefficient D according to[13]:

$$E = E_0 \exp(-DF) \tag{3}$$

with

$$F = \gamma^2 t_{180}^3 \left[\frac{2}{3} g_1^2 + \left(\frac{2}{3} + \frac{5}{4\pi^2}\right) g_2^2 + \left(\frac{4}{3} + \frac{1}{\pi^2}\right) g_1 g_2\right]$$

Here E_0 is a constant for constant time and γ is the gyromagnetic ratio. The quantity F will be called the 'field-gradient term'.

Compared with the usual pulsed field-gradient techniques[12-14], the sinusoidal gradient/amplitude variation method has the advantage of easily controllable eddy currents in the pole caps of the magnet which merely lead to a small and constant phaseshift of the field gradient against the programming voltage. Secondly, we have the possibility of measuring at a constant diffusion time (in our case 20 ms). As discussed below, this simplifies the interpretation in cases of broad chain length distributions and if internal field gradients are present.

Figure 1 shows a block diagram of the apparatus. It consists of the following four main components: a pulsed n.m.r. r.f. unit, the field-gradient power supply, the probehead with integrated gradient coil, and the data recording and evaluation system.

The time dependence of the field gradient is produced by a waveform generator (Marconi TF 2120). From the same source, the time intervals of the r.f. pulses are derived. A commercial pulsed n.m.r. spectrometer (Bruker, Minispec P40, 40 MHz proton resonance frequency) was used. Thus the r.f. pulses can be adjusted to coincide with the minima of the field gradient.

The power supply for the field-gradient current (Kepco BOP 15–20M) produces an output current corresponding to equation (2):

$$I(t) = I_1 + I_2[1 - \cos(\omega_g t)] \qquad (4)$$

Here I_2 is varied between 0 and 20 A, and $\omega_g/2\pi = 100$ Hz was found to be the highest field-gradient frequency compatible with the full output current of the power supply. It also ensured a sufficient length of diffusion time. The small and constant current I_1, the purpose of which is to stabilize the spin echoes, is directly controlled by the computer system using a digital-to-analogue converter.

Figure 2 shows a cross-section of the probehead. The field gradient is produced by a quadrupole coil[15] (2 × 60 windings of copper wire, 0.71 mm diameter, with high-temperature insulation).

The Joule heating produced in the coil can exceed 200 W. Therefore the coil and the brass coil former are cooled by a closed circuit of (proton-free) Frigen 113 TRT (Hoechst), which is kept at a constant temperature of 10°C.

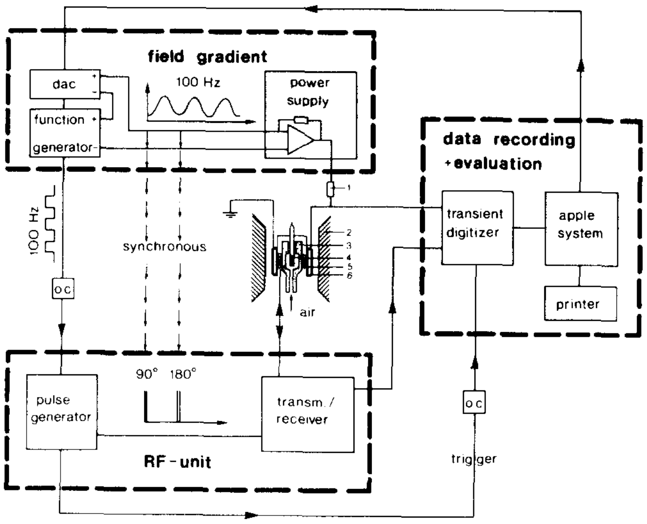

Figure 1 Block diagram of the apparatus used for the self-diffusion measurements: OC, opto coupler; DAC, digital-to-analogue converter; 1, serial resistor; 2, magnet pole caps; 3, tempering cell and r.f. coil former; 4, sample; 5, r.f. coil; 6, gradient coil

