Effect of molecular mobility on the decay of free radicals in amorphous polymers: a Monte Carlo study

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An algorithm has been formulated for studying the diffusion-controlled reactions in amorphous polymers. A method has been proposed based on molecular mobility and leading to migration of radical centres, their approach and decay. In a volume of dimensions 70 × 100 × 123 Å, using boundary periodic conditions, an amorphous polymer system and free radicals are simulated on a diamond lattice by the Monte Carlo method. Owing to crank, kink and crankshaft motions, some of them approach one another and decay. A change in the concentration of free radicals with time and temperature has been observed by the method described.

(Keywords: amorphous polymer; free-radical decay; molecular mobility; Monte Carlo)

INTRODUCTION

Radical processes in solid polymers have recently been thoroughly examined experimentally. Either a decay of the whole set of radicals from the overall spectra was studied or decay characteristics of the individual types of radicals were done separately. Some peculiarities in the behaviour of radicals in solid polymers were observed in both cases. One of them is their relatively long lifetime, which is due to the fact that the reactions are diffusion-controlled. The diffusion coefficient in the solid phase is generally low, but depends on temperature, and the decay curves of free radicals are therefore functions of temperature. The radicals are stable at temperatures well below T_g (in poly(methyl methacrylate) (PMMA) and polystyrene (PS), for example, radicals formed by γ-radiation are stable even at room temperature[1]). Under gradual heating of the sample, the concentration of radicals decreases and all radicals usually decay at T_g. This trend varies with a change of conditions leading to a change in T_g of the polymer (external pressure[2], modification of the original polymer structure, copolymerization[3], cross-linking, etc.). However, these facts indicate unambiguously that there is connection between the stability of free radicals and molecular mobility in solid polymers. In addition to a purely kinetic approach to radical processes developed mainly by Dole[4], attention has also been directed towards aspects of radical decay taking account of their diffusion.

The classical papers of Smoluchowski[5] dealing with the problems of diffusion-controlled reactions were later followed by studies of simpler systems[6] and then of polymers[7–10]. Although remarkable results were achieved mainly in the area of understanding many experimental results[8,9], it always happened after simplifications that usually do not allow solutions of concrete polymeric systems and provide more qualitative insight into experimentally obtained results.

In this paper we intend to study the problems of the decay of radicals from a different point of view. Instead of the analytical formulation of the problem of diffusion of active particles in a polymeric system, radical decay will be examined by the Monte Carlo method. The rotational isomeric-state (RIS) model will be used[11]. Various types of elementary motions of the various segments of the polymer chain will take place on a diamond lattice as a function of temperature. During these motions, transport of centres, where an unpaired electron is localized, is observed, which enables transfer or decay of radicals according to the character of the environment of a radical.

THEORETICAL BACKGROUND

Rotational isomeric-state model

The use of the RIS model is popular mainly in connection with the modelling of polymers on a tetrahedral lattice. One idea of the procedure, namely that the conformation of a macromolecule goes through a finite number of possible minima on the potential energy curve for rotation around a bond, is applied in the Monte Carlo process of chain building[10–14]. The probability of occurrence of the conformation, $P(\phi)$, defined for a set of angles $\{\phi_i\}$, is given by the product of probabilities $p\{\phi_{i-1}, \phi_i\}$. Here $p(\phi_{i-1}, \phi_i)$ is the probability that the conformation of the bond i ($i \neq 2$) is ϕ_i at the given ϕ_{i-1} for the preceding bond. Thus:

$$P(\phi)=p(\phi_2)p(\phi_2, \phi_3)\cdots p(\phi_{N-2}, \phi_{N-1}) \qquad (1)$$

In the RIS model, three values are usually assigned to the angle ϕ, and the corresponding bond conformations are denoted as t ($\phi=0°$), g^+ ($\phi=120°$) and g^- ($\phi=-120°$) with respect to the conformations of the preceding bonds. N is the number of bonds in the chain; $p(\phi_2)$ is the probability that the second bond will be in the conformation ϕ_2. The conditional probability $p(\phi_{i-1}, \phi_i)$ for the rotational state of bond i represented

