

Molecular motion in polymer melts:

2. Interpretation of relaxation data of poly(ethylene oxide)

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N.m.r. relaxation data of molten poly(ethylene oxide) are quantitatively analysed by the aid of the three components of molecular motion, defined previously. Polymer motion is described by the crankshaft fluctuation of orientation conserving defects and by longitudinal chain diffusion. Furthermore, a rotational diffusion of the local chain orientation is discussed. The theory explains the molecular weight dependence of the T_1 dispersion, the size of T_2 , the different behaviour of highly concentrated solutions and the temperature dependence of T_1 . The parameters, used for the description of the relaxation data, are compatible with data derived from other investigations. In addition, dielectric and mechanical relaxation data are qualitatively compared with the proposed model. The essential relaxation features of all methods agree well with the predictions of the three component description.

INTRODUCTION

In previous papers^{1,2} we have given an analytical and a numerical treatment of relaxation phenomena in polymer melts. Now we wish to compare the theoretical model calculations with diverse experiments performed on poly(ethylene oxide) melts.

The applied theory depends on the characteristic times of the three components of molecular motion²: τ_s (anisotropic segment reorientation by defect steps and flip-flops), τ_l (longitudinal chain diffusion within the surrounding tube as a consequence of defect diffusion) and τ_r (configurational fluctuation of the surrounding tube). The correlation function of anisotropic segment reorientation has been simplified as an exponential plus a constant, thus neglecting effects occurring at the highest available frequencies. The theoretical molecular weight dependences are^{1,2}: $\tau_s = \text{constant}$, $\tau_l \propto M$, $\tau_r \propto M^3$. Thus the molecular weight dependence of the relaxation data will be of special interest.

The investigation of polymer melts by relaxation methods is restricted to a relatively small range of temperatures, given by the melting point and the decomposition of the material. As a consequence, it is essential that frequency ranges as great as possible are applied. In this direction experimental efforts with diverse methods have been carried out.

Using a field modulation technique, n.m.r. relaxation times of poly(ethylene oxide) melts could be measured in the frequency range 10^3 – 10^8 Hz^{3–5}. Mechanical relaxation (MR) measurements could be extended over a range of 10^{-4} – 10^7 Hz^{6–8}, using diverse experimental methods. In the case of dielectric relaxation (DR) a range from 10 to 10^{10} Hz is available^{9,10}. The interpretation of these latter measurements at low frequencies, however, becomes difficult because of the influence of electric conductivity.

MOTION OF ORIENTATION CONSERVING DEFECTS IN POLY(ETHYLENE OXIDE)

In poly(ethylene oxide) (PEO) $[-(\text{CH}_2\text{CH}_2\text{O})_n-]$ there are

two types of main chain bonds: C–C and C–O. Both have rotational potentials with three-fold symmetry. Some characteristic energy data of these potentials are given in Table 1. All calculations, mentioned below, were performed using these data.

According to the values of Table 1, we expect an intramolecular defect energy for kinds ($gt\bar{g}$ or $gttt\bar{g}$ sequences)¹⁵ of 1.0 and 2.8 kcal/mol depending on whether the *gauche* positions are at two C–O bonds or at one C–C bond and one C–O bond (compare with Table 2). All other orientation conserving defects (e.g. torsions) are expected to have higher energies and are, therefore, not taken into consideration.

In Table 2 we give the possibilities of kink rearrangement in the special case of PEO. There are processes which shift the defect (steps) and reorientations without displacement of the defect (flip flop motions). The activation energies for the diverse processes are listed in the last column of Table 2. Furthermore, we have to deal with the simultaneous annihilation and creation (in a certain distance) of defects (jumps). The probable range of activation energies of jumps can be derived from the data given in Table 3.

Later we discuss the application of several relaxation methods for PEO melts. The question is to what extent the methods are sensitive to the processes. Nuclear magnetic relaxation has a strong sensitivity to a process, if H–H vectors of neighbouring protons are strongly disoriented. In the case of dielectric relaxation the disorientation of the

Table 1 Literature data of potentials in PEO. The values concern different model compounds and various methods, and should be taken as approximate estimations. For our purpose however, the accuracy is completely sufficient. E_1 is the energy in the *gauche* position; $E_{2,3}$ is the height of the potential barriers. All energies refer to the *trans* position

Bond	E_1 (kcal/mol)	$E_2 \approx E_3$ (kcal/mol)
C–C	–0.4 (ref 11)	3.0 (ref 13)
C–O	1.4 (ref 12)	2.7 (ref 14)