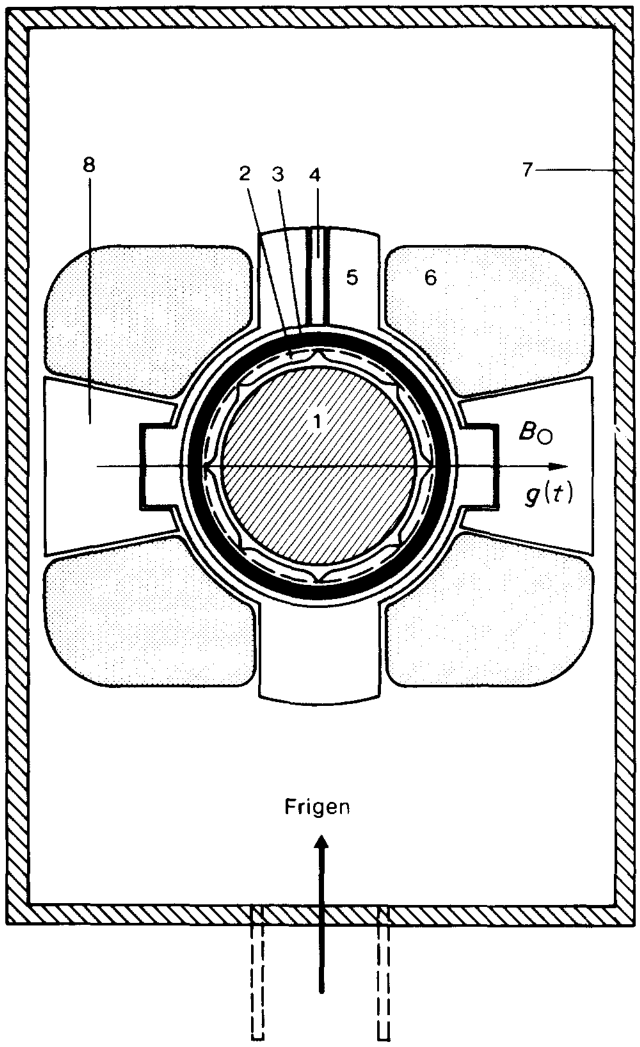

Figure 2 Cross-section of the probehead (to scale): 1, sample; 2, poly(tetrafluoroethylene) r.f. coil former and tempering cell; 3, r.f. coil; 4, poly(vinyl chloride) spacer; 5, brass form; 6, quadrupole coil; 7, brass case; 8, coil former (has been removed after winding and fixing the gradient coil)

Deviations from constancy of the field gradient in the sample volume of about 1 cm^3 are less than 3%. The highest gradient safely reached is 800 G cm^{-1}. The field-gradient current is measured by a low-temperature coefficient resistor (0.04 Ω), whose temperature is controlled by the same Frigen bath mentioned above. The field gradient has been calibrated using a Hall probe inserted instead of the sample. The position of the Hall probe can be adjusted using a micrometer screw.

The sample temperature is controlled by compressed air and two-stage heating. Temperatures up to 250°C with gradients less than 6°C within the sample volume can be achieved. The relatively low temperature gradient is ensured by having an unconstrained air flow around the sample and by avoiding any direct contact of the sample tube with the r.f. coil former in the vicinity of the sample material. In order to prevent convectional flow at low viscosities, a dense texture of glass fibre has been incorporated into the samples. The estimated volume fraction of the glass fibre is less than 7%. With high-

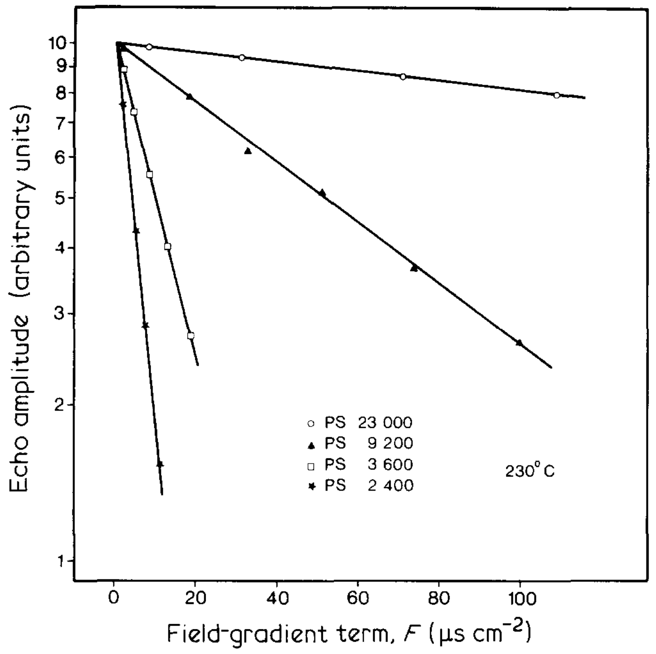

Figure 3 Echo amplitude vs. field-gradient term F for an exemplary set of polystyrene fractions (M_w)

viscosity samples, where convection is negligible, no influence of the glass fibre has been found, so that surface effects are ruled out.

