

The Density Effect on the Diffusion and Decay of Free Radicals in Amorphous Polymers

J. TIÑO, J. URBAN, and V. KLIMO

Polymer Institute, Slovak Academy of Sciences, CS-842 36 Bratislava

Received 7 May 1991

A Monte Carlo method has been used for studying the influence of the molecular mobility on the decay of free radicals in amorphous polymers. We worked on a tetragonal lattice with different degrees of the occupation of lattice points (density). The diffusion of radicals is shown to be strongly dependent on density – it increases with increasing density. The decay of radicals in the time scale is more effective at lower densities. Cooperative motions are particularly sensitive to density.

Stochastic approaches to the study of the decay of free radicals in the solid phase provide a comprehensive picture of the general laws of the process of the decay and enable to explain some qualitative properties of decay characteristics. A deeper insight into the reasons that lead to the meeting of free radicals and their decay requires an investigation of the mechanisms at a molecular level. Recently we proposed an algorithm which allows relation of the molecular mobility with the transfer of a radical centre [1–3]. Several types of motions chosen as models are at present considered as most probable in solid polymers: crank, crankshaft, and kink. Then, at higher temperatures, cooperative motions are generated on their basis. The cooperative motions should correspond to relaxation motions in the α region [4, 5] and should lead to the diffusion of radicals throughout the volume contrary to local motions which mediate transfer of radical centres to neighbouring chains in a one-step process. The decay curve of radicals shows that the motions without cooperation are not able to completely describe the radical decay. At a rather high concentration of radicals, saturation is reached, and by increasing the number of attempts the concentration of radicals does not change any more [3]. After introducing cooperative motions, the concentration of radicals is substantially reduced. The effectiveness of the individual types of motions depends on the density of the polymer studied (in our algorithm the ratio between the number of the occupied sites of the lattice and their total number).

Some investigators have begun with both theoretical [6–8] and experimental [4, 5, 9–11] studies of the idea of cooperativeness. *Berstein* and his coworkers [4, 5, 9–11] carried out several reasonable experiments leading to the following conclusions: *i*) the molecular motions in β relaxa-

tion region are performed at the level of the Kuhn segments, *ii*) on going to α relaxation region, the size of the moving segment does not increase but cooperation during the motion occurs. The temperature is decisive for the development of cooperation since the activation barrier considerably increases by transition from local motions to the cooperative ones. On the tetragonal lattice the process is carrying on in such a way that if a segment is thermally activated to move, it runs into the neighbouring chain and if its energy is sufficient to initiate the segment motion on that chain, it need not return to the original position but it is transferred to the freed locus. The following segment can do the same, *etc.* Thus the situation arises when local motions are transferred to motions in which more chains participate.

In this paper we study the effect of the density of the system on the efficiency of molecular motions during transition and the decay of free radicals in amorphous polymers without cooperation and during cooperative motions.

MODEL

The Monte Carlo method is used for building an amorphous polymer on a tetragonal lattice as has been described elsewhere [1]. Since no concrete type of polymer is investigated, we use model values of the barriers for individual types of motions [1, 2]. After constructing the volume, free radicals are generated by random choice on the chain and the system starts to move. In Ref. [2] we reported on the radical generation in traces as if the radicals were formed by generating rays in radiation. In this paper we predict homogeneous distribution throughout the volume. During the segmental motion, two cases may occur: *i*) the segment contains free radical; the radical

follows the motion of the segment and comes to a different position, different surrounding. If there is another radical around 3×10^{-10} m, both radicals decay. If there is no free radical, the radical centre can be transferred with the probability $w = \exp(-E_t/30 RT)$ [2] (E_t is the barrier of a radical centre transfer) to the chains in the 3×10^{-10} m surroundings. *ii*) No free radical occurs on the moving segment. A transfer of the radical centre from the area of 3×10^{-10} m can take place if any radical occurs there. During cooperative motion, such a transfer can take place to the distances greater than in simple motions.

In the model applied we work with the excluded volume up to the distance of 3×10^{-10} m. This is the upper limit of the occupation of the lattice (density). The decay of free radicals depends on density. It should become particularly evident at higher temperatures, where generation of cooperative motions is more probable.