Table 2 Rearrangement of segments by orientation conserving defects. As an example a $2g1$ kink ($gt\bar{g}$ sequence) is considered. Double-kinks ($gt\bar{g} \text{ } tt \text{ } \bar{g}tg$ sequences) have similar relaxation features. The motions of higher order kinks ($2gn, n > 1$) and chain torsions are less probable because of energy reasons (inter- and intra-molecular respectively). The activation energies are calculated with the values of *Table 1*

Kink type	Process	Type of motion	Defect trans-lation?	Activation energy (kcal/mol)
I		Step	Yes	4.0
I		Flip-flop	No	4.7
I		Step	Yes	^c 4.3 ^d 6.1
II		Flip-flop	No	2.6
II				

Table 3 Activation energies (kcal/mol) for annihilation and creation of kinks in PEO according to data given in *Table 1* (elongation and contraction of chains are not taken into account). The activation energy of jumps depends on the cooperation of the annihilation and creation processes. If the processes are considered to be rigidly coupled, the values of annihilation/creation pairs have to be added. In reality the cooperation may be less strong leading to lower activation energies. The most probable processes are the annihilation of a kink type II and the creation of a kink type I or II

Kink type	Annihilation	Creation
I	4.7	5.7
II	2.6	5.4

C–O dipoles is relevant, while mechanical relaxation is sensitive to defect displacements. According to these differences the processes may appear at different frequencies with the diverse methods and may be more or less 'broadened'.

LONGITUDINAL N.M.R. RELAXATION

In contrast to transverse relaxation, the effect of a possibly heterogeneous microstructure usually does not affect the exponential behaviour of the longitudinal relaxation because of spin diffusion. If this averaging process is rapid enough compared with relaxation times then a distribution of correlation functions is obtained. As can be seen in part I of this series, the correlation functions themselves inherently contain a distribution involving the distance of the nearest chain bend from a reference segment. Both distributions will mix to one effective T_1 formula, and a distinction between both distributions is principally problematic.

In the following comparison with experiments, the T_1

formulae given in ref 2 are used without heterogeneity distribution. In other words, the given distributions are considered as limiting cases between which the real behaviour (including a possible heterogeneity distribution) is expected.

In *Figures 1–3* the theoretical curves according to the formulae in *Table 1* of ref 2 are compared with the T_1 dispersion of PEO melts and concentrated solutions reported in ref 4 and 5*. In fact three dispersion regions according to the three components of molecular motion can be separated: at the highest frequencies, anisotropic segment reorientation determines the dispersion. The theoretical description of this part is simplified because the broadening of this process expected by environmental fluctuation^{2,16} has been omitted. Principally, this broadening can easily be included in the theoretical curve at the expense of some additional parameters. The slowly rising dispersion region at medium frequencies is dominated by longitudinal diffusion of chains within the surrounding tube. The plateau occurring at the lowest frequencies is finally due to the fluctuation process of the surrounding tube.

In *Figure 1* the results for four molecular weights ($M_w/M_n < 1.5$) are plotted. Three of them ($M_n = 4000$, $M_n = 10\,000$ and $M_n = 27\,000$) are beyond the entanglement length, and the molecular weight dependence of the characteristic times are used as previously given^{1,2} ($\tau_l \propto 1/D_1 \propto M$; $\tau_r \propto M^3$). The lowest molecular weight ($M_n = 1000$), however, lies below the entanglement value. Thus, the configurational fluctuation of the surrounding tube should show a different dependence on the molecular weight. Remembering that this process is determined by the viscosity, we could achieve a slightly better fitting with⁷ $\tau_r \propto \eta \propto M^{0.9}$ for this particular value of the molecular weight.

* In ref 5 a mistake has occurred in the legends of the *Figures*. *Figure 1e* should be interchanged with *Figure 1f* and *Figure 1g* with *Figure 1h*.