The n.m.r. signals and the course of the field gradients are simultaneously recorded by a two-channel transient recorder (Datalab DL 922, 8 bit, 20 MHz) interfaced to the computer system (Apple II Europlus, 48k). The accumulation program (ASSEMBLER) for the n.m.r. signals involves an artifact rejection procedure. Only echoes appearing within an appropriate time window and exceeding 80% of the optimum amplitude are accumulated. The width of the time window and the optimum amplitude are determined in a series of test scans preceding each experiment. The final evaluation of D according to equation (3) is carried out with a BASIC evaluation and plotting program.

The whole apparatus and the data recording system have been checked by measuring the temperature dependence of the self-diffusion coefficient of a water-free glycerol sample (with glass-fibre texture). Literature data[14] have been reproduced in perfect agreement over several orders of magnitude.

The lower limit of diffusion coefficients which can be determined by our technique is about 10^{-10} cm^2 s^{-1}. The experimental error is about 10% or less. The mean displacements in the diffusion time of 20 ms are at least 350 Å so that they exceed the random coil dimensions of the polymer chains with all fractions used. Our results are therefore attributed to centre-of-mass diffusion rather than to internal fluctuations[11].

SAMPLES

The experiments have been carried out with narrow fractions of linear polyethylene (PE) and atactic polystyrene (PS). The polyethylene fractions in part were gifts of Dr Goldbach, Hüls AG, Marl, FRG, and Dr Asbach, Abt. Experimentelle Physik, Universität Ulm. The rest was purchased from Knauer, West Berlin, Polymer Laboratories, Shawbury, UK, and Humphrey, North Haven, Conn., USA. The ratios of the weight and number average molecular weights, M_w/M_n, ranged from 1.1 to 1.5. Gel permeation chromatography curves of some of the samples have been published previously[16]. Perdeuterated polyethylene (PE$_D$, $M_w = 431\,000$, $M_w/M_n = 2.4$) was purchased from Merck AG, Darmstadt, FRG. The n.m.r. signal of the residual protons was negligible.

The polystyrene samples either were gifts of Dr Münstedt, BASF, Ludwigshafen, FRG, or were purchased from Knauer, West Berlin, and Pfannenschmidt, Hamburg, FRG. The ratio M_w/M_n in all cases was about 1.1 or less. Deuterated polystyrene (PS$_D$, $M_w = 31\,700$, $M_w/M_n = 1.85$) was purchased from Merck AG, Darmstadt, FRG. The n.m.r. signal of the residual protons was again negligible.

The samples (about 1 cm^3) have been pressed in cylindrical form after having incorporated a texture of glass fibre (see above). Volatile constituents have been removed by evacuating the samples at least overnight before they were sealed in the evacuated state ($\simeq 10^{-4}$ mmHg).

Mixtures have been prepared by thoroughly mixing the powdery materials and thereafter applying the same procedure as above. The homogeneity of the mixture could be controlled by the exponentiality of the longitudinal n.m.r. relaxation curves and is confirmed by the observation of matrix effects[11].

Below we will indicate the fractions by the abbreviations PE, PE$_D$, PS, PS$_D$, respectively, followed by the weight average molecular weight.

EVALUATION

In *Figure 3* we have plotted the echo amplitudes measured with four exemplary polystyrene fractions *versus* the field-gradient term F. Obviously the data can be described by single exponentials, so that the self-diffusion coefficients can easily be evaluated according to equation (3). The results are plotted in *Figures 5* and *6*.

In the case of polyethylene, we have to deal with chain length distributions that are broad compared with those of the polystyrene samples. Broad chain length distributions reflect themselves in a distribution of diffusion coefficients so that the evaluation curves are no longer exponential (*Figure 4*).

Chain length distributions also lead to distributions of transverse relaxation times[16] T_2, so that the spin echo amplitudes at different times can be governed by different fractions of the chain length distribution. As the diffusion time is constant in our experiments and as we keep it as short as is compatible with the dominance of centre-of-mass diffusion, we do not expect any strong convolution effect of the T_2 distribution on the evaluation curves. Rather we interpret and evaluate the non-exponential decays as a linear superposition of (a few) exponentials with different diffusion constants. The weighted average of these fractional coefficients should then closely correspond to the proper *weight average* of the diffusion constant.

