

Molecular motion in polymer melts:

1. Description by components and n.m.r. relaxation behaviour

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A separation of molecular motion in polymer melts into three components is proposed on the basis of local defects. The components are: (a) defect reorientation with environmental fluctuation, leading to a rapid anisotropic segment motion; (b) longitudinal chain diffusion (de Gennes' reptation), and (c) configurational deformations of the surrounding tube. Analytical formulas for the longitudinal and transverse relaxation rates are given. The relaxation behaviour shows model specific features, which allow the proposed model to be checked with experiments.

INTRODUCTION

Molecular motion in polymer melts has been studied by several authors^{1,2} on the basis of fluctuating and diffusing local defects (rotational isomers of a few neighbouring segments). According to such local defect models a special type of chain motion, called 'reptation'¹, should occur. The purpose of this paper is to derive the n.m.r. relaxation behaviour, expected for the typical components of molecular motion which are related to local defect models. Thus, over all changes of the chain configurations will finally be described as the effect of thermally excitable elementary processes such as the hindered crankshaft rotation of segments.

As pointed out in recent papers^{3,4}, there are two main components of molecular motion in polymers: firstly we have to deal with the anisotropic motion of the segments, leaving a non-zero value of the correlation function in the limit of infinite times. This means that (a) the dipolar broadening of n.m.r. lines cannot be averaged out by this component alone, even if the motion is very rapid, and that (b) the final low frequency plateau of the T_1 dispersion cannot be attained by this part of the polymer motion. The remaining contribution, we have to consider, consists of any type of overall chain motion such as longitudinal diffusion and configurational fluctuations. If rapid enough, these components will cause the final averaging out of the dipolar broadening.

Previously, we have given an expression for the longitudinal relaxation time T_1 due to the reptation mechanism^{3,5}. In ref 6, the basic assumption that the reptation mechanism obeys the one-dimensional diffusion equation within the range of interest, has been discussed with the aid of a Monte Carlo simulation of the system. We now wish to extend the calculations to include configurational fluctuations of the 'tube', within which the reptation mechanism is assumed. Furthermore, the transverse relaxation time T_2 is drawn into consideration. Two different orientation correlation functions of the chains are assumed in order to obtain an idea of the influence of the type of these functions.

DEFINITIONS

The longitudinal relaxation rate in the case of dipolar interaction between equal nuclei with spin 1/2 is given by⁷:

$$\frac{1}{T_1} = \frac{9}{8} \gamma^4 \hbar^2 \sum_l c_l \sum_k [I_{k,l}^{(1)}(\omega_L) + I_{k,l}^{(2)}(\omega_L)] \quad (1)$$

In this formula, we have included the case of different phases of spins, denoted by the index l and weighted by the probability c_l . Among the diverse phases a rapid material or spin diffusional exchange compared to the inner-phase relaxation times is assumed⁸ according to the usually observed exponential relaxation curves. The sum over k comprises all nuclei interacting with a reference nucleus within a phase l . For simplicity, the summations over k and l are omitted in the following sections.

As to the transverse relaxation rate a situation of convenient simplicity arises if the dipolar broadening is averaged out. Otherwise the definition of transverse relaxation times becomes problematic. Furthermore, spin diffusion does not affect the transverse relaxation behaviour. If the material exchange is slow compared to the transverse relaxation processes, the relaxation curves should be composed of several exponential functions⁹. One component corresponding to the phase l of nuclei relaxes as⁷:

$$\frac{1}{T_2} = \frac{3}{16} \gamma^4 \hbar^2 \sum_k \left[\frac{3}{2} I_{k,l}^{(0)} + 15 I_{k,l}^{(1)}(\omega_L) + \frac{3}{2} I_{k,l}^{(2)}(\omega_L) \right] \quad (2)$$

Subsequently, we will again omit the indices k and l and the summation over k .