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by one of the values of the angle ϕ_i will be determined by the statistical weight matrix $\mathbf{U}_i$ introduced by Flory[11]:

$$\mathbf{U}_i = \begin{array}{c} \\ (t) \\ (g^+) \\ (g^-) \end{array} \begin{array}{c} \begin{array}{ccc} (t) & (g^+) & (g^-) \end{array} \\ \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{pmatrix}_i \end{array} \tag{2}$$

where $u(\phi_{i-1}, \phi_i) = \exp[-E(\phi_{i-1}, \phi_i)/RT]$ and $E(\phi_{i-1}, \phi_i)$ represents the relative energy of the nearest-neighbour interactions. Symbols for statistical weights corresponding to particular combinations of the sequences of bonds i and $i-1$ are evident from (2). According to Flory (for alkane chains) $\sigma = \exp(-0.5\,\mathrm{kcal\,mol^{-1}}/RT)$, $\omega = \exp(-2\,\mathrm{kcal\,mol^{-1}}/RT)$. The method of determination of $p(\phi_{i-1}, \phi_i)$ so that the chain conformation would correspond to condition (1) has been reported elsewhere[15]. (Detailed discussion of the problem of the determination of the p values is given in ref. 28.) We have:

$$p(\phi_{i-1}, \phi_i) = p(\phi_2) u(\phi_{i-1}, \phi_i) [\mathbf{U}^{N-i-1} q]_{\phi_{i-1}} / [\mathbf{U}^{N-i} q]_{\phi_i} \tag{3}$$

where $[\ \ ]_{\phi_i}$ means that the element of the vector in brackets is taken such that it corresponds to the rotational state of the respective bond. If ϕ_i is t, g^+, g^-, the first, second and third elements respectively are taken; q is the (column) vector $(1, 1, 1)^{\mathrm{T}}$.

In building the chains by the Monte Carlo method, condition (1) is fulfilled as follows[12]:

(i) Elements of the matrix of the conditional probabilities $\mathbf{P}$ for the ith bond will be denoted by $p_{i,ab}$; $p_{i,ab}$ is the probability that configuration b corresponds to the angle ϕ_i of bond i $(2 < i < N-1)$ given that bond $i-1$ is in conformation a. The symbols a, b, c show that the angle ϕ corresponds to t, g^+ and g^-, respectively.

(ii) From the three possible isomers of the ith bond, an isomer will be chosen with respect to the bond $i-1$ according to the interval into which a random number ξ will fall in terms of the following conditions:

$$\begin{array}{lll} p_{i,aa}, & p_{i,aa} + p_{i,ab}, & 1 \\ p_{i,ba}, & p_{i,ba} + p_{i,bb}, & 1 \\ p_{i,ca}, & p_{i,ca} + p_{i,cb}, & 1 \end{array} \tag{4}$$

If the $(i-1)$th bond is in the state a, then it is chosen according to the first row of (4). If random number $\xi \leqslant p_{i,aa}$, ϕ_i is an angle corresponding to state t. If $\xi < p_{i,aa}$ ξ is compared with $p_{i,aa} + p_{i,ab}$, and if $\xi \leqslant p_{i,aa} + p_{i,ab}$, ϕ_i assumes the value corresponding to g^+, etc. In agreement with Flory[11], configurations $g^{\pm} g^{\mp}$ are refused $(\omega = 0)$.

(iii) In chain building, we shall consider an excluded volume with a sphere of radius 3 Å.

Chain building proceeded on a tetrahedral lattice in volumes with edges L_1, L_2 and L_3 with periodic boundary conditions. With regard to the problem being solved, i.e. free-radical decay, we do not insist on the same chain lengths. The beginnings of chains and the orientation of the first two chain bonds are selected at random by means of random numbers. The development of the chain follows from the above procedure, applied until a 'cul-de-sac' is reached. Then the chain is built up from the other end until it stops in a 'cul-de-sac'. Then we start with a new chain.