The evaluation procedure can be checked in the reverse direction by investigating mixtures of different fractions. In *Figure 4*, the decay curve measured with a mixture of

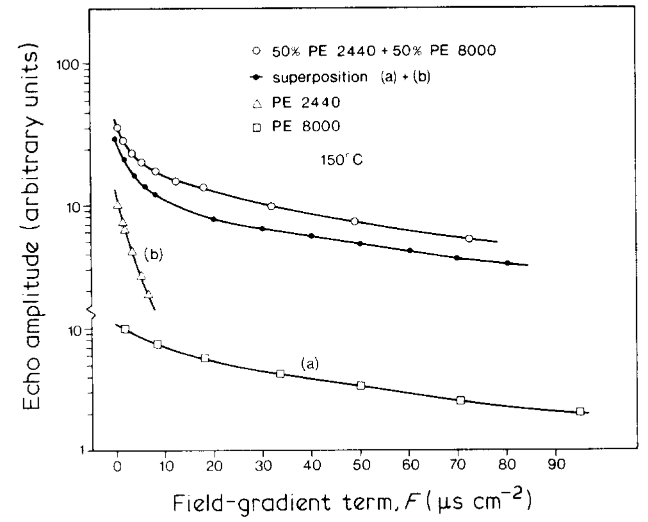

Figure 4 Echo amplitude vs. field-gradient term F for the polyethylene fractions PE 2440 and PE 8000 and a 1:1 mixture by weight of these fractions. The numerical superposition of the two polyethylene fractions is shown to be in agreement with the direct measurement

50% PE 2440 and 50% PE 8000 is compared with the decay curve calculated from the data of pure constituents. Obviously the superposition corresponds to the effect of the artificial broadening of the chain length distribution.

A similar test has been carried out with polystyrene. A blend of 50% PS 2400 and 50% PS 3600 shows an average diffusion coefficient $D = 1.0 \times 10^{-7} \mathrm{cm}^2 \mathrm{s}^{-1}$ at 230°C, while a pure fraction PS 3000 is expected to have a value $1.15 \times 10^{-7} \mathrm{cm}^2 \mathrm{s}^{-1}$ according to *Figure 5*. Thus the evaluation procedure yields diffusion constants virtually representing weight averages.

MOLECULAR WEIGHT DEPENDENCE

Figure 5 shows the molecular weight dependence of the diffusion coefficient in linear polyethylene and polystyrene melts. For comparison we have also plotted the i.r. data of Klein[4] and one tracer data point of Bueche[17]. In all cases the proportionality $D \sim M_w^{-2.0 \pm 0.1}$ has been verified. Merely near or below $M_w \simeq 10^3$ slight deviations from this relation appear. In particular the slopes are not altered at the critical molecular weights M_c.[18,19]

The data point of Bueche[17] for polystyrene fits very well with our n.m.r. results. We have also observed the same molecular weight dependence as Klein[4] in his polyethylene study. The absolute values of the i.r. data, however, are smaller by a factor of roughly 7. The investigations of Klein were carried out with deuterated fractions, so that the question arises whether there is an isotopic effect. Also, in contrast to the almost monodisperse polystyrene fractions, the diffusion coefficients of polyethylene represent averages according to the chain length distributions. The broader distributions and the different averaging procedure used by Klein again might have consequences concerning the absolute values. Possibly the deviation is also due to a kind of bottleneck effect appearing at the more or less imperfect interface between the deuterated and undeuterated films used with the i.r. technique[4].

With the polyethylene fractions we have carried out two series of measurements at 150°C and 200°C. The apparent activation energy which must be attributed to

