Cooperative motion in amorphous polymers: application to the study of free-radical decay in solids

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A method for the simulation of cooperative motion in amorphous polymers has been proposed. The influence of this motion on the free-radical decay in solid polymers is studied. The cooperative motion is shown to extend beyond the local regions and lead to diffusion of radicals throughout the volume.

(Keywords: amorphous polymers; free-radical decay; molecular mobility; Monte Carlo; cooperative motion)

INTRODUCTION

In recent papers[1,2] we have proposed a method for studying the effect of elementary molecular motions on radical reactions in solid polymers. We used a Monte Carlo method for selecting realizable motions at the chosen temperature on the basis of rotational barriers of the individual motion types (crank, crankshaft, kink). If the moving segment contains an unpaired electron, it changes its position. If the unpaired electron is near the new position of another radical centre (less than 3 Å), a reaction may take place and both radicals decay. If another chain without an unpaired electron occurs at a distance less than 3 Å from the new position of the radical centre, a transfer of the radical centre to this chain may take place.

There is still a problem of the proper characterization of the motional state of the polymer system, i.e. which structural units are moving at the particular temperature and which types of motion they undergo at that temperature. The above-mentioned types of motion which derive from the rotational isomeric state (RIS) model[3,4] are generally discussed. But a more important problem is that of the size of a segment, its vibrational and rotational state corresponding to the temperature of the system and the temperature dependence of its size. In the sequence of relaxation regions from γ to α, the activation energy increases. The increase can be (and usually is) interpreted mechanically as an increase in the size of the moving segment. If polymers are without side groups, motions can only take place within chains. We should here differentiate vibrational motions from rotational ($t \rightarrow g^{\pm}$). On the basis of the analysis of i.r. spectra of a series of polymers, Ryzhov and Berstein[5] came to the conclusion that only vibrations (librations) occur up to the temperature $T_2 = (0.7\text{–}0.8)\ T_g$ (K). From T_2 (β-region), rotational transitions are observable.

The findings of Berstein *et al.*[6–8] show that, on going from the β to the α relaxation region, the size of the segment does not change significantly. The increase in the activation energy in this region is caused by cooperative motions. The authors state that it is always Kuhn segments that realize vibrational, rotational or cooperative (multisegment) motions. The conclusions of these authors seem to be convincing and we shall use them in the following considerations. In this paper we shall extend the motion regime in solid polymers from the β-relaxation region[1,2] to the α-region on the basis of the realization of cooperative motions.

THEORETICAL BACKGROUND

We have so far worked merely in the β-region without taking account of another type of motion – vibrational motion[1,2]. On a tetrahedral lattice, the rotational motion of chain ends around the second and third bonds (crank), segmental motion along the chain, (three- and five-bond) crankshaft and kink (double kink) can occur. The last belongs to a group of cooperative motions. The motions contribute in various amounts to radical decay (the most efficient being a double kink[2]). As a result of these motions, the concentration of radicals is reduced by 65% of its original value. The reduction is in agreement with the fact that the complete decay of radicals in amorphous polymers is not recorded until the α-relaxation region is reached. If we want to raise the efficiency of the molecular mobility, all motions have to be taken into account in this region.

D.s.c. measurements and the results from i.r. measurements[5–9] show that it is the motion of Kuhn segments that is responsible for relaxation processes in polymers. For example, in experiments with alkanes of different degrees of polymerization[8] saturation is reached on the curve of the plot of intensity of spectral line *versus* chain length. The intensity is no longer a function of the number of monomers in the chain beyond a particular chain length. A similar effect is also seen with crosslinked polymers. The intensity of an i.r. spectrum decreases with network density when the distance of crosslinked atoms is comparable with the Kuhn segment of the particular polymer[6]. D.s.c. measurements of polymers filled with

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plasticizers show that the α-relaxation maximum observed in a pure polymer decreases with increasing concentration of plasticizer and completely disappears when the amount of plasticizer reaches 50%. By combining these results, the authors devised a model for the dynamics of a polymer chain in which the motion of the Kuhn segment is always involved in the motion of the chain. The α-relaxation region is characterized by the cooperative motion of these segments.

Model

The idea of cooperative motion is used for explaining many properties of polymers[10–12]. It is based on mutual interactions, ranging from chemical bonds to excluded volume. There are domains suitable for cooperative motion, where the displacement of a given segment depends upon correlated displacement of others in that domain. The size of the domain reflects the complexity of motion.

We propose a model which is a continuation of our algorithm[1] for the selection of types of motion and their application to the diffusion of radical centres along the system and their decay. The choice of types of motion is bound by our basic assumption – the use of a lattice. If the starting positions of atoms and their positions after performing movements are on the lattice, then the concept[13–15] that the strict constancy of bond angles and bond lengths should not necessarily be maintained during the central bond transition cannot be taken into account. On the other hand, in more concentrated solutions and bulk polymers, as distinct from dilute solution, crankshaft may be important as a local motion. Other types of motion applied by us (kink and crank) are also considered to be acceptable.