The relaxation rates depend on the intensity functions $I^{(i)}$ given as the Fourier transform of the correlation function $G^{(i)}(\tau)$:

$$I^{(i)}(\omega^{(i)}) = \int_{-\infty}^{+\infty} G^{(i)}(\tau) \exp(i\omega^{(i)}\tau) d\tau \quad (3)$$

where $i = 0, 1, 2$; $\omega^{(0)} = 0$; $\omega^{(1)} = \omega_L$; $\omega^{(2)} = 2\omega_L$ (ω_L is the Larmor frequency).

The correlation function can be expressed by⁷:

$$G^{(i)}(\tau) = \iint W(\mathbf{r}', 0 | \mathbf{r}'', \tau) \phi^{(i)}(\mathbf{r}') \phi^{(-i)}(\mathbf{r}'') d\mathbf{r}' d\mathbf{r}'' \quad (4)$$

where

$$W(\mathbf{r}', 0 | \mathbf{r}'', \tau) = p(\mathbf{r}') W^c(\mathbf{r}', \mathbf{r}'', \tau)$$

[$p(\mathbf{r})$ represents the *a priori* probability of finding the spin-spin vector \mathbf{r} ; $W^c(\mathbf{r}', \mathbf{r}'', \tau)$ represents the conditional probability of finding the spin-spin vector \mathbf{r}'' after a time τ if there was an initial vector \mathbf{r}' ; $W(\mathbf{r}', 0 | \mathbf{r}'', \tau)$ represents the probability of finding \mathbf{r}' at a time 0, and \mathbf{r}'' after a time τ ; $\phi^{(\pm i)}(\mathbf{r})$ represents the dipolar interaction function for the vector \mathbf{r} as defined in ref 7 p 289.]

In the case of a finite set of N discrete interaction states we obtain:

$$G^{(i)}(\tau) = \left(\phi^{(i)}(1) \dots \phi^{(i)}(N) \right) \begin{pmatrix} p(1) & \dots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \dots & p(N) \end{pmatrix} \quad (5)$$

$$\begin{pmatrix} W^c(1, 1, \tau) & \dots & W^c(1, N, \tau) \\ \vdots & \ddots & \vdots \\ W^c(N, 1, \tau) & \dots & W^c(N, N, \tau) \end{pmatrix} \begin{pmatrix} \phi^{(-i)}(1) \\ \vdots \\ \phi^{(-i)}(N) \end{pmatrix}$$

where we have replaced the spin-spin vectors by interaction state numbers.

If the initial interaction state is not correlated to the final states, which have been reached after the responsible process has occurred, then:

$$G^{(i)}(\tau) = \langle W^c(\mathbf{r}', \mathbf{r}', \tau) |\phi^{(i)}(\mathbf{r}')|^2 \rangle_{\mathbf{r}'} \quad (6)$$

Finally, if this process is a Poisson process (i.e. if there are equal probabilities for the occurrence of the process at all time intervals of equal length) the correlation function becomes exponential:

$$G^{(i)}(\tau) = \exp(-|\tau|/\tau_c) \langle |\phi^{(i)}(\mathbf{r}')|^2 \rangle \quad (7)$$

where τ_c is the correlation time.

In the following, anisotropic motions are discussed. This means that the correlation function due to these motions does not fall to zero in the limit of long periods τ . Consequently, we define the remainder of the correlation function in this limit $G^{(i)}(\infty)$ which is a measure of the anisotropy of the motion. The consequence of this remainder is a strong secular term concerning the transverse relaxation rate and, by circumstance, a remaining dipolar broadening.

COMPONENTS OF MOLECULAR MOTION AS EXPECTED IN THE LOCAL DEFECT MODEL

The conformation of the chains is considered to be highly distorted in the sense of rotational isomerism. An almost saturated concentration of defects is assumed (e.g. *gtg*-sequences) and the following features of defects are emphasized. (a) A reference segment within a defect can suffer a finite set of dipolar interaction states when the defect is diffusing across this segment. (b) Defects are generally able to diffuse in a series of steps or jumps¹⁰. (c) Defects contain stored length, i.e. a segment, which is passed by a defect, is displaced.

The latter two points imply the possibility of chain diffusion according to the de Gennes reptation model¹.

In order to define separable components of molecular motion in polymer melts, an arbitrarily chosen chain conformation is considered as shown in *Figure 1*. Three partial motions are expected for the representative chain part 1.