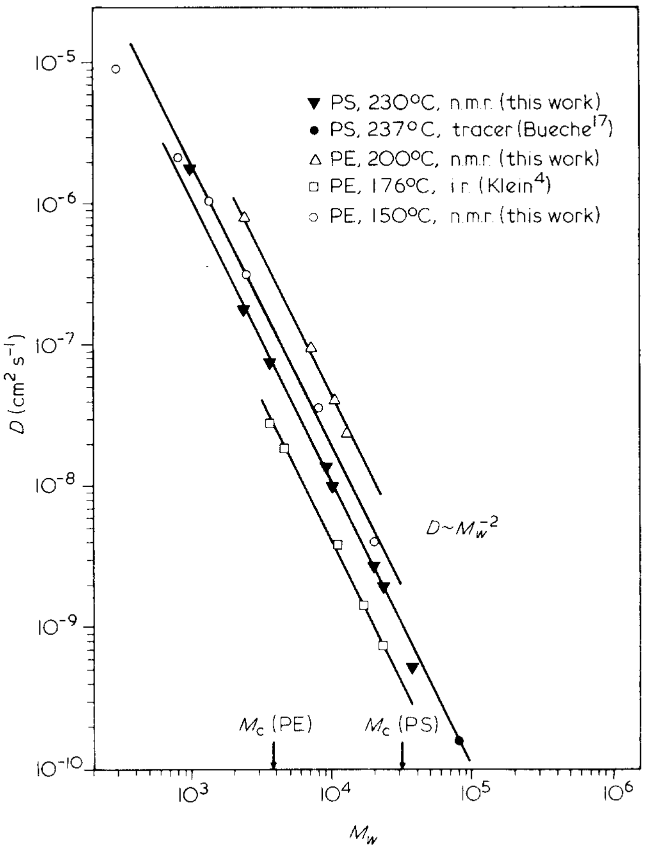

Figure 5 Molecular weight dependence of self-diffusion coefficients. Our polystyrene data can be considered to represent virtually monodisperse samples, while our polyethylene values are weight averages (see 'Evaluation' section)

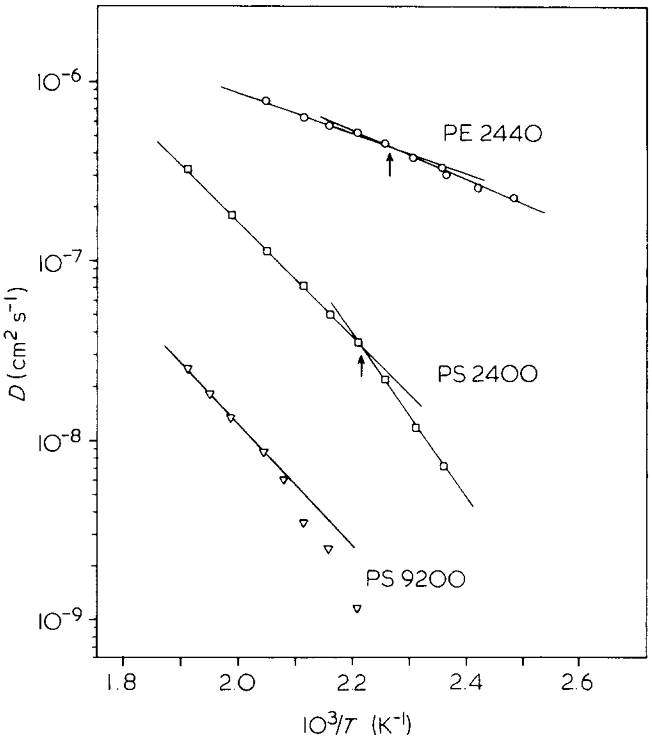

Figure 6 Temperature dependence of self-diffusion coefficients (see legend of *Figure 5*)

the temperature effect fits very well with the 28 kJ mol^{-1} found in relaxation studies[16,20].

In several other studies, molecular weight dependences deviating from the M^{-2} power law have been reported. Tanner *et al.*[10] found $D \sim M^{-1.7}$ for poly(ethylene oxide) and poly(dimethylsiloxane) with a pulsed field-gradient method[21]. Kumagai *et al.*[7] measured different proportionalities ranging from $D \sim M^{-2.7}$ to $D \sim M^{-1.0}$ in polystyrene. These authors used a tritium tracer technique. On the other hand, in both papers it was concluded that M_c has no influence on the molecular weight dependence.

Little information concerning the chain length distributions and their variation with the diverse fractions has been given in most of the previous diffusion studies. Possibly one has to look here for the reason for the observed deviations. With polystyrene, however, this should normally be no problem. Nevertheless, the results of Kumagai *et al.*[7] are very different from ours (including the tracer data point of Bueche[17]). Very likely there is an effect of the very thin films ($\simeq 10\,\mu$m) used by Kumagai *et al.* in their tracer technique. It is known that thin films of polymer melts show partial ordering phenomena[22,23] which might account for the different behaviour. In the light of the reptation model of self-diffusion[1,2,11], non-randomly coiled chains are expected to show a flatter molecular weight dependence as has been reported by Kumagai *et al.* for the case of constant matrices.

