A Monte Carlo study of free radicals decay in amorphous polymers

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Dedicated to Professor Ľ. Treindl, DrSc., in honour of his 60th birthday

The Monte Carlo method was used for a theoretical study of the diffusion and decay of free radicals in solid polymers. A model of amorphous polymer was built up on a tetrahedral lattice of $(36 \times 62 \times 43) \times 10^{-30}$ m³ dimensions. Three types of molecular motions — kink, crank, and crankshaft — were initiated at various temperatures and changes in the concentrations of free radicals were followed as a function of the number of attempts to do motions, of temperature and density.

Монте-Карло метод был использован для изучения диффузии и гибели свободных радикалов в аморфных полимерах. Модель полимера была подготовлена на диамантовой решетке в объеме с размерами $(36 \times 62 \times 43) \times 10^{-30}$ м³. Молекулярные движения осуществлялись при различных температурах при помощи трех элементарных типов: кинк, кранк и кранкшафт. Была установлена зависимость гибели свободных радикалов от числа попыток для осуществления движений, температуры и плотности.

We have discussed relationship between the decay of free radicals in amorphous polymers and molecular motions in our recent paper [1]. In our opinion, three types of molecular motions are responsible for diffusion and decay of radicals in solid polymers: crankshaft, crank, and kink. Each of these motions has the final value of the barrier dependent on the morphology of the system studied and on the surroundings of the bond during inner rotation. The energy of the mobile chain segment (at a particular temperature) may cause that the segment is capable of gaining sufficient amount of energy to overcome local barrier. If such a segment contains unpaired electron, motion will translate it to another position where it can either meet other unpaired electron and recombine, or diffuse throughout the system by virtue of further thermal motion.

Generally it is possible to calculate the energy barrier of each motion of the segment considered [1] but it is a very time-consuming procedure. In this paper we use the actual value of the barrier which originates from intramolecular interaction of atoms in the neighbourhood of the rotated bond and the average value for intermolecular interaction of the surrounding atoms with the atoms of

the rotated segment. This approximation could influence the results but the aim of the present calculation is not to reproduce experimental results of any polymers. We would like to demonstrate on a model system how individual types of motion influence the concentration of free radicals and to show how polymer density can change the course of the decay process.

Theoretical

The process of the building up of volume of the polymer sample and distribution of free radicals in it has been described in detail earlier [1]. Here we give a brief outline of the procedure used.

We start from the rotational isomeric-state model (RIS) [2]; the conformation of macromolecules is connected with three minima on the potential energy curve for the rotation around the bond t, g^+, g^-. During the volume building up, the polymeric chains are located on tetrahedral lattice. The beginnings of chains and orientation of the first two chain bonds are selected at random. Further growth of the polymer chain follows from the procedure according to which one of the three possible positions is chosen for the following atom dependent on statistical weights of t, $g^\pm$. These serve as a basis for the choice using the Monte Carlo method. The length of chains and their number in volume can be chosen at will. In our calculations we worked with restriction, which eliminated any possibility of approximation of two atoms to the distance smaller than 3×10^{-10} m. Periodic boundary conditions are used.

In building up of the volume with the defined density, free radicals are generated. A system of random numbers is used so that the first number will determine the chain and the second the atom at which the free radical will be localized. Free radicals may be generated with the restriction determined in advance, if required by the accord with the experimental approach. For example, on irradiating the sample, radicals may arise in the traces of rays and then they will not be randomly distributed throughout the volume. During mechanical destruction [3], radicals are formed on the surface of the sample, *etc.*

Free radical decay in solid polymers may be characterized by two stages [4]: mutual approximation (diffusion) and recombination (or disproportion). We shall follow here diffusion of radicals and assume that the probability of the reaction after approximation of two radicals is equal to 1. The process of radical approximation is mediated by the motion of submolecular structures. We start from the RIS model and tetrahedral lattice. Thus the number of possible motions is reduced to several types: i) crank, ii) crankshaft, and iii) kink. The crank motion is rotation of chain end around the bond (Fig. 1) from the i position to the position j, i and j representing one of the three conformations t,