(a) Rapid anisotropic segment rearrangement by defect steps. In other words, this type of motion can be described by the crankshaft rotation of neighbouring segments, i.e. simultaneous rotation around parallel main chain bonds. Because of the mutual hindrance of defects, this type of motion will be 'modulated' by a fluctuation of the environment of a reference segment.

(b) Longitudinal chain diffusion (reptation) as a consequence of defect diffusion.

(c) Configurational fluctuation of the 'tube' surrounding the reference chain as a consequence of the reptation of the neighbouring chains. This component is understood to comprise all motions not involved in (a) and (b). In this way, the configuration of the tube itself is time dependent.

It is assumed that all three components are stochastically independent. The independence of components (a) and (b) from (c) is plausible because reptation and defect fluctuation are intrachain effects while the configurational fluctuation of the tube is an interchain effect. Components (a) and (b) are, strictly speaking, not stochastically independent: the reptation process is a consequence of defect fluctuation. In the time scale, however, in which reptation influences n.m.r. relaxation, each segment has re-oriented many times. In other words, reptation is caused in this limit by the movement of a large ensemble of defects and is thus practically uncorrelated to the diffusion steps of a single defect.

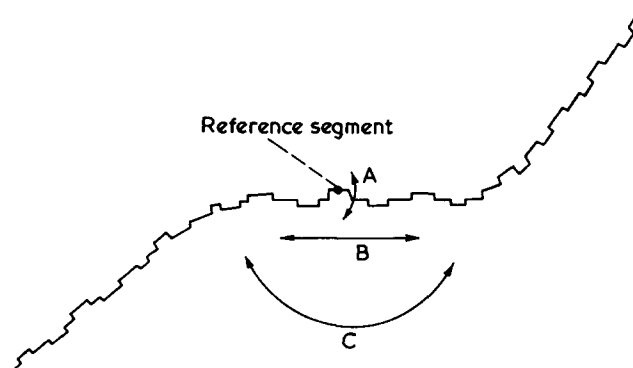


Figure 1 Schematic representation of the considered components of molecular motion in a chain entangled by neighbouring chains: A, segment reorientation with environmental fluctuation; B, chain diffusion ('reptation'¹); C, configurational fluctuation of the surrounding 'tube'

The resulting correlation function has then a form:

$$G^{(i)}(\tau) = A^{(i)}(\tau)b(\tau)c(\tau) \quad (8)$$

The letters A , b , c refer to the contributions defined above. $b(\tau)$ and $c(\tau)$ are reduced correlation functions because the dipolar interaction functions are included in $A^{(i)}(\tau)$.

Consequently

$$b(0) = c(0) = 1$$

and

$$b(\infty) = c(\infty) = 0$$

in contrast to

$$A^{(i)}(0) = \int p(\mathbf{r}') |\phi^{(i)}(\mathbf{r}')|^2 d\mathbf{r}' = \langle |\phi^{(i)}|^2 \rangle$$

and

$$A^{(i)}(\infty) = \iint p(\mathbf{r}') p(\mathbf{r}'') \phi^{(i)}(\mathbf{r}') \phi^{(-i)}(\mathbf{r}'') d\mathbf{r}' d\mathbf{r}'' = \langle \phi^{(i)} \rangle^2$$

REARRANGEMENT OF SEGMENTS

In ref 3 the rearrangement of segments in crystalline structures due to kink diffusion was treated by a random walk formalism as a 'one particle problem', i.e. mutual hindrance of kinks (environmental fluctuations) was neglected. As a consequence the diffusion effect was dominating. In polymer melts, however, defect concentrations are high and mutual hindrance of defects plays an essential role. In this sense we are dealing with a many particle problem.

There are two ways to treat such problems: either an approximate but analytical theory is used or a computer Monte Carlo simulation of the segment motion is carried out. Two models concerning the first method have been treated as Markov chains in ref 3. The second method is described in detail in ref 6.