Matrix variation, on the other hand, may be connected with a strong variation of the free volume as will be discussed in the following section. This especially holds true if the temperature is relatively low. Kumagai *et al.* have measured at 150°C, while our polystyrene data have been recorded at 230°C, where matrix effects are weak[17].

THE INFLUENCE OF THE MATRIX

In order to detect matrix effects, we have carried out two experiments in which we have observed a small amount of undeuterated material dissolved in a deuterated matrix. The results are given in *Table 1*.

The most probable reason for matrix effects is the alteration of the free volume provided that the fluctuation of free volume is rate-limiting[11,24–26]. The molecular weight dependence of the specific volume can be described by empirical formulae which have been reported for polyethylene[27] and polystyrene[28]. According to these findings, matrix effects are expected to be strong only in connection with low molecular weights and low temperatures. As a matter of fact, no or only rather weak matrix effects have been observed with PS 80 000 at 237°C [17] and with PE 3600 or PE 23 000 at 176°C.[5]

Our own investigations (*Table 1*) refer to lower molecular weights and, hence, the effect is stronger. PS 3600 dissolved in deuterated PS 31 700 has a diffusion coefficient 2.4 times smaller than in the pure melt at 230°C. Thus the diffusion coefficient of the dissolved chains varies considerably more weakly than the matrix chain length even in this short-chain regime, where the free volume is linearly related to M^{-1}.[28]

With PE 2440 dissolved in deuterated PE$_D$ 431 000 the effect is of one order of magnitude. It is inconceivable that this result is solely due to a corresponding alteration of the free volume, because rheological studies near 200°C do not indicate such a strong molecular weight dependence of free volume[29]. Also the results of Klein[5] do not suggest an effect of this magnitude. Thus we try the following explanation specifically valid for n.m.r. experiments with polyethylene.

In a previous paper[16], we have shown that polyethylene melts imply internal magnetic field inhomogeneities which have been attributed to the occurrence of (fluctuating) voids. By taking into account the right value of the magnetic susceptibility (in ref. 16, a factor of 4π erroneously has been omitted), it can be estimated that the n.m.r. lines should be broadened by up to 10^3 Hz. Void and chain fluctuations, if fast enough (as is the case with short chain lengths), lead to full or partial motional narrowing[16]. In a matrix with very long chains, however, as in the experiment referred to, motional averaging can be incomplete, and we have to take into account a substance internal field gradient superimposed on the external gradients, equation (2). The order of magnitude can easily exceed that of the applied gradients, so that we have to discuss possible consequences.

Diffusion of chains in a fluctuating internal field gradient effectively means that the local resonance frequency fluctuates with a rate f. In an n.m.r. self-diffusion experiment the relevant diffusion interval is t_{180} (see equation (3)). The effect of internal gradients will be averaged out if:

$$2\pi f t_{180} \gg 1 \tag{5}$$

In our case t_{180} is equal to 10 ms, so that the critical fluctuation rate of the local resonance frequency is:

$$f_{\text{crit}} = (2\pi t_{180})^{-1} \simeq 16\ \text{s}^{-1} \tag{6}$$

Only for $f \gg f_{\text{crit}}$ are the internal gradients negligible. (Note that this condition is less restrictive in the present case than that for motional narrowing of the inhomogeneously broadened lines connected with a timescale of only $(\Delta\omega)^{-1} = (2\pi \times 10^3\ \text{Hz})^{-1} = (2\pi)^{-1}$ ms.[16])

Rate f can be estimated by the Carr–Purcell–Gill–Meiboom experiments[12]. Variation of the 180° pulse spacing permits us to find the limit where the diffusion effect within the pulse intervals becomes negligible, or, in

Table 1 Self-diffusion coefficients of undeuterated chains ($M_w^{(1)}$) dissolved in deuterated matrices ($M_w^{(2)}$)

	θ (°C)	$M_w^{(1)}$ (undeut.)	$M_w^{(2)}$ (deut.)	p_1 (% w/w)	$D(M_w^{(1)})$ (cm^2 s^{-1})	D_{mix} (cm^2 s^{-1})
PE	200	2440	431 000 (M_w/M_n = 2.4)	10	6.7×10^{-7}	(3.8×10^{-8})*
PS	230	3600	31 700 (M_w/M_n = 1.9)	20	7.0×10^{-7}	2.9×10^{-7}

* As discussed in the text, the D_{mix} value of polyethylene is an apparent one which is influenced by internal field gradients

other words, where the local resonance frequency becomes quasi-stationary.