RESULTS AND DISCUSSION

In the calculations used in the present work we have chosen model rotational barriers for individual types of motions [1]. The corresponding probabilities which are decisive for the choice of segments for motions at the chosen temperature are temperature-dependent and therefore motions with higher barriers are introduced with increasing temperature. The barriers are chosen so as to define the differences in individual types of motions from the qualitative point of view correctly.

Cooperative motions are done at higher temperatures at which the segments have sufficient amount of energy not only for implementing their own rotation, but also for initiating the motion of another segment which hinders their motion. The choice of motions is based on the probabilities which are determined from the rotational barriers for individual motions. The exact values of the barriers for cooperative motions are not known. Our procedure is as follows. We choose the type of motion (crank, crankshaft, kink) by random number. By another random number the size of the barrier ϵ of cooperative motion is selected from the interval $(E_b, 3 E_b)$ (E_b is the barrier of a simple motion of the corresponding type). An attempt for simple motion is done if $\epsilon < 1.2 E_b$. For $1.2 E_b \leq \epsilon < 2 E_b$ an attempt is done for cooperative motion of the two segments, at $2 E_b \leq \epsilon < 3 E_b$ an attempt for the cooperative motion of the three segments is done.

Calculations are done according to the procedure described elsewhere [1]. At first, a volume of the amorphous polymer is formed, free radicals

are generated, and the system is set in motion. The barriers for the individual types of motions are the same as given elsewhere [1] and follow from several basic values: 11.3 kJ mol^{-1} rotation around the bond $t \rightarrow g^+$, 8.8 kJ mol^{-1} $g^+ \rightarrow t$, 17.2 kJ mol^{-1} $g^+ \rightarrow g^-$. Barrier for intermolecular interaction is determined for each motion separately so that the value of 4.4 kJ mol^{-1} is ascribed to each CH_2 group. The intramolecular 1,3 transfer of unpaired electron proceeds with a barrier of 130 kJ mol^{-1} [12]. We used four density values: 0.08, 0.1, 0.2, 0.25. The number of radicals in the volume is corresponding: 200, 250, 500, 626.

Cooperation during motion involves segments of various chains but also segments from the same chain if they are in the neighbourhood owing to the favourable chain conformation.

The effectiveness of the cooperative motions is connected with the density of the polymer studied. At low densities, the mean value of the distances between the chains is high; therefore, even at higher temperatures, when the segments have the energy high enough to perform cooperative motions, the motions of segments are simple because they have enough free volume for this purpose. On the other hand, at low temperatures and at these densities, the simple motions are easier to be carried out because of the larger free volume. The situation changes on transfer to higher densities.

Table 1 illustrates the role of density; it contains not only the data on the number of decayed radicals but also on how many radical centres have been transferred during the segmental motion from the chain studied to other chains in the vicinity (transfer of the type 1) and how many of them have been transferred from the surrounding chains to the chain studied (transfer of the type 2). Please note that the transfer with the probability $w = \exp(-\epsilon/30 RT)$, ϵ being the respective barrier [2], can take place both when the motion is realized and when the motion is not realized if by an attempt at motion the chains approach to the distance smaller than 3×10^{-10} m. The number of these transfers will obviously be greater at higher densities and Table 1 shows that it is so at all temperatures except for 100 K where the molecular mobility is low. This fact is affected by higher radical concentration at higher densities which has been chosen for calculation so as at each density each chain would be assigned approximately the same number of radicals. The standardized values of transfers (per 1 radical) are given in Table 1. They provide a picture of the processes at particular temperatures. At 100 K, the mobility is low and mainly the decay of radicals close to each other takes place and motions

Table 1. The Number of Transferred Radical Centres (N) and Variation of the Concentration of Radicals (C/C_0) as a Function of Density and Temperature

T K	Density	N		C/C_0^a
		Type 1	Type 2	
100	0.08	0	7	0.19
	0.1	—	—	0.17
	0.2	1	4	0.26
	0.25	0	8	0.15
200	0.08	24	128	0.19
	0.1	37	181	0.41
	0.2	59	247	0.20
	0.25	74	372	0.32
300	0.08	32	92	0.37
	0.1	63	197	0.16
	0.2	85	299	0.41
	0.25	180	381	0.21
		0.29	0.61	

a) The number of radicals decayed divided by the original number of radicals in the volume.

needed for an approach should not be very energy-demanding. By and large, the decay at this temperature appears to be almost the same at all densities. The most favourable from this viewpoint is the density of 0.2 at which most radicals decay.