Cooperative motion (intra- and intermolecular) is realized at higher temperatures, where segments have enough energy not only for rotation but also for the excitation of the motion of another segment which hinders their own motion. We do not know the exact value of the energy applied to realize cooperative motion. We shall work in our model with random choice from the interval (E_b, $3E_b$).

Procedure

(i) The type of motion is chosen by random number ξ.

(ii) Using another random number η the size of the barrier E of the rotation of the given segment in the interval (E_b, $3E_b$) is chosen. To consider energetic demands of individual types of motion in our model we divided this interval into three parts: if $E < 1.2E_b$ a simple motion is realized; for $1.2E_b \leqslant E < 2E_b$, a correlated motion of two segments is realized; for $2E_b \leqslant E \leqslant 3E_b$, a correlated motion of three segments is realized.

(iii) The motion will be selected if $w < \mu$ (μ being a random number); w is determined from the motion barrier: $w = \exp(-E/30RT)$ (Ref. 2).

Steps (i)–(iii) have been described in detail in a previous paper[1] where the procedure in (iii) is described in more detail. If there are no atoms of its own or other chains within 3 Å (which represents approximately twice the C–C bond length (1.54 Å) used here as a spacing of lattice) of the chosen segment after rotation, motion is realized. If the lattice points within 3 Å of the new position of the moving segment are occupied, an attempt follows at cooperative motion, in that the segment of a neighbouring chain makes an attempt at motion. Its behaviour is determined in the same way as that of the first segment (if there are no atoms within 3 Å after motion, motion is realized; if atoms are present within 3 Å an attempt is made at cooperative movement). The cooperative movement is completed by the motion of the third segment. If the third segment cannot move because of geometrical hindrance, the whole procedure returns to point (i). Radicals may decay in these motions if they approach closer than 3 Å or transfer of the radical centre may take place in any stage of the cooperative motion if, after approaching the adjacent (or its own) chain, the distance is smaller than 3 Å.

The probability of radical decay in this stage of the modelling is equal to one. The probability of radical centre transfer is calculated from the transfer barrier (see Results and discussion).

RESULTS AND DISCUSSION

The main aim of these calculations is the investigation of the concentration of radicals as a function of temperature and time. If c_0 is the initial concentration of radicals and c is the concentration at time t and temperature T, then we shall follow changes in c/c_0 resulting from the molecular mobility of a polymer system. Since at this stage we are still dealing with a model calculation, rotational barriers are idealized too but they are selected so as to qualitatively express differences between individual motion types.

Calculations are made according to the procedure described elsewhere[1]. At first, the volume of the amorphous polymer is formed, free radicals are generated ($c_0 = 500$) and the system is set in motion. Barriers for individual types of motions are the same as those described elsewhere[1] and follow from several basic values: rotation around the bond $t \rightarrow g^{\pm}$ – 11.3 kJ mol^{-1}; $g^{\pm} \rightarrow t$ – 8.8 kJ mol^{-1}; $g^{\pm} \rightarrow g^{\mp}$ – 17.2 kJ mol^{-1}. The part concerning the intermolecular interaction consists of contributions due to cohesive energy and is determined for each motion separately so that the CH_2 group has the value of 4.4 kJ mol^{-1} (ref. 16). The intramolecular 1–3 transfer of an unpaired electron is carried out[16] with the barrier 130 kJ mol^{-1}.

Figure 1 shows the course of c/c_0 for three temperatures and various types of motion. The density of lattice occupation (i.e. the ratio of occupied points to all points, 15000) is 0.2. By selecting all motions without any possibility of cooperative motion (curve 3), the concentration of radicals is stabilized in the particular sample volume at a value of 0.35. Introduction of cooperative motions lowers this value to 0.16. The concentration of radicals is not yet stabilized at that number of attempts. For other motions, 10^6 attempts is sufficient in all cases to reach a stabilized level of radicals (*Figure 1*). A greater number of attempts is needed for cooperative motions. We have made such a calculation and *Figure 2* shows the result. Here, at 200 and 300 K, the number of attempts rose to 4×10^6. At 200 K, the concentration of radicals was stabilized, at 300 K the curve was still descending.