In the case of the PE 2440/PE_D 431 000 sample this limit was found to be of the order of 10 ms pulse spacing. We conclude that in this mixture $f \lesssim f_{crit}$. Therefore, the internal gradients have not been averaged out, and the evaluation of the diffusion diagram (*Figures 3* or *4*) on the basis of equation (3) leads to *apparent* values of D considerably *less* than the actual diffusion coefficient. The reason is that at small external field gradients the internal gradients even dominate so that the variation of the term F causes minor effects on the echo amplitudes. The average slope in the diffusion diagrams (*Figures 3* or *4*) therefore appears to be flatter than it would be in the absence of internal gradients. Thus the D value for polyethylene given in *Table 1* must be considered to be an apparent one.

The 'matrix' chain lengths effective for the polyethylene data in *Figure 5*, on the other hand, are considerably smaller ($M_w \lesssim 20000$). In these cases Carr–Purcell–Gill–Meiboom experiments indicate that $f \gg f_{crit}$, so that the internal field gradients have no effect and the true diffusion coefficients have been measured. (Simultaneously, motional narrowing of the inhomogeneous broadening has been observed in this range of molecular weights[16].)

The peculiar diffusion results obtained by Zupančič *et al.*[30] can also be explained on the basis of internal field-gradient effects. In contrast to our experiments, these authors have varied the diffusion times from 3 ms up to 1 s at an unspecified temperature. With PE 30000 and an assumed temperature near the melting point they therefore initially have a situation $f \lesssim f_{crit}$, while at long diffusion times $f \gg f_{crit}$ is reached. Thus, according to their evaluation method, they initially measure an *apparent* diffusion coefficient considerably *higher* than the true value obtained after a long diffusion time (apart from any chain length distribution effect).

Above we have argued that, in the context of our technique, the internal field gradients by circumstance can lead to apparent diffusion coefficients *smaller* than in reality. In the experiment of Zupančič *et al.*[30] we expect the opposite effect. This is no contradiction. In our technique the echo amplitudes are evaluated as a function of the external field-gradient *amplitude* while in the conventional method the diffusion *time* is the parameter varied in the experiments. The variation of the echo amplitude caused by internal gradients is just opposite for the two types of experimental parameters.

With polystyrene, the free-induction decays did not indicate any perceptible field inhomogeneity effect in the absence of external gradients. The echo amplitudes varied identically with the free-induction decays. Thus the diffusion coefficients evaluated for the external field gradient must be considered to have the actual values.

TEMPERATURE DEPENDENCE

In *Figure 6* we have plotted the temperature dependence of D for three exemplary fractions of polyethylene and polystyrene. The curves obviously do not correspond to a simple Arrhenius behaviour. Rather, a bend has been observed in all three cases. The bend temperature (defined by the intersection of the straight lines) and the apparent activation energies above and below the bend of PE 2440 are 168.5°C, 21.6 kJ mol^{-1} and 26.3 kJ mol^{-1}, respectively. PS 2400 has a bend temperature of 178.5°C and apparent activation energies of 62.2 kJ mol^{-1} and 87.8 kJ mol^{-1}, respectively. In ref. 31, bend phenomena have been reported which have been observed for PE 2475 with quite different techniques. Almost the same bend temperature has been derived.

With polystyrene, on the other hand, a transition at a molecular weight dependent temperature T_{ll} well above the glass transition has been reported[32], which does not fit to the bend temperatures in *Figure 6*. Thus the phenomena represented by the bends in *Figure 6* must be of a different nature.

INTERPRETATION AND CONCLUSIONS

A crucial prediction[1,2,11] of the reptation model of self-diffusion in polymer melts is the proportionality, equation (1). This molecular weight dependence has been verified (*Figure 5*), so that the model must be considered to be confirmed. A more extensive discussion of the origin of this power law can be found, for example, in ref. 11.

