ELSEVIER

Polymer 43 (2002) 997–1001

polymer

www.elsevier.com/locate/polymer

Theoretical aspects of free radical decay in polyethylene and comparison with experimental results☆

J. Tiňo, I. Koreň*

Polymer Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, Bratislava 842 36, Slovak Republic

Abstract

Results of the study of stability of free radicals using electron spin resonance suggest a close relationship between the glass transition temperature (T_g) and free radical decay. In a detailed study of radicals in polyethylene (PE) [J. Polym. Sci. A2 6 (1968) 1435] in the sixties, it was concluded that the decay of radicals in solid polymers is connected to molecular mobility. In this report on molecular mobility using a Monte Carlo method we show with the example of PE that it is the motion of molecular structures, which, depending on temperature, lead to a transfer of radical centers and thus to the approach of radicals and their decay. Theoretical and experimental decay curves for PE are compared and based on their close correspondence it is concluded how the individual types of motions affect the stability of free radicals.

Keywords: Polyethylene; Free radical; Mobility

1. Introduction

Already in the sixties it was recognized that the free radicals in solid polymers decay as a result of molecular mobility [1]. The decay curves showed that the decay of interchain radical pairs occurs at first [2], with radicals in the crystalline regions being relatively stable. Alkyl radicals in the amorphous regions decay generally below the T_g. Later, it was observed [3–5] that high pressure has a stabilizing effect on concentration of free radicals, which also points to the idea of molecular mobility as the origin of radical decay.

The idea of determining types of motions in solid polymers and their individual temperature-dependant roles in the transfer of free radical centers, can be realized by modeling. The Monte–Carlo (MC) method, formulated [6] and elaborated in recent studies [7,8], is well suited to the purpose. Considering a model polymer, it was shown that (i) submolecular structures exist that exhibit different mobilities depending on the temperature, (ii) at temperatures considerably lower than the T_g, only libration motions take place, (iii) on increasing the temperature, the amplitude of libration increases and can lead to the approach of adjacent radical centers and their decay, (iv) at temperatures close to the T_g, the angle of deflection of molecular segments in libration can exceed the rotational barrier on the potential energy hypersurface and the segment can jump to another local minimum. A detail discussion of the size of the chain segment and of the temperature of decay of free radicals was presented [7,8]. The effect of pressure on the decay of free radicals, using ESR, was experimentally studied [3–5]. Also, using the MC method, the effect of density on radical stability was simulated. The measurements have shown that high pressure has a stabilizing effect on the free radicals. The MC method provided results showing that the increased density of the polymer system leads to limited mobility of submolecular units and consequently to stabilization of radicals. Since, under the influence of increased pressure, the free volume is decreasing and the density is increasing, both of these results correlate and lead to a conclusion that high pressure reduces the molecular mobility and stabilizes the radicals.

In this paper we compare experimental results on free radical decay in low-density polyethylene (PE) with results on amorphous PE provided by MC simulation. The experimental decay curves originate from detailed ESR studies of Japanese authors [1,2,9–12], in which they account for crystallinity (e.g. [1]), isolated chains [10,13] and a decay of radical pairs [2]. The MC procedure [6–8] has the power to account for all of these peculiarities and calculate the respective decay curves.

☆ This paper was originally submitted to *Computational and Theoretical Polymer Science* and received on 4 December 2000: received in revised form on 23 February 2001: accepted on 17 April 2001. Following the incorporation of *Computational and Theoretical Polymer Science* into *Polymer*, this paper was consequently accepted for publication in *Polymer*.

* Corresponding author. Tel.: +421-7-5477-3488; fax: +421-7-5477-7409.

E-mail address: upolkori@savba.sk (I. Koreň).

0032-3861/02/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0032-3861(01)00590-0

2. Model

One model applied to the study of molecular mobility in polymers uses several submolecular structures through which the polymer mobility is realized [6–8]. In accord with the experimental observation of Berstein et al. [14–16], when going from α to β relaxation regions, the length of the moving segment does not vary but cooperative motions take place in the system. Hence the length of selected submolecular structures is not changed with temperature. On increasing the temperature, cooperative motions are included gradually. Apart from this, for the process of approach of radical centers, the librational motions of macromolecular structures are also important, which, due to theirs small energetic demand, can be realized well below the T_g and can enable the approach of radicals and decay of radical pairs. Details on the conditions of realization of librational motions, including the determination of the extent of deflection depending on the temperature, are reported in our previous work [7].

For the MC method [6–8] and the case of the simulation of amorphous PE with the decay of free radicals, a volume of the size $36 \times 62 \times 43$ Å^3 was used. The radical decay was examined by the RIS modeling of polymeric chains [17] on a tetrahedral lattice. In this model, united atoms (H atoms contracted into C pseudo-atoms) were used, with three potential minima and a spherical excluded volume of radius 3 Å. Periodic boundary conditions were applied. In this work, we considered a volume comprising 34 chains of length equal to 100 groups at density 0.85 g cm^{-3}, which is very close to the established experimental value for amorphous PE [18].