Both methods lead to a correlation function of the type:

$$A^{(i)}(\tau) = \sum_j \tilde{A}^{ij} \exp(-|\tau|/\tau_j) + \tilde{A}^{i0} \quad (9)$$

The constant quantity \tilde{A}^{i0} characterizes the anisotropy of segment reorientation and dominates at long times compared with the fluctuation times τ_j . This process is 'broadened' because of the environmental fluctuation, as indicated by the different exponentials in equation (9).

The anisotropic remainder of equation (9) finally decays to zero if there is any process changing the local chain orientation. Longitudinal chain diffusion around bends of the surrounding tube is the first possibility for the final loss of correlation.

CHAIN DIFFUSION

We assume the validity of the one-dimensional diffusion equation for the chains reptating on a curvilinear path. In ref 6 this assumption has been shown to be justified within the time scale relevant for the interpretation of T_1 dispersion measurements.

Following the treatment in ref 3, the chain diffusion factor in equation (8) is given by the ensemble averaged probability that a reference segment with a given initial orientation has the same orientation after a time τ :

$$b(\tau) = \int_0^\infty \rho(\bar{x}) 2 \int_0^{\bar{x}} \eta(x, \tau) dx d\bar{x} \quad (10)$$

$\rho(\bar{x})$ is the probability that the nearest bend of the surrounding tube is at a distance \bar{x} from the reference segment. The factor 2 is necessary because there are final positions with the same tube orientation on both sides of the reference segment. $\eta(x, \tau)$ is the probability that the reference segment diffuses a distance x within a period τ .

Thus, $\int_0^{\bar{x}} \eta(x, \tau) dx$ is the probability that the reference segment is in the range $0 \leq x \leq \bar{x}$ after a period τ . The exterior integration gives the average over all lengths \bar{x} .

The solution of the diffusion equation yields¹¹:

$$\eta(x, \tau) = \frac{1}{2(\pi D_1 \tau)^{1/2}} \exp(-x^2/4D_1 \tau) \quad (11)$$

Generally we have to assume a time dependence of the curvilinear diffusion coefficient D_1 , i.e. $D_1 \tau$ should be replaced by:

$$\int_0^\tau D_1(t) dt$$

where

$$D_1(t) = \frac{1}{2} \frac{d\langle r^2 \rangle}{dt}$$

In ref 6, however, it can be seen that at times, large compared to the correlation times of defect sequences, an effective and constant diffusion coefficient can be used to a good approximation.

Thus we obtain:

$$2 \int_0^{\bar{x}} \eta(x, \tau) dx = \operatorname{erf} \left(\frac{\bar{x}}{(4D_1 \tau)^{1/2}} \right) \quad (12)$$

The analytical form of $\rho(\bar{x})$ depends on the microstructure. Two limiting cases will be considered in order to learn something about the influence of $\rho(\bar{x})$ on the final results:

(a) The unidirectional distance-distribution is rectangular, i.e. all unidirectional parts of the surrounding tube are of equal length:

$$\rho(\bar{x}) = \frac{1}{2l} \text{ for } 0 \leq \bar{x} \leq 2l$$

= 0 otherwise

$2l$ is the total length of the unidirectional parts of the surrounding tube.

(b) The other, more plausible case is an exponential distance-distribution of the nearest tube bend, which means that there is the same probability at each segment that the surrounding tube changes its orientation:

$$\rho(\bar{x}) = \frac{1}{l} \exp(-\bar{x}/l) \quad (14)$$

$2l$ is now the mean distance from one bend to the next. For case (a) we obtain:

$$b(\tau) = \operatorname{erf} \left(\frac{l}{(D_1|\tau|)^{1/2}} \right) + \frac{\exp(-l^2/D_1|\tau|) - 1}{l \left(\frac{\pi}{D_1|\tau|} \right)^{1/2}} \quad (15)$$

The result in case (b) is:

$$b(\tau) = \left\{ 1 - \operatorname{erf} \left[\frac{(D_1|\tau|)^{1/2}}{l} \right] \right\} \exp(D_1|\tau|/l^2) \quad (16)$$

The characteristic time of this function is the medium diffusion time for a distance l :

$$\tau_l = l^2/2D_1$$

CONFIGURATIONAL FLUCTUATION OF THE SURROUNDING 'TUBE'

This component will be due to changes in the environmental microstructure of a chain, allowing the chain to alter its conformation without diffusing in the longitudinal direction. We assume that the conformational changes of this kind are of equal probability in all time intervals of equal length, i.e., we have a Poisson process. A justification of this assumption is the fact that the 'tube' is formed by many neighbouring chains, entangling the reference chain. The

removal of any one of them via reptation can cause this type of fluctuation.