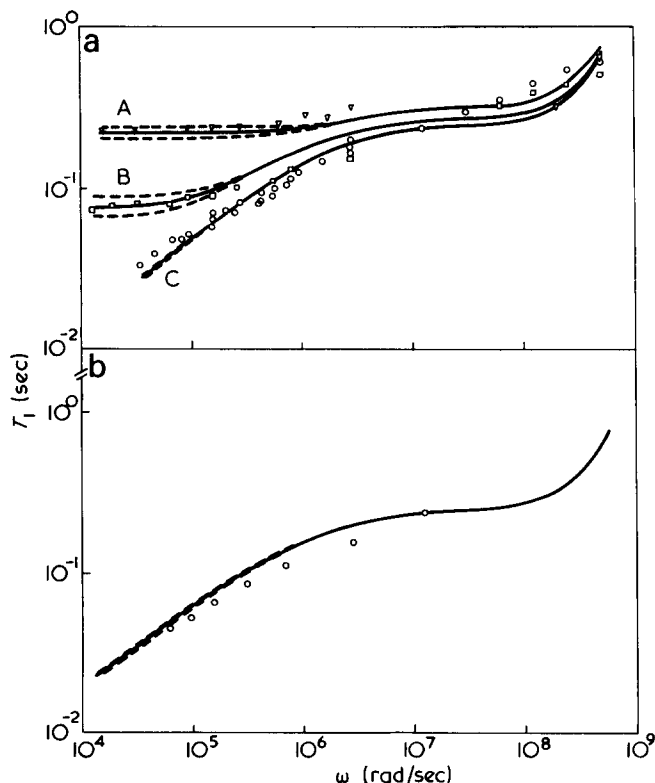


Figure 1 T_1 dispersion in PEO melts for various molecular weights (experimental data from ref 5). The fitted parameters (together with the confidence limits) are: the anisotropy parameter $p = A^{(i)}(\infty)/A^{(i)}(0) = 9.2 \times 10^{-3} \pm 15\%$; the mean correlation time for segment reorientation $\tau_s = 1.4 \times 10^{-9} \pm 10\%$ (sec); the diffusion time for the mean equally oriented reptation path within the surrounding tube $\tau_l = 4 \times 10^{-12} \times M \pm 40\%$ (sec) (M = molecular weight); the mean correlation time for the fluctuation of the surrounding tube $\tau_r = 7 \times 10^{-17} \times M^3 \pm 30\%$ (sec) (for $M = 1000$ this value must be multiplied by 6 as this molecular weight lies below the entanglement length)⁷. —, are theoretical curves for an exponential orientation correlation function of the surrounding tube²; ---, indicate the expected shift of the experimental points when the molecular weight is changed by $\pm 10\%$ (a) A, $M = 1000$; B, $M = 4000$; C, $M = 27000$. $\theta = 70^\circ\text{C}$. (b) $M = 10000$. $\theta = 70^\circ\text{C}$

The result of a least squares fit is plotted in *Figure 1*. Apart from the characteristic times the ratio $p = A^{(i)}(\infty)/A^{(i)}(0)$ of the squared interaction amplitudes of the correlation function for anisotropic segment fluctuation has been fitted. This parameter contains the information of the anisotropy of segment reorientation. $p = 1\%$ means that the total correlation function is reduced to 1% of the initial value by segment reorientation. In other words, segment reorientation averages out most of the dipolar field components. Consequently, rather small bends of the surrounding tube or slight deformations of its configuration are sufficient to reduce the remaining correlation to zero.

The parameter τ_s , representing segment reorientation, should be one order of magnitude longer than the actual reorientation times of segments, because our discussion includes only the mean value of this broadened process¹. In fact, the value derived in this way is compatible with the activation energies given in *Table 2* and with the experimental value of dilute solutions¹⁷.

Figure 2 shows the T_1 results at a higher temperature. Theoretical curves have been obtained with characteristic times calculated from the above given values (*Figure 1*) and activation energies 4, 4.5 and 5 kcal/mol (*Table 2*). In this

energy range, nearly identical high temperature curves have been found. Furthermore the T_1 dispersion of a concentrated solution in D_2O is shown in *Figure 3*. The theoretical parameters are the same as in *Figure 1* with the exception of p , which was found to be smaller than the melt value. This result is plausible because the incorporation of solvent molecules allows a greater space angle of spin-spin vectors to be reached by anisotropic segment fluctuation within the 'tube'.

Recently, longitudinal ^{13}C relaxation times independent of molecular weight have been reported¹⁸. The plateau of the T_1 versus M_n curve, found at high molecular weights, is completely compatible with the presented model (compare with *Figure 2* of ref 2).

In ref 5 a fit to the experimental results has been attempted using a translational diffusion model. This theory implies, however, that the distance of neighbouring spins is continuously changing according to the diffusion equation. This process could therefore only account for intermolecular interaction, the influence of which is rather small.