Tetrahedral lattice

The strategy of building up of the chains and the motion of their segments is very simple when using vector symbols developed by Wall *et al.*[13,14]. All bond conformations, the whole chain and its configurational changes on a tetrahedral lattice may be described by four vectors α, β, γ, δ defined by the components listed in *Table 1*. The absolute values of all components are equal to 1 and the absolute value of vectors is therefore $\sqrt{3}$. The chain is built up as a sum of vectors from *Table 1*, a positive vector always being followed by a negative vector and vice versa. The negative vector (or its components) is denoted by a bar over the symbol (see *Table 1*).

A step chosen as described above (in subsection on RIS model) is characterized by one of the vectors. Here we can formulate several simple rules:

(i) A vector is never followed by its negative.

(ii) A chain with all bonds in *trans*-configuration is described as simple alternation of two symbols, e.g. $\alpha\bar{\beta}\alpha\bar{\beta}\cdots$.

(iii) When the number of bonds is even and if all vectors appear twice with reverse sign, the chain is closed, e.g. $\alpha\bar{\beta}\gamma\bar{\alpha}\beta\bar{\gamma}$.

(iv) To an arbitrary sequence of vectors, which defines the chain, e.g. $\bar{\alpha}\delta\bar{\alpha}\cdots$, the zero vector may be added as a sum, e.g. $\gamma\bar{\gamma}$, and the resulting position of the chain will be the same; that is, $\bar{\alpha}\delta\bar{\alpha}$ ends in the same place on the lattice as $\bar{\alpha}\gamma\bar{\alpha}\delta\bar{\gamma}$ (commutability of vectors in vector sum and rule (i) were taken into account).

Intra- and intermolecular interactions

The energy of the chain corresponding to these interactions is composed of bond rotational energy and the energy due to the interaction of non-bonded atoms in the molecule and in other molecules. Thus the energy E is expressible as:

$$E = \sum_{i=2}^{N-1} u_i^{\mathrm{R}}(\phi_i) + \sum_{\substack{m=1 \\ l > m+3}} \sum_{l} u(r_{lm}) \tag{5}$$

The first summation runs over the bonds of the polymer chain, the second through atoms of its own and other chains in the system. $u_i^{\mathrm{R}}(\phi_i)$ is the energy corresponding to the rotational state of the ith bond and for alkanes it has the form:

$$u_i^{\mathrm{R}}(\phi_i) = \sum_{n=0}^{5} a_n \cos^n \phi_i \tag{6}$$

with $\sum_{n=0}^{5} a_n = 0$ so that the zero of energy is *trans*. The molecule is modelled as a chain of $N-1$ bonds that connect n vertices. Each vertex represents a carbon atom and its substituents. Parameters in (6) may be chosen, for example, according to Skolnick and Helfand[16] or according to Montgomery *et al.*[17] $u(r_{lm})$ is the energy of

Table 1 Components of vectors in tetrahedral lattice

Vector	Components		
	x	y	z
α	1	1	1
β	1	$\bar{1}$	$\bar{1}$
γ	$\bar{1}$	1	$\bar{1}$
δ	$\bar{1}$	$\bar{1}$	1

interaction of a pair of atoms l, m situated at a distance r_{lm}. The second sum of the RHS of (5) covers all the distinct pairs formed by atoms that are separated further than third nearest neighbours of the same molecule and all atoms belonging to different molecules.

There are several empirical potentials used for the representation of $u(r_{lm})$[18]. We shall use a Lennard-Jones potential:

$$u(r_{lm})=4\varepsilon^*\left[\left(\frac{r_0}{r_{lm}}\right)^{12}-\left(\frac{r_0}{r_{lm}}\right)^{6}\right] \qquad (7)$$

where r_0 is defined so that $u(r_0)=0$; $-\varepsilon^*=u(r_{lm})_{\min}$. Since, from the form of (7), it follows that the value of $u(r_{lm})$ decreases rapidly with increasing r_{lm}, in our considerations we shall assume that $u(r_{lm})=0$ for $r_{lm}>6$ Å.