From the point of view of our study – the effect of the density on the efficiency of the cooperative motions – the most interesting temperature at which these motions can be applied, is that of 300 K. At 200 K, the most favourable density for the decay is 0.1, at which the free volume is sufficient for segmental motion and the density is sufficient to enable to reach the distance between the chains by simple motions at which radicals can decay.

The main component of the decay at 300 K are cooperative (inter and intra) motions. The motions are most efficient at the density of 0.2 ($\rho = 0.75 \times 10^3 \text{ kg m}^{-3}$). At lower densities, the cooperation between the chains is less efficient for larger free volume where simple motions can be done without any problem and at the density of 0.25 ($\rho = 0.95 \times 10^3 \text{ kg m}^{-3}$) it is rather difficult to apply intermolecular cooperative motions because of the small free volume. A rather large decay at this temperature was observed at the density of 0.08. This is mainly a result of a considerable efficiency of 1,3 intramolecular transfer. Fig. 1 depicts the situation better and shows how the effect of

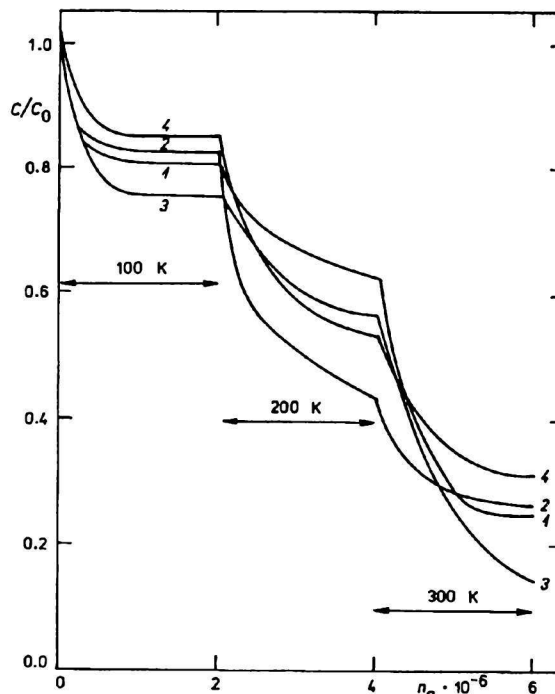


Fig. 1. A variation of the concentration of radicals with temperature and number of attempts (n_a) for four densities: 1. 0.08, 2. 0.1, 3. 0.2, 4. 0.25.

individual motions at respective densities varies with temperatures. We can see e.g. that at the density of 0.2, most radicals decay as a result of cooperative motions. The density of 0.25 represents an extremely dense system ($\rho = 0.95 \times 10^3 \text{ kg m}^{-3}$) and as the pressure measurements in EPR spectroscopy indicate [13], the radical decay is retarded owing to the high pressure. This agrees with our observations.

REFERENCES

1. Tiño, J., Urban, J., and Klimo, V., *Polymer* 30, 2136 (1989).
2. Tiño, J., Urban, J., and Klimo, V., *Chem. Papers* 44, 711 (1990).
3. Tiño, J., Urban, J., and Klimo, V., *Polymer*, submitted for publication.
4. Ryzhov, V. A. and Berstein, V. A., *Vysokomol. Soedin.* 29, 1852 (1987).
5. Berstein, V. A., Razgulyaeva, L. G., Galperin, V. M., Egorov, V. M., Kolosova, T. O., and Sinani, A. B., *Vysokomol. Soedin.* 20, 1885 (1978).
6. Adachi, K., *Macromolecules* 23, 1816 (1990).
7. Pakula, T., *Macromolecules* 20, 679 (1987).
8. Mazur, S. J., *Chem. Phys.* 91, 7236 (1989).
9. Berstein, V. A. and Pertsev, N. A., *Acta Polymerica* 35, 575 (1984).
10. Berstein, V. A. and Egorov, V. M., *Vysokomol. Soedin.* 27, 2440 (1985).
11. Berstein, V. A., Ryzhov, V. A., Ganitscheva, S. I., and Ginzburg, L. I., *Vysokomol. Soedin.* 25, 1385 (1983).
12. Bartoš, J. and Tiño, J., *Polymer* 27, 281 (1986).
13. Szöcs, F., *J. Appl. Polym. Sci.* 14, 2629 (1970).

Translated by A. Rebrová