

## Analysis of the dynamics of molten polyethylene in three components by proton relaxation spectroscopy of an isotopically diluted system

In this letter we report nuclear magnetic relaxation measurements on molten polyethylene in the frequency range  $10^4$  to  $10^8$  Hz. In previous papers<sup>1,2</sup> we have described the dynamics of molten polymers by three components.

Starting with the most elementary component which is directly accessible to thermal activation, we consider at first the anisotropic segment reorientation as a consequence of defect jumps. This process reduces the correlation function with a correlation time  $\tau_s$  down to a fraction  $a_2:a_1$  of the initial value.  $\tau_s$  can be interpreted as the mean defect jump time. A further reduction is achieved by two secondary processes.

Defect migration is connected with a material transport<sup>3</sup>. Thus we expect longitudinal chain diffusion within a 'tube' formed by the surrounding chains. As this displacement occurs along the conformation of that tube, we have to deal with a diffusion controlled loss of local orientation of the chain axis. Introducing an exponential orientation correlation function with a correlation length<sup>1,4</sup> we can define the mean diffusion time  $\tau_l = l^2/2 D_1$  as a characteristic time parameter.  $D_1$  is the curvilinear diffusion coefficient of the chains. As  $D_1$  is proportional to the inverse of the molecular weight<sup>6</sup>  $M$ , it holds for  $\tau_l \sim M$ .

The conformation of the surrounding tube is now not static, and we introduce the conformational fluctuation of that tube as the third component. This process can be considered to be competitive with the second component, because longitudinal chain diffusion as well as the tube fluctuation influence the local orientation of the chain axis. The reason for the conformational fluctuation is again given in our molecular picture of the longitudinal chain diffusion, but now also involves that of the neighbouring and entangling chains. The conformation of the 'tube' can be changed when an entanglement is untied. This means that the entangling chain of length  $L$  has to diffuse a mean square

displacement proportional to  $L^2$  on a curvilinear path. Thus it holds for the corresponding correlation time:

$$\tau_r \sim L^2/D_1 \sim M^3$$

Nuclear magnetic relaxation dispersion of polymer melts can now be described on the basis of this picture by the aid of the intensity function<sup>1</sup> given in equation (1)

In equation (1) the quantities are defined as follows:

$$K^{(j)} = \{1 + [\omega\tau_c^{(j)}]^2\}^{1/2}$$

$$\frac{1}{\tau_c^{(1)}} = \frac{1}{\tau_s} + \frac{1}{\tau_r} \approx \frac{1}{\tau_s}$$

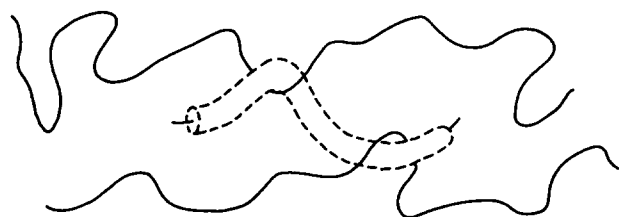
$$\frac{1}{\tau_c^{(2)}} = \frac{1}{\tau_r}$$

$a_2$  is the value of the dipolar correlation function to which this function would decay in the absence of the secondary processes;  $a_1$  is the initial value of the correlation function. (This expression is a somewhat more convenient version of the expression given for exponential orientation correlation functions in Table 1 of ref 1.)

It is possible to fit the time parameters  $\tau_s$ ,  $\tau_l$  and  $\tau_r$  of equation (1) to experimental data. This becomes the less ambiguous the more the molecular weight dependence of these parameters can be taken into account<sup>2</sup>. Nevertheless it was desirable to have an experimental tool to distinguish the individual components. In fact, direct evidence for the three component behaviour can be demonstrated by an experiment illustrated in Figure 1.

By measuring the proton  $T_1$  dispersion of diluted short chains dissolved in a matrix of long deuterated chains, one

$$I(\omega) = \sum_{j=1}^2 a_j \frac{2\tau_c^{(j)} + \tau_c^{(j)3/2} \tau_l^{-1/2} (1 + K^{(j)})^{1/2}}{K^{(j)2} + \frac{1}{2}\tau_c^{(j)} \tau_l^{-1} K^{(j)} + \tau_c^{(j)1/2} \tau_l^{-1/2} [(1 + K^{(j)})^{1/2} + \omega\tau_c^{(j)} (K^{(j)} - 1)^{1/2}]} \quad (1)$$



Observation of SHORT CHAINS  $\rightarrow \tau_l$   
in "tubes"  $\left. \begin{array}{l} \rightarrow \tau_s \\ \rightarrow \tau_r \end{array} \right\}$   
Formed by LONG CHAINS (deuterated)

Figure 1 Illustration to the isotopic dilution experiment

can artificially separate the intermolecular from the intramolecular components.  $\tau_l$  is then determined by a low molecular weight while  $\tau_r$  corresponds to the high molecular weight of the deuterated matrix. This experiment has been carried out with an apparatus described elsewhere<sup>5</sup>. The experimental data (Figure 2) have been obtained from normal polyethylene ( $M_n = 2200$ ;  $M_w/M_n = 1.11$ ) dissolved in deuterated polyethylene ( $M_n = 180\,000$ ;  $M_w/M_n = 2.4$ , degree of deuteration  $> 99\%$ ). The concentration of the PE 2200 was 10% by wt. No signal from the residual protons of the deuterated polyethylene was detectable. The results are just as expected from the model discussed above: the low frequency plateau of pure PE 2200 is shifted outside of our frequency range in the mixture as a consequence of the strong increase of  $\tau_r$ . The low frequency dispersion is then given by  $T_1 \sim \omega^{1/2}$  (equation 1). At high frequencies,

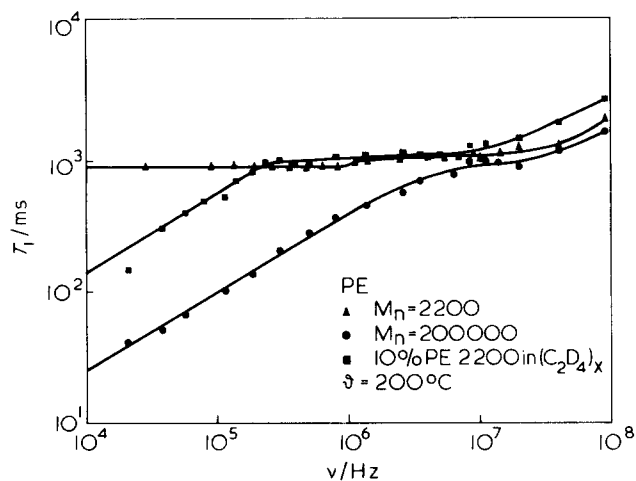


Figure 2 Frequency dependence of the longitudinal proton relaxation time  $T_1$  of various polyethylene samples at 200°C

where the anisotropic segment reorientation dominates, no essential alteration occurs. The somewhat higher values in the mixture are due to the fact that the intermolecular interaction has no influence here. For comparison we have plotted the  $T_1$  dispersion of undeuterated PE 200 000 in Figure 2.

We conclude that the three-component description of molecular dynamics together with experiments on iso-

topically diluted polymer melts allow a separate study of longitudinal chain diffusion and conformational fluctuations. We hope that the detailed analysis of the n.m.r. experiments presented here and of those currently in progress can clarify the discussion on polymer diffusion in the melt or in concentrated solutions<sup>6-9</sup>.

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