Generation of free radicals

Free radicals are prepared experimentally by several methods. During mechanical destruction of the sample, radicals are formed via skeletal bond rupture. Radicals are usually in a thin surface layer of small pieces of destruction products and primary radicals are of the end type. Another widespread method is radiation, which generates radicals over the whole volume and, in addition to end radicals, radicals may also be formed on the chain. The generation of radicals via a chemical route is a less often used method. It is mainly applied in connection with the application of high pressure, which stabilizes polymer radicals by shifting T_g to higher values and allows the use of peroxide radicals for reactions with polymers[19]. This method forms radicals over the whole volume.

To study radical decay by the Monte Carlo method, free radicals are generated in the whole volume with the polymer sample prepared (see 'RIS model' above) in agreement with the method of preparation of radicals in the particular experiment. The system of random numbers will be used so that the first will determine the chain and the second the atom where the free radical will be located. Various restrictions following from the experiment may be introduced by additional conditions. Without them, the distribution of radicals in the volume should approach the experimental distribution observed after long sample irradiation.

Decay of free radicals

At very low temperatures, the radicals are stable. They decay stepwise with increasing temperature[20]. On increasing the temperature, the concentration changes remarkably in a relatively short time and, if the temperature remains constant, the concentration of radicals is stabilized. As the temperatures, at which the radicals are stable, increase, radical pairs decay at first (their distance apart being 10 Å). Deviations of chain segments from the energy minimum are often sufficient for their decay. Most probably, however, it is simple motion with low activation energy that contributes to their approach. With increasing temperature, motions of larger extent occur, leading to migration of the radical centres and their decay.

Types of molecular motions in solid polymers

We start from our model, where everything takes place on a tetrahedral lattice. This fact reduces the number of possible motions in real systems to several types. This, on the one hand, facilitates theoretical procedures but, on the other, it means that bonds and bond angles are fixed and only discrete types of motions connected with rotation around bonds are considered. Two simplifications are used, the RIS approach and restriction to a tetrahedral lattice.

If the rotational energy minima are well defined, a tangible physical basis exists for adoption of the RIS scheme. The potentials affecting torsional rotations ϕ about single bonds of the chain backbone usually possess minima separated by barriers at least several times the thermal energy kT[21]. With judicious choice of rotational states, the error involved using the RIS scheme is generally within the limits of accuracy of basic information on bond rotations, non-bonded interactions, and so forth[11].

The question of how further restriction to tetrahedral lattice affects the results has been studied in detail[22–24]. The result is not unambiguous. Fixman[22] proposed an effective potential that compensates the error from the use of constant inner coordinates; however, the computational effort involved in the repeated calculation of the metric tensor, which enters the theory, is so large that it is questionable[23] whether this is a simplification with respect to the use of the model without a lattice. The results obtained from ref. 24 show that the tetrahedral lattice is an acceptable approximation to the rotational states of the carbon backbone if second-neighbour interactions are considered. It has to be elucidated whether small flexibility in real bonds and bond angles has any significance in large-system motions[23].

We study three types of molecular motions, which are real in amorphous polymers: crank, crankshaft and kink. All these motions are possible in solid polymer systems[25] and allow migration and approach of radicals that were originally spatially separated. The extent of these motions depends, of course, on the polymer and mainly on temperature. There are several possibilities for the realization of each of them. For instance, in crank motion, there may be rotation of two, three, four and more chain-end bonds, of course, with activation energy that increases with the increasing number of bonds in the moving group. Similarly, crankshaft motion may be simplest—three-bond (Boyer crankshaft)—or multi-bond[26]. Kink motion may occur in various surroundings and the activation energy will also depend on the cohesion energy. Northrup[27] found that the existence of a kink on its own or on the neighbouring chain lowers the barrier for the formation of another kink. This provides a starting point for the choice of the type of motion in the Monte Carlo method. The type of motion attempted is determined by the choice of random number between 0 and Z, where Z is the sum of all probabilities of attempting each particular type of motion (all types of crank, crankshaft motions, kink formation, migration and annihilation).