The segmental motions were divided in two types: (i) chain-end motions and (ii) local motions within a polymer chain that do not affect the position of other segments [6]. Four-bond kink and two-bond crank chain-end motions were used in our model. The longer chain-end segments (three or more bonds crank) were not taken into account due to the high energetic demands and lattice occupation. The local motions within the chain were divided into three groups: (i) three-bond crankshaft, (ii) five-bond crankshaft and (iii) five-bond double kink. These motions are defined on cubic lattices. As we used a tetrahedral lattice, our crankshaft motions were really crankshaft-like ones.

A definite minimum activation energy is required to make a transition of a segment from one equilibrium position to another. In our model, this energy consisted of the energy required for bond rotation and a contribution derived from cohesive energy [6]. Our model used the following values of energies for bond rotation:

E_{intra}:
11.3 kJ mol^{-1} for transition $t \rightarrow g^{+,-}$;
8.8 kJ mol^{-1} for transition $g^{+,-} \rightarrow t$;
17.2 kJ mol^{-1} for transition $g^{+,-} \rightarrow g^{-,+}$.

E_{inter} [19]:
4.19 kJ mol^{-1} for CH_2 group;
9.64 kJ mol^{-1} for CH_3 end group.

We distinguished 17 energetically different states of motions in our model. Each of them involved several conformational sequences that occurred with various frequencies. The sum of frequencies of the conformational sequences of a given energetic state formed one element of the vector of relative frequencies of types of motion. Choice of the applied motion was determined by the relative frequency of its occurrence in the volume and this selection was accomplished by choosing a random number from a uniform distribution. At higher temperatures, where the moving segment possessed additional energy from the activation of a neighboring segment, the cooperative intermolecular type of motion was introduced [20].

3. Results and discussion

Free radicals in PE appear after the application of γ-radiation (e.g. [1,12,13,21]), or mechanical stress [22]. After irradiation of PE at the temperature of liquid nitrogen, alkyl radicals are stabilized on the chains. By gradually increasing the temperature, these radicals start to decay. The observed decay curves show that a considerable decrease of free radicals starts only above the temperature of 100 K [1,10]. In reports concerning the decay of radicals, two types of decay are recognized: a fast and a slow decay. Since in experimental studies, there is always some crystallinity present in PE, the slow decay is attributed to the radicals in the crystalline regions or to allyl or polyene radical (see the discussion in Ref. [23]). The fast decay is unambiguously ascribed to the alkyl radicals in amorphous region or amorphous radicals trapped in the proximity of crystallities.

In this work attention is concentrated on the study of the mechanism of radical decay in the amorphous regions of alkyl radicals situated in the chain over the temperature range 80–350 K. The shape of the ESR spectrum of the alkyl radicals in the chain was analyzed in detail previously [23,24]. In these papers the structure of radicals pertaining to the parameters of the respective ESR spectra were described.

When studying radical decay, it is interesting to know the mechanism that leads to the approach of radicals and to their decay. Some of the radicals on adjacent chains can be in close proximity and a librational motion enables their approach to the distance required for the formation of a new bond and the radicals disappear. These radicals form radical pairs that can be experimentally verified by measurement at a half-field resonance [25]. Such measurements were performed, e.g. Ref. [2]. The authors concluded that: (i) radical pairs form ca. 0.3% of the total concentration of radicals and (ii) these are mostly interchain. The average

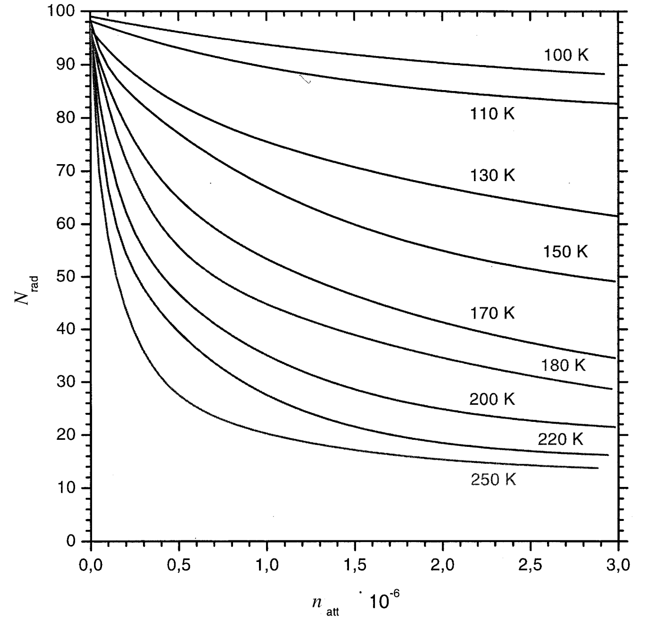

Fig. 1. Variation of the normalized concentration of free radicals (N_{rad}) calculated by the MC method with number of attempts (n_{att}) at various temperatures (100, 110, 130, 150, 170, 180, 200, 220, 250 K).

distance of radicals in radical pairs was estimated to be ca. 4 Å.