Figure 1 also shows that at low temperatures, processes with high barriers (cooperative motion) are not selected and are mostly selected at high temperatures, where simple motions do not lead to a change of radical concentration. A separate test has shown that transfer

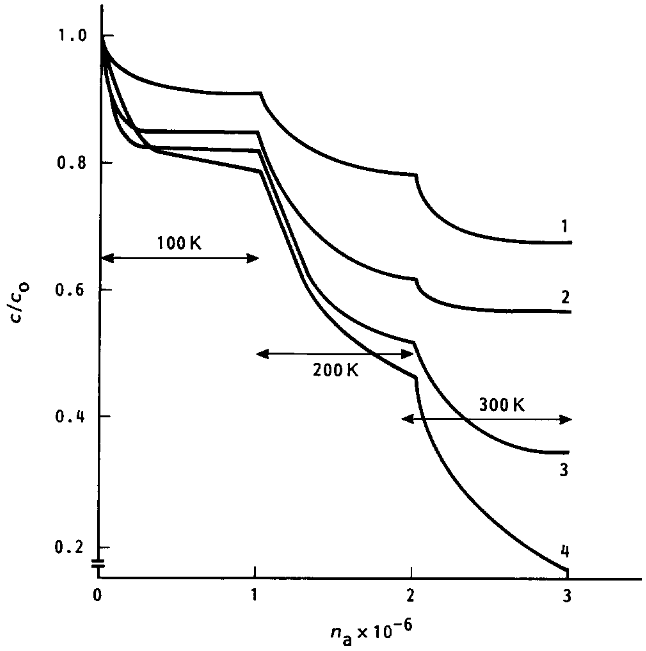

Figure 1 Plot of changes of the concentration of radicals *versus* the number of attempts at the realization of motions (n_a) for various types of motion: 1, crank + crankshaft; 2, motion 1 + kinks + double kinks; 3, all motions (except cooperative ones); 4, motion 3 + cooperative motions

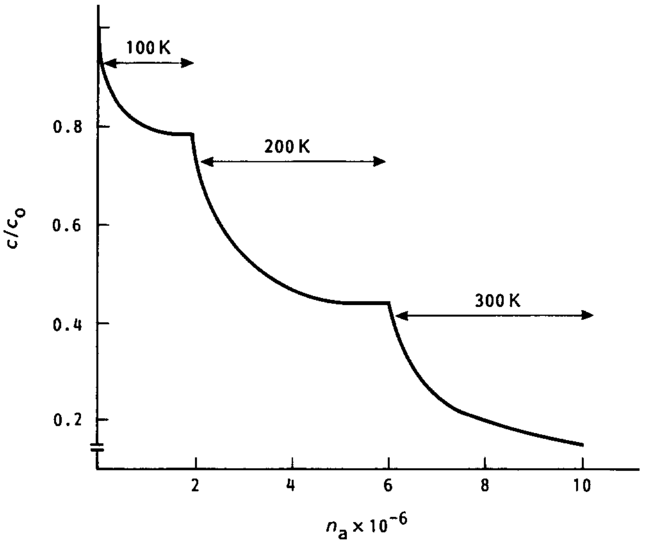

Figure 2 Plot of changes of the concentration of free radicals *versus* the number of attempts at the realization of motions (n_a) for all motion types at various temperatures

along a chain does not lead to a decay of radicals until the temperature reaches 300 K. Simple motions are mainly efficient at short distances. The extent of their influence is restricted and after decay of radicals from domains where local motions occur, c/c_0 does not change until the temperature increases (*Figure 1*). This is an effect known from experimental measurements and leads to a stepwise decay of radicals (*Figure 3*).

Cooperative motions are activated in the region where local motions no longer lead to radical decay and substantially reduce c/c_0. We have not incorporated vibrational (librational) motion into our model. It exists at all temperatures and by raising the temperature

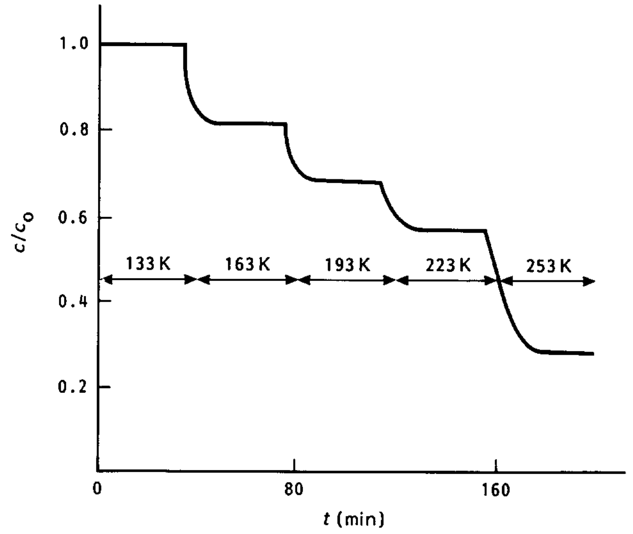

Figure 3 Plot of changes of the concentration of free radicals generated by the γ-radiation of atactic polypropylene *versus* time at five temperatures

deviation from the equilibrium position increases according to the following relation[17] (valid for *gauche* states at ±120°C):

$$\overline{\cos\varphi} = \frac{1 - \exp(-\Delta E/RT)}{1 + 2\exp(-\Delta E/RT)}$$

$\Delta E = E_t - E_{g^\cdot}$ at vibrations around the minimum in the *t* position. These motions can then also support an approach of chain segments and a transfer of the radical centres or decay of radicals. A study of this problem is in progress in our laboratory.

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