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g^+, g^-. The motion in solid polymers is restricted to a few end bonds. Crankshaft is simultaneous rotation around two bonds. The rotating rigid segment between these two bonds may have several bonds. Fig. 2 shows three- and five-bond crankshaft motions. The kink motion is a rapid succession of the two rotations, which transfer the moving chain segment to the parallel position with the original course (Fig. 3a). In the solid phase of the amorphous polymer, this type of motion is only realizable at the chain end. Inside the chain, compensation motion has to take place, to be able to keep the chain residue in the original position (Fig. 3b).
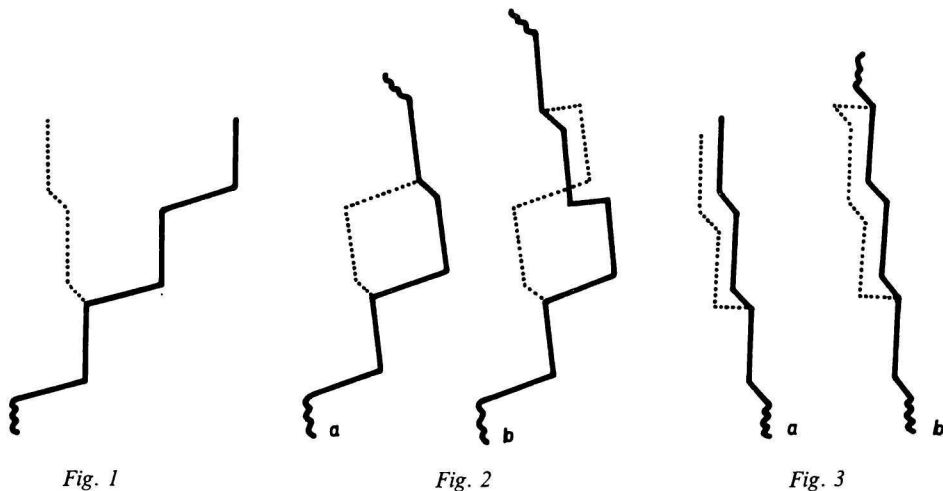

Fig. 1   Fig. 2   Fig. 3

Fig. 1. Crank motion ($tttt \rightarrow tg^+tt$).

Fig. 2. Crankshaft motion: a) three-bond ($tttg^+t \rightarrow tg^+tg^-t$); b) five-bond ($tttg^-tg^-t \rightarrow tg^+tg^-tg^-t$).

Fig. 3. a) Kink motion ($ttttt \rightarrow tg^+tg^-t$); b) double kink ($ttttt \rightarrow tg^+tg^-tg^+$).

When selecting individual motions, one starts from particular barriers (E_b) (close description of energy barrier calculation can be found in Ref. [1]). Boltzmann factor is then calculated

$$w_i = \exp\left(-E_b^{(i)}/RT\right) \qquad (1)$$

determining in Monte Carlo procedure which of the motions will be selected. At first we find a random number ξ_1, which determines the type of motion, then another random number ξ_2 that will determine which of the motions will be considered. The random number ξ_3 serves as a test whether the chosen motion takes place at a given temperature. If $\xi_3 \leq w_i$, motion can take place; otherwise it is rejected. To perform motion, one has to fulfil another condition: chain

Table 1

Values of the Boltzmann factor w_i determined from relations (1) and (3) for two temperatures and five values of E_b

| $E_b/(\text{kJ mol}^{-1})$ | w_i | | | |
| | Eqn (1) | | Eqn (3) | |
	$T = 100$ K	$T = 300$ K	$T = 100$ K	$T = 300$ K
0.4	0.8×10^{-3}	0.85	0.98	0.99
4	8×10^{-3}	0.20	0.865	0.95
20	4×10^{-11}	3×10^{-4}	0.475	0.77
50	8×10^{-27}	2×10^{-9}	0.13	0.51
70	3×10^{-37}	6×10^{-13}	0.06	0.39

atoms cannot approach one another closer than 3×10^{-10} m. The only exception is the case, when the rotating segment and the chain segment which the rotating segment approaches, contain unpaired electrons: the radicals decay. If an unpaired electron is on one of them only and their distance is less than 4×10^{-10} m, transfer of the radical centre takes place with the probability 0.5.

In connection with Monte Carlo method, a problem which arises as a result of the great difference between E_b and RT has often been discussed [5]; w_1 are then very low and almost all motions are rejected. In our case we have to solve a similar question. Rotation around the bond is not only a consequence of thermal energy accepted by this bond but also by the surrounding degrees of freedom.