The reduced correlation function is then:

$$c(\tau) = \exp(-|\tau|/\tau_r) \quad (17)$$

where τ_r is the rotational correlation time of the local tube orientation. τ_r will be determined by lateral diffusion of chain parts. This implies that at high molecular weights the mean life time of chain entanglements will dominate. If L is the mean chain length, we obtain¹²:

$$\tau_r \propto L^2/D_1 \quad (18)$$

RESULTING RELAXATION FORMULAS

In order to obtain the final relaxation formulas equations (1) and (2), we have to Fourier transform the correlation equation (8):

$$I^{(i)} = \mathcal{F}^{(i)}\{G^{(i)}(\tau)\} = 2 \operatorname{Re} \mathcal{L}^{(i)}\{G^{(i)}(\tau)\} \quad (19)$$

($\mathcal{F}^{(i)}\{\}$) signifies Fourier transformation with respect to frequency $\omega^{(i)}$; ($\mathcal{L}^{(i)}\{\}$) corresponds to the Laplace transformation. It should be noted that the correlation function is even). The Laplace transform pairs, needed for equation (19), can be found in ref 13. The results are given in Table 1 and Figure 2.

The expected features of the frequency dependence of T_1 (Figure 2) can be summarized as follows: (a) a low frequency plateau due to configurational fluctuation of the surrounding 'tube'; (b) a flat dispersion region at medium frequencies due to longitudinal chain diffusion; (c) the high frequency behaviour will be dominated by anisotropic seg-

Table 1 Intensity functions for both orientation correlation functions discussed in this paper. The n.m.r. relaxation rates are given by equations (1) and (2)

Distance distribution, ρ	Intensity functions, $I^{(i)}(\omega^{(i)})$
Exponential, equation (14)	$\sum_j 2\bar{A}^{i,j} \frac{\delta_j + 2a b_{i,j} \cos \phi_{i,j}}{b_{i,j}^4 + 4a^2 b_{i,j}^2 + 4ab_{i,j}(\delta_j \cos \phi_{i,j} + \omega^{(i)} \sin \phi_{i,j})}$
Rectangular, equation (13)	$\sum_j 2\bar{A}^{i,j} \left\{ \frac{\delta_j - \exp\left(-\frac{b_{i,j}}{2a} \cos \phi_{i,j}\right) \left[\delta_j \cos\left(\frac{b_{i,j}}{2a} \sin \phi_{i,j}\right) - \omega^{(i)} \sin\left(\frac{b_{i,j}}{2a} \sin \phi_{i,j}\right) \right]}{b_{i,j}^4} \right. \\ \left. + 2a \frac{\exp\left(-\frac{b_{i,j}}{a} \cos \phi_{i,j}\right) \left[\cos\left(\frac{b_{i,j}}{a} \sin \phi_{i,j} + 3\phi_{i,j}\right) + \frac{b_{i,j}}{a} \cos\left(\frac{b_{i,j}}{a} \sin \phi_{i,j} + 2\phi_{i,j}\right) \right]}{b_{i,j}^3} \right. \\ \left. - \frac{2a}{b_{i,j}^3} \cos 3\phi_{i,j} \right\}$

where:

$$\delta_j = \frac{1}{\tau_j} + \frac{1}{\tau_r} \approx \frac{1}{\tau_j} \quad (j \neq 0); \quad \phi_{i,j} = \frac{1}{2} \arctan \frac{\omega^{(i)}}{\delta_j}; \quad \omega^{(i)} = i\omega_L$$

$$\delta_0 = \frac{1}{\tau_r}; \quad b_{i,j} = (\delta_j^2 + \omega^{(i)2})^{1/4}; \quad i = 0, 1, 2$$

$$a = \frac{1}{2l} D_1^{1/2} = \frac{1}{2(2\tau_l)^{1/2}}; \quad j = 0, \dots, n [n \equiv \text{number of exponentials contributing to } A^{(i)}(\tau)]$$