TRANSVERSE N.M.R. RELAXATION

The sample with the highest molecular weight ($M = 27000$) showed a non-exponential T_2 behaviour. There are several reasons for the occurrence of non-exponential transverse relaxation decays^{4,19}: either there is a residual dipolar broadening or (and) the sample is heterogeneous in the sense of differing microstructures or molecular weights and consequently different relaxation times T_2 . Even-

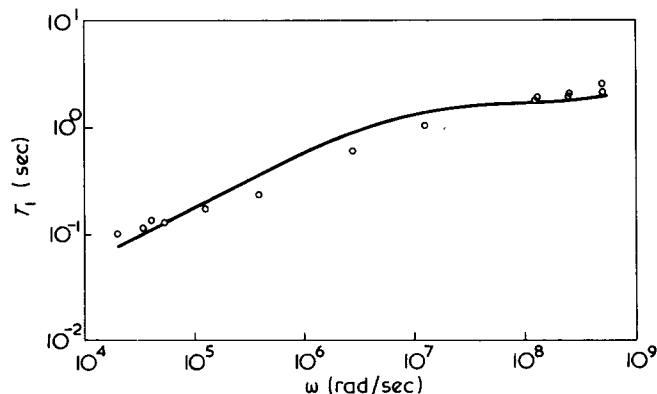


Figure 2 T_1 dispersion of molten PEO ($M = 27000$) at a higher temperature (158°C). The theoretical curve is obtained by extrapolating the correlation times fitted to the 70°C curves (*Figure 1*) with an activation energy 4.5 kcal/mol

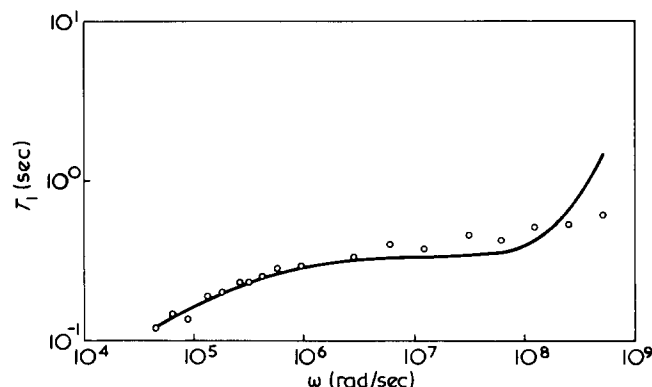


Figure 3 T_1 dispersion of a concentrated aqueous PEO solution ($M = 27000$; $C = 1\text{gPEO}/1\text{gD}_2\text{O}$). The correlation times given in the legend of *Figure 1* have been extrapolated to 50°C with an activation energy 4.5 kcal/mol. The amplitude ratio has been fitted to $p = 3.1 \times 10^{-3}$, indicating a greater motional freedom for segment reorientation

Table 4 T_2 values of PEO melts (70°C). The experimental values have been taken from ref 4

M	ν (MHz)	T_2 , exp. (msec)	T_2 , calc. (msec)
1000	32	168	270
4000	10	137	135
27 000	42	>9	6

tually, the inhomogeneous broadening due to an anisotropic susceptibility also plays a role. The influence of distributions of the molecular weight could be separated in ref 19. The PEO samples, discussed in this paper, have a rather narrow distribution of molecular weights ($M_w/M_n < 1.5$). Therefore, it is expected that one of the other reasons is responsible for the non-exponential T_2 behaviour. The high value of τ_r in the order of milliseconds suggests that the motional narrowing is incomplete for this sample. Furthermore the condition $T_2 \gg \tau_r$ is only unsufficiently fulfilled. Thus the usual T_2 theory can only yield a rough description of the transverse relaxation.

In part 1 of this series², we have shown that T_2 is strongly dependent on the reptational correlation time τ_l . Therefore, the range of T_2 can be used to check the parameter τ_l fitted to the T_1 dispersion. In Table 4, the T_2 range, found by Preißing⁴, is compared with the theoretical values, calculated with the parameter set of the T_1 dispersion (Figure 1).

COMPARISON WITH OTHER RELAXATION METHODS

The model theory derived in ref 2 in principle can be transferred to other relaxation methods. In this paper, however, we merely wish to check the compatibility of the previous discussion with dielectric and mechanical relaxation measurements.

The high frequency processes in PEO solutions and melts have been investigated in refs 9, 20 and 21 (compare also ref 22). Activation energies between 2.4 and 2.7 kcal/mol have been found in contrast to the 4 kcal/mol derived from nuclear magnetic relaxation¹⁷. This fact clearly shows the differences in the sensitivity of the methods to the diverse processes occurring in PEO. According to Table 2 the maximum of the dielectric loss curve could be dominated by the flip-flop motion of kink type II, while the observed distribution of relaxation times should involve all other relevant processes. Moreover, the studies in solution can be influenced by chain ends where the condition of orientation conservation is less stringent for a defect to reorientate. Therefore, low activation energies arising from rotations around single bonds contribute to the resulting distribution of relaxation times. The low frequency dielectric loss behaviour unfortunately allows no conclusion on molecular motions because of conductivity mechanisms^{9,10}.