In the rate processes this fact is considered by expression $(E_b/RT)^s$ within the preexponential factor [6]; s is the number of active degrees of freedom. A disadvantage of this approach is that s is the parameter, which we do not know in the actual situation. In our case, we chose scaling method [5], which shifts w_i to higher values. We use this procedure and finding of *Heijboer* [7] that the relation (2) holds between the activation energy (E_a) and the secondary loss maximum temperature (T_m)

$$E_a = a T_m \qquad (2)$$

where a for the frequency 1 Hz is 0.25 (activation energy E_a in kJ mol^{-1} and T_m in K). Relation (2) was advantageously used in the interpretation of the results in a series of other experiments [8, 9]. In our approach it means that w_i has to be calculated not on the basis of eqn (1) but from the following equation

$$w_i = \exp{(-E_a^i/30\,RT)} \qquad (3)$$

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Table 1 contains values of w_i obtained from expressions (*1*) and (*3*), respectively, for activation energies over 0.4—70 kJ mol^{-1}. The study of molecular mobilities in solid polymers [10, 11] and ESR measurements [12] show that activation energies vary within this region or are higher. According to the results from relation (*1*), almost no motions would occur to 300 K with $E_a >$ > 4 kJ mol^{-1}, although it is known that in many amorphous polymers up to T_g all radicals generated in a polymer matrix decay. The scaling used in eqn (*3*) agrees with these observations.

Results and discussion

Using the procedure described in detail earlier [1], we built up a model of amorphous polymer (PE) in volume with dimensions $(36 \times 62 \times 43) \times 10^{-30}$ m^3 and with chains containing 100 CH$_2$ groups. The energy difference between *gauche* and *trans* conformations is 2 kJ mol^{-1} [2]; *i.e.* that the respective statistical weight σ at 300 K ($\sigma = \exp(-\Delta E/RT)$) is 0.43. We shall demonstrate how the decay of free radicals depends on the number density ($n = N_{occ}/N$, N_{occ} is the number of occupied lattice points, N is the number of all points in volume). We therefore prepared several models with the values $n = 0.06$, 0.1, and 0.2. This corresponds to the density values in 10^3 kg m^{-3}: 0.23, 0.38, and 0.75.

Table 2

Rotational energy barriers for the motion of submolecular structures

Type of motion		$E_b/(\text{kJ mol}^{-1})$		
		E_b^{intra}	E_b^{inter}	E_b^{total}
Crankshaft	3-bond	22.6	8.8	31.4
	5-bond	22.6	17.6	40.2
Crank	around 2nd bond $\quad t \to g^{\pm}$	11.3	18	29.3
	$g^+ \to t$	8.8	18	26.8
	$g^{\pm} \to g^{\mp}$	17.2	18	35.2
	around 3rd bond $\quad t \to g^{\pm}$	11.3	26.8	38.1
	$g^{\pm} \to t$	8.8	26.8	35.6
	$g^{\pm} \to g^{\mp}$	17.2	26.8	44.0
Kink	$t \to g^{\pm}$	11.3	35.2	46.5
	$g^{\pm} \to t$	8.8	35.2	44.0

Four types of motions of submolecular structures were considered. Each type has moving segment of several kinds according to the size as seen from Table 2. The choice of motions was done according to a scheme described in Theoretical (w_i was determined from relation (3)). The initial number of radicals in volume in all cases is 500.

The figures show the change in radical concentration as a function of the number of attempts at motions. Fig. 4 shows a typical decay curve. The decay was observed at $n = 0.1$ with inclusion of all motions listed in Table 2 at three temperatures. The decay curve shows stepwise decay as is usually observed in experiments in solid polymers [13, 14].
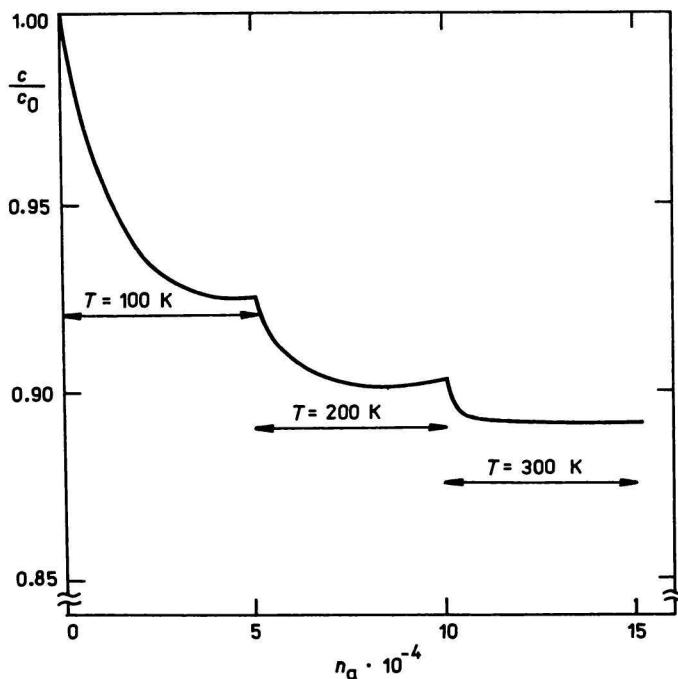