To calculate the probability of transition, one has to know the barrier of the corresponding motion (E_b). All motions occur by rotation around a bond (for crankshaft motions about two bonds simultaneously). In addition, since there is no motion of an isolated chain, a barrier is formed as a result of interactions of the rotating segment with the surrounding atoms (Δu_b). Thus

$$E_b=u_b^R+\Delta u_b \qquad (8)$$

where u_b^R is the barrier for rotation around the bond,

$\Delta u_b = u(R^*) - u(R)$, where $u(R^*)$ is the value in the saddle-point of the hypersurface of the potential energy of the system[16], and $u(R)$ is the energy of the system in the starting configuration (see equation (5)).

Mechanism of free-radical decay

In the volume with amorphous polymer prepared on a tetrahedral lattice and with a distribution of free radicals, motions occur that lead to transfer of individual beads of polymer chains. Since this process results in transfer of the free valency in the system, it provides simultaneously information on the mechanism of free-radical decay. The following cases may in general occur:

(1) A segment of a chain, which is by random choice selected for motion, contains an unpaired electron. The realization of its motion is connected with the conditions of the surroundings, into which it is placed due to motion: (a) In the 3 Å surrounding the new segment position, there is no chain—motion takes place. (b) In the 3 Å surrounding the new segment position, there is part of another or the same chain with an unpaired electron—motion takes place, and radicals decay. In the first approximation, we shall assume that they will decay with probability $p = 1$. In general, we have to consider also a barrier to the bimolecular reaction formulated in this way. (c) In the 4 Å surrounding the new position of the chain, there is part of another or of the same chain without an unpaired electron—transfer may occur. In the first approximation, we shall assume that the transfer will take place with probability $p = 0.5$. This process has in general a non-zero value of the barrier and has to be taken into account in this problem.

(2) The moving chain segment does not contain any unpaired electron. Three situations exist in this case according to the surroundings of the new position of the segment: (a) In the 3 Å surroundings, there is no chain—motion takes place. (b) In the 3 Å surroundings, there is part of the same or of another chain without an unpaired electron—motion does not take place. (c) In the 4 Å surroundings, there is part of the same or another chain with an unpaired electron—the same as the case 1(c).

From this analysis it follows that only one type (1(b)) of the six possible types leads to the decay of radicals. Other types contribute either to electron transfer (1(c), 2(c)) or to motion of the beads of chains, which is only significant from the point of view of the increase in the probability that the situation 1(b) will arise.

Model calculation. We give a simple example as an application of the model proposed. The preparation of amorphous polymer was carried out according to the programme mentioned. In the building up of the chains, ignoring the effects of $g^{\pm}g^{\mp}$ sequences, conditional probabilities $p_{i,ab}$ were determined on the basis of the scheme described in ref. 28 for the simplified case of the reduction of calculation to the maximum eigenvalue of the matrix $\mathbf{U}$. Using the values $\sigma = 0.43$ and $\omega = 0$, the matrix $\mathbf{P}$ has the form:

$$\mathbf{P} = \begin{pmatrix} 0.59 & 0.20 & 0.20 \\ 0.74 & 0.25 & 0 \\ 0.74 & 0 & 0.25 \end{pmatrix} \tag{9}$$

In chain building, we start from the conditional probabilities, instead of *a priori* ones, since at the decision about the conformation of the *i*th bond, we start from the known conformation of the preceding one (see 'RIS model' above). In the volume, 80 chains (with length of 100 beads) and 1190 free radicals were generated.