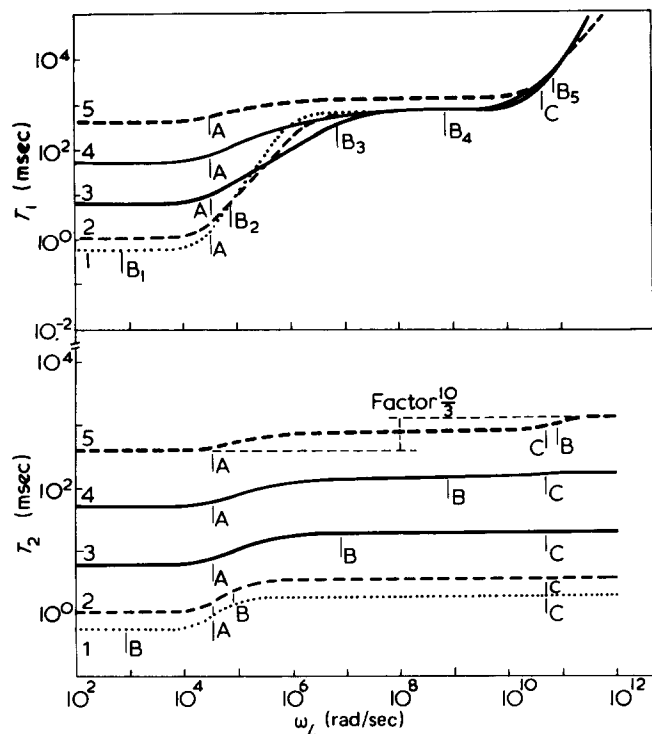


Figure 2 T_1 and T_2 dispersion for a homogeneous phase of spin pairs with exponential orientation correlation function according to Table 1. The curve parameter is the mean diffusion time τ_l for the correlation length l . In this plot, we have used for simplicity one exponential of equation (9) with the correlation time τ_s . Parameters other than indicated in the plots:

$$\frac{9}{8} \gamma^4 \hbar^2 G^{(1)}(0) = 2.7 \times 10^9 \text{ sec}^{-2};$$

$$l(0) : l^{(1)}(0) : l^{(2)}(0) = 6 : 1 : 4;$$

$$\bar{A}^{1,1} : \bar{A}^{1,0} = 10^3$$

The time constants for segment fluctuation (τ_s), longitudinal chain diffusion (τ_l) and the fluctuation of the surrounding tube (τ_r) are given by positions A, B and C, respectively: A, $\omega_L \tau_r = 1$; B, $\omega_L \tau_l = 1$; C, $\omega_L \tau_s = 1$

ment reorientation finally leading to a high frequency limit $T_1 \sim \omega_L^{-2}$. [In Figure 2, only one exponential of equation (9) has been used for simplicity. This process will, however, be 'broadened' in reality by environmental fluctuations.]

Provided that reptation (b) is slow enough, the dispersion of T_2 will be characterized by a single step (curves 1 to 3 in Figure 2). It should particularly be noted that the high frequency process does not essentially influence the T_2 dispersion in this case, because the secular term is dominating.

The comparison of the curves for exponential and rectangular distance distributions of nearest chain bends shows that the type of distribution causes no remarkable change of the dispersion curves. The deviations of both types of curves are less than 20%. Consequently we expect that the analysis of experimental relaxation dispersion data does not essentially depend on the chosen distribution.