Analogous to nuclear magnetic relaxation the molecular weight dependence of the components of the complex shear modulus varies with the applied frequency⁶. There is a strong temptation to use the previously explained components of molecular motion without modification for the description of the mechanical relaxation results. While in n.m.r. the behaviour of a set of spin-spin vectors is representative, mechanical relaxation is sensitive to the microstructural renewal processes within a volume element. This means, that the reorientation time of segments by crankshaft motions and the mean life time of entanglements can be interpreted as time constants determining mechanical relaxation at very low and very high frequencies. The latter time constant is proportional to the configurational fluctua-

tion time of a chain together with its surrounding tube. Thus the previously defined time constants τ_r and τ_s and their molecular weight dependence again become essential.

For $\tau \gg \tau_r$, the volume elements have lost their memory to the initial configurations of the included polymer chains. This means that for $\omega \ll 1/\tau_r$ the limits²³ $G' \propto \omega^2$ and $G'' \propto \omega$ are expected and observed (compared with the n.m.r. limits $T_1, T_2 = \text{constant}$). From this limit one derives the viscosity $\eta = G''/\omega$. The molecular weight dependence of the viscosity has also been directly determined^{7,15} and was found to be $\eta \propto M^{2.9}$ above the entanglement length as predicted by the model theory ($\lim_{\omega \rightarrow 0} G''/\omega \propto \tau_r \propto M^3$). In this way the three component description of polymer motion could be tested against experimental data for molecular weights up to 6×10^6 .

DISCUSSION

In the previous sections theoretical curves, based on essentially one single set of parameters, have been compared with experimental values which have been obtained under different conditions and with different samples. Nevertheless, the agreement between theory and experiments is satisfying, suggesting that the important features of molecular motion in polymer melts are included. It should, however, be noted that the theory is simplified in some aspects.

The anisotropic segment reorientation, which is responsible for the high frequency process, is influenced by environmental fluctuation, leading to a broadening of this process¹⁶. This leads to a far better description of the T_1 dispersion at high frequencies. Unfortunately, the theory extended in this way, requires some additional parameters. Therefore, the fitted value of τ_s should be regarded as a mean value of the various time constants determining this process.

A further question is the reality of the reptation mechanism (longitudinal chain diffusion by defects²⁴). There are some additional experimental facts, which support the existence of this type of motion, apart from the successful description of relaxation data: the diffusion coefficient D is clearly not affected by the so called entanglement length²⁵. The explanation could be that longitudinal diffusion is dominant in the experimental determination of D , while viscosity measurements will be influenced by the possibility of lateral chain movement too. The activation energy of the diffusion coefficient is smaller than that of the viscosity, probably for the same reason as mentioned above²⁶.

Tanner *et al.*²⁵ have found that at concentrated solutions the diffusion coefficient does not depend on the concentration, a fact which can easily be explained by the reptation mechanism because defect step times are not severely influenced by the solvent. On the other hand, dilute solutions show a proportionality $D \propto M^{-0.6}$ in contrast to $D \propto M^{-5/3}$ for bulk material. The latter result is compatible with the reptation mechanism¹, while in dilute solutions other diffusion processes are expected in agreement with the weak molecular weight dependence of D (lateral displacements).

Finally, the low frequency process due to the configurational fluctuation of the surrounding tube should be considered. Again we have assumed that this process is Poisson-like. This motion is, however, connected with the diffusion of neighbouring chains and diffusion processes normally deviate from a Poisson behaviour. On the other hand, each chain is surrounded by a huge number of chains. Therefore, the total effect of these chains might well be Poisson like. This means, that in equal time intervals, the same probability

for the process holds. Minor deviations from the Poisson behaviour will not be detectable because of the superposition of the reptation process.

In this paper a first analysis of relaxation data with respect to the suggested three components of molecular motion in polymer systems is reported. For the distinct observation of only one or two of these components, a couple of experiments are in preparation. Narrow fractions of higher molecular weight will separate the specific dispersion regions of the components according to their different dependence on the molecular weight. Crosslinkage of the molecules will prevent reptation. Finally, T_2 dispersion data are desirable because the transverse relaxation time specifically monitors low frequency processes.

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