In that paper we have argued that there is a factor n^{-1} (n = number of segments per chain) due to the uncorrelated directions of the instantaneous segment velocities. On the other hand, a factor n_d^{-1} (n_d = number of defects per chain) arises from the random distribution in forward/backward direction of the defect velocities. Thus

$$D \sim (nn_d)^{-1} \tag{7}$$

At first sight, one expects a proportionality $n_d \sim n$. However, in ref. 11 we have shown that many experimental findings with polymer melts can be explained by the introduction of the so-called contour length fluctuation of the chains. This means that the chain part which is rate-limiting for reptative whole-chain displacements has a reduced length given by:

$$L = L_0[1 - (\Delta_0/L_0)^{0.5}] \tag{8}$$

(Δ_0 = average length per fold). Hence a reduced number of defects has to be inserted in equation (7) leading to the proportionality:

$$D \sim n^{-2}[1 - (\nu_0/n)^{0.5}]^{-1} \tag{9}$$

(ν_0 = average number of segments per fold). Equation (9) can be approximated over at least two orders of magnitude by[11]:

$$D \sim n^{-2.1} \tag{10}$$

This proportionality still lies within the limits of the experimental errors. Interestingly it coincides with a finding published by Klein and Briscoe some years ago[4].

At high molecular weights ($M_w \overset{=}{<} M_c$) and high temperatures ($\simeq$200°C), the free volume[27,28] is virtually independent of chain length. Thus, even if free volume fluctuations were rate-limiting to self-diffusion, no additional dependence is expected, as has been demonstrated by matrix variation (see the n.m.r. relaxation experiments in ref.11 and the discussion above). Only for $M_w \ll M_c$ can an influence of that kind become strong. Apart from matrix variation experiments, this also seems to be indicated by the diffusion coefficient of PS 1000 which is somewhat higher than predicted by the M_w^{-2} law (*Figure 5*).

Polyethylene, on the other hand, for $M_w < 10^3$ shows diffusion coefficients falling below the M_w^{-2} line (*Figure 5*, cf. ref. 4). This is very likely due to the beginning transition from random coil conformations of long chains to conformations of short paraffins ($L \lesssim \Delta_0$). Neutron scattering studies[33,34] of the radius of gyration indicate that this transition becomes perceptible just at these molecular weights. Deviations from random coil conformations, however, lead to weaker molecular weight dependences[2,11] and, finally, to the breakdown of the reptation model. Simultaneously, a diffusion mechanism competitive with reptation should become relevant. This process can be imagined on the basis of contour length fluctuation[11] which provides lateral displacements. Thus, in contrast to PS 1000, the free volume effect is considered to be overcompensated by the reduced molecular weight dependence of the intrinsic factors (equation (7)).

We conclude that the molecular weight dependence of the self-diffusion coefficient in polymer melts has three sources in addition to the 'random direction' factor n^{-1}: (i) the intrinsic molecular weight dependence of curvilinear reptative diffusion ($\sim n_d^{-1}$); (ii) the molecular weight dependence of free volume (tendency to concave $\log D$ *versus* $\log M$ curves); and (iii) lateral displacements on the basis of contour length fluctuation as a mechanism competitive with reptation (tendency to convex $\log D$ *versus* $\log M$ curves).

The latter two influences are expected to compensate each other to a certain degree. However, they can be strong only far below M_c, where free volume depends sensitively on chain length and where contour length fluctuation reduces more and more the 'tube core' (see equation (8)) whose renewal is governed by reptative whole-chain displacements rather than by contour length fluctuation[11]. Note that the effectiveness of this core is expected to be different for zero-shear viscosity and lateral diffusion. As long as there is a finite core length (equation (8)) embedded in a quasi-stationary matrix, lateral diffusion will be prevented while tube renewal as the mechanism responsible for the viscous zero-shear behaviour can nevertheless have reached a high degree. Thus, contour length fluctuation will govern zero-shear viscosity for $M < M_c$, but will be less effective for self-diffusion in the vicinity of M_c. Also, contour length fluctuation is expected to be more sensitive to free volume than curvilinear reptative motions as discussed in ref. 11.

On the other hand, a mechanism on the basis of contour length fluctuation might be of special importance for diffusion of star-branched polymers, where whole-chain reptation is prevented. Star-branched polymer chains are confined to star-branched tubes. A disengagement of the tube arms is possible by contour length fluctuation. If this fluctuation reaches contour length zero, which means that the whole branch consists of a fold just near the branching point, tube renewal will be complete. As long as an arm has contour length zero it will provide only minor resistance to displacements of the branching point. Thus the rate of branching point displacements is given by the contour length fluctuation rate. It would be interesting to combine relaxation[11] and diffusion data in a model on this basis.

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