DISCUSSION

The suggested separation of molecular motion into three components is quite general. The question remains, how-

ever, whether the components can be experimentally distinguished. There are three reasons, why such a distinction can be expected to be possible. (A) The time scales, within which the processes occur, are very different, because configurational fluctuation of the surrounding tube is the consequence of reptation while reptation is the result of defect diffusion i.e. segment reorientation. The diffusion lengths, determining the time scales of reptational and configurational fluctuations, are also quite different, provided that the chains are longer than the entanglement length. (B) The relaxation time dispersions of the components sensitively depend on the type of the motions. (C) All components have quite different dependences on the molecular weight. In ref 6 we have shown that $D_1 \propto M^{-1}$. Thus $\tau_l \propto D_1^{-1} \propto M$ and $\tau_r \propto L^2 D_1^{-1} \propto M^3$ while the elementary process for all components, i.e. the defect motion, is independent of the chain length.

The high frequency process (segment reorientation) is somewhat difficult to analyse because only rough estimations of the distribution of exponentials in equation (9) are possible. Therefore, T_2 relaxation measurements have the advantage, essentially not to be influenced by this process. On the other hand, problems not arising in T_1 dispersion appear. Any kind of heterogeneity in the sample will cause a multicomponent transverse relaxation if the material exchange between the diverse components is slow compared with T_2 . (This phenomenon often does not occur in T_1 relaxation because of the effect of spin diffusion.) If chain diffusion and configurational fluctuation of the surrounding tube are slow compared to the inverse dipolar line width, a residual dipolar broadening will be left. Thus, the analysis of transverse relaxation curves becomes problematic.

It will be valuable to consider all kinds of relaxation measurements for a comparison. There is a great deal of experimental material in the literature, requiring an extensive comparative study. This will be carried out in part 2 of this series. Especially, the contribution of the diverse components, introduced in this paper, will be discussed in detail.

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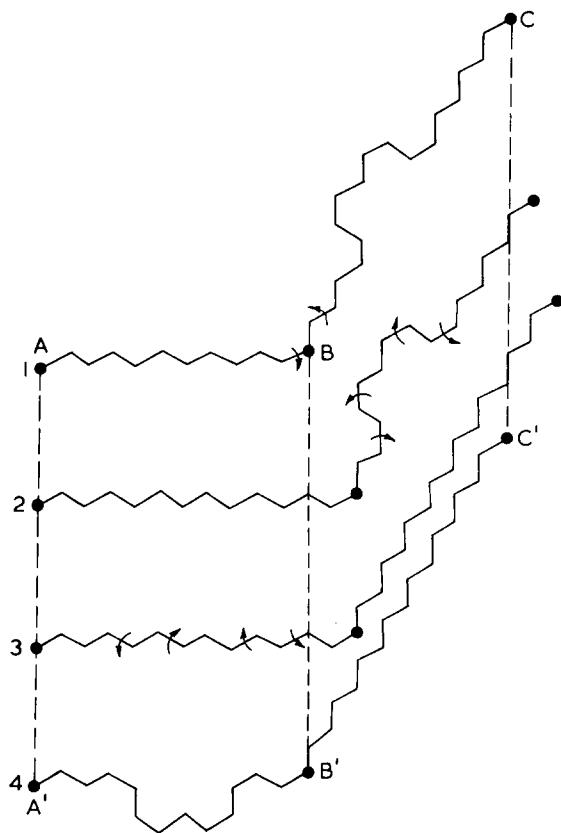


Figure A1 The indicated processes refer to the text

APPENDIX

Exemplary process of defect diffusion across gauche bends

The reptation model requires defects which are able to diffuse along the chain. The question is now whether such defects can cross *gauche* bends of the main chain orientation. In polymer melts, all possible crankshaft motions of the main chain are excited to a very high degree. So, combinations of such processes lead to the possibility that defect states are *effectively* transported across *gauche* bends of the chain.

In order to demonstrate this, *one* example of such a process is considered. This process is separated into three intermediate steps which should occur practically simultaneously (Figure A1). The first step is a crankshaft motion, shifting the *gauche* position at point B together with the right hand part of the chain to the right (1 → 2). The displacement of the right-hand chain part can be removed by annihilating the existing double kink and creating a new double kink on the *left-hand* side of the *gauche* position (2 → 3 → 4).

The net effect of the total process is that a double kink or two bond lengths have effectively been transported across the *gauche* bend from the right to the left.