Crank and three-bond crankshaft motions were applied at the temperatures 200, 250 and 300 K, respectively. Barriers for individual motions consist of two contributions: (i) rotation around a bond for isolated chains (in crankshaft motion, double values (for $t \rightarrow g^+$, 22.6 kJ mol^{-1})); (ii) cohesion energy corresponding to the particular rotating segment (to CH_2 group, 4.4 kJ mol^{-1})[29]. In crank motions, if the chain ends with a methyl group, barriers for motion around the second or third bonds are given in *Table 2*.

In the terms of the subsection on 'Types of molecular motions', individual motions (attempted motions) have been chosen randomly. The procedure is similar to that in 'RIS model'. The respective probabilities for scheme (4) were determined from the barriers for individual motions. To prevent needless tests (not every sequence in the chain is suitable for performing a particular motion), we set in order the sequences formed suitable for this purpose into vectors and the selection was only done within these sequences.

If we denote by $w_i^{(l)}$ the weight proportional to the probability of attempting motion of type l ($l = 1$, three-bond crankshaft; $l = 2$, two-bond crank; $l = 3$, three-bond crank) of the ith component of the appropriate vector, then we can define:

$$Z = \sum_{i=1}^{n_1} w_i^{(1)} + \sum_{i=1}^{n_2} w_i^{(2)} + \sum_{i=1}^{n_3} w_i^{(3)} \tag{10}$$

where $w_i^{(l)} = \exp(-E_i^l/RT)$, E_i^l is the barrier to appropriate motion (see e.g. *Table 2*), and n_l ($l = 1, 2, 3$) gives the number of components of the lth vector. Probabilities for scheme (4) can then be calculated from:

$$q_i^l = w_i^{(l)}/Z \tag{11}$$

Sequences for individual motions in the volume prepared with amorphous polymer were selected in this way for three temperatures, and the decay of free radicals was examined as a function of the number of attempted motions. The result is seen in *Figure 1*. The curve shows the change in radical concentration with the number of attempts. The radicals decay at first more rapidly; later, as the number of attempts increases, their concentration varies slightly. As the temperature increases, the concentration again rapidly decreases.

This model calculation involves remarkable simplifications. Despite these, it is seen that such a simulation of the changes in radical concentration shows a similar course of the radical decay (stepwise) as has been observed in experiments[20]. A more precise study requires inclusion of further possible motions (see 'Type of

Table 2 Barriers for crank motion around the second and third bonds

		E_{inter} (kJ mol^{-1})		E_{total} (kJ mol^{-1})	
Type of motion	E_{intra} (kJ mol^{-1})	Two bonds	Three bonds	Two bonds	Three bonds
$t \rightarrow g^{\pm}$	11.3	18	26.8	29.3	38.1
$g^{\pm} \rightarrow t$	8.8			26.8	35.6
$g^{\pm} \rightarrow g^{\mp}$	17.2			35.2	44.0

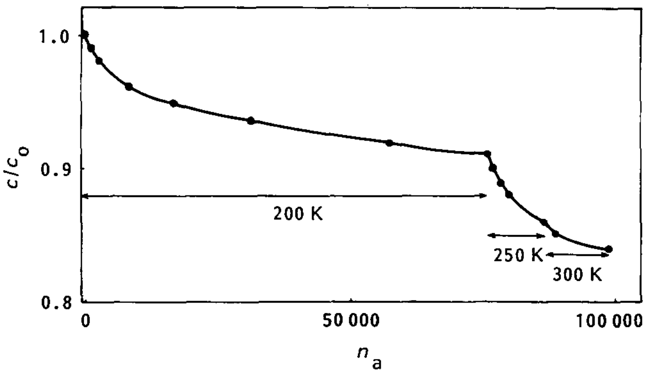

Figure 1 Dependence of concentration of free radicals c/c_0 on the number of attempted motions n_a

molecular motions') and employment of more realistic entry data. This will be the subject of our future study.

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