Fig. 4. A plot of the concentration of free radicals c/c_0 on the number of attempted motions n_a ($n = 0.1$).

Not every motion contributes equally to diffusion and decay of free radicals. The efficiency of several types of motions is limited because they can take place at chain ends only (crank, kink). Fig. 5 illustrates how the individual types of motions affect the change in the concentration of radicals, if taken separately. The smallest amount of radicals decays when only crank motion is considered, which includes rotation around the second or third bonds from the end of the

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chain. Crankshaft (three- and five-bond) is more efficient since it can take place over the whole chain. The most effective are motions of the type kink and double kink.
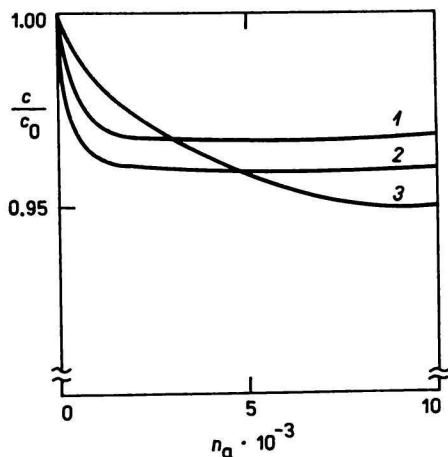

Fig. 5. Decay curves of free radicals for individual types of motions: *1.* crank; *2.* crankshaft; *3.* kink + double kink ($n = 0.1$; $T = 300$ K).
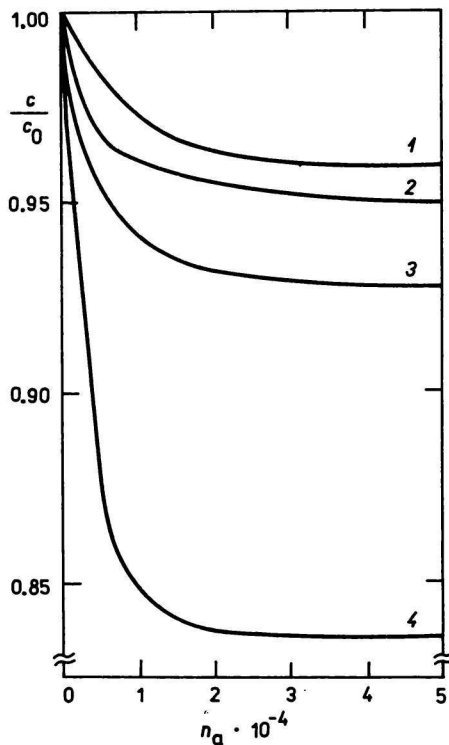
Fig. 6. Decay curves of free radicals at 300 K and different number densities *n*. *1.* $n = 0.25$; *2.* $n = 0.2$; *3.* $n = 0.1$; *4.* $n = 0.06$.

The rate of free radicals decay also depends on the density in volume. At high densities, the mobility is limited and diffusion of radicals is slower. Fig. 6 demonstrates how the density influences the decay of radicals.

Conclusion

Decay curves of free radicals in amorphous polymers obtained on the basis of the model of the motion of submolecular structures are of similar (stepwise) character as the curves obtained experimentally. The rate of radicals decay in computer experiment depends on the density of occupation of points on tetrahedral lattice. High occupation $n = 0.25$ ($\varrho = 0.94 \times 10^3$ kg m^{-3}) leads to the decrease of mobility in this model and the decay of radicals is slower. Individual

types of motion influence the decay process in different way. The most effective is double kink.

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