The overall picture on the radical decay in PE can be obtained by the simulation of molecular motions. From these simulations it follows (Fig. 1) that, at temperatures around 80 K, the radicals do not decay at all, at 100 K the radicals are relatively stable and an intensive decay sets in only when $T = 150$ K is reached. In agreement with the experimental results, Fig. 2 demonstrates that mostly librational motions, that enable the radicals to approach to a distance where decay is possible, would be responsible for radical decay at temperatures between 80 and 100 K.

At higher temperatures, rotational and cooperative motions start to apply as well. Hori et al. [10] observed the stability of radicals in PE in urea–polyethylene complex (UPE) and normal PE. In the case of UPE, the PE chains are mutually isolated and radicals can decay via intrachain migration only. On the contrary, in normal PE the chains can interact and radicals can migrate between the chains (interchain migration). It was established that the alkyl radicals trapped in UPE were very stable up to 350 K while the alkyl radicals in the normal PE had almost vanished at this temperature. It was concluded that the rate of free-radical migration across the chains is much faster than that along the chains. In our simulations, we have taken into account this finding and we considered only the interchain migration of radicals.

Experimental results on ESR measurement in PE, that are the closest to our MC model of simulation, are presented in the work of Nara et al. [1]. For these measurements the authors used PE with crystallinity in the range of 51–89% and, for the individual samples, they reported different decay curves. While, for PE with a crystallinity of 51%, the alkyl radicals have almost entirely disappear at 250 K, for PE with a crystallinity of 89% the radicals only started to decay at this temperature. The samples with a crystallinity of 51% resemble our model most closely and we will discuss our results by comparison with curve 1 in Fig. 3.

Fig. 4 depicts the decay curve of alkyl radicals in PE calculated by the MC method (see the model description). At 80 and 100 K, the decay occurs mainly via the libration of submolecular structures (see Figs. 2 and 5). We deduce

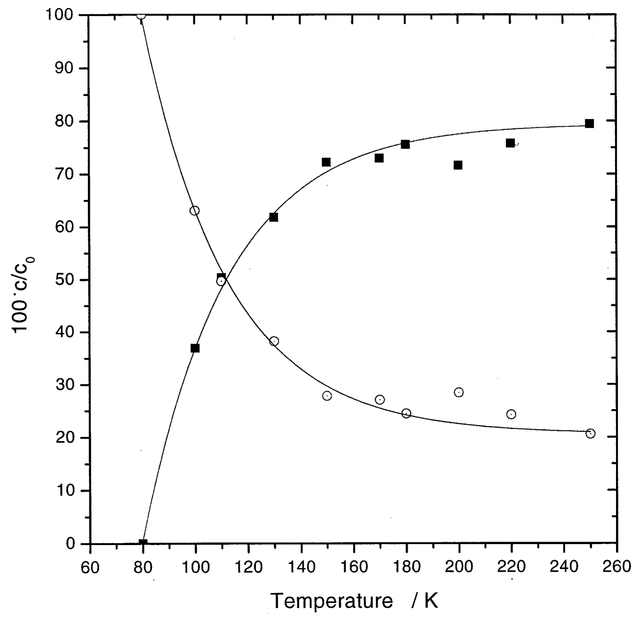

Fig. 2. Percentage of rotational (■) and librational (○) motions in the decay of free radicals in amorphous PE of density $\rho = 0.85$ g cm^{-3}.

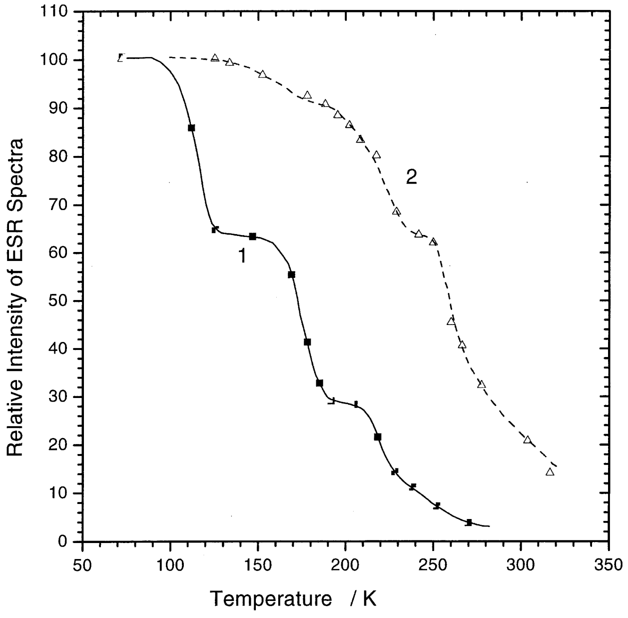

Fig. 3. Decay of free radicals in irradiated PE of two crystallinities: 51% (1) and 89% (2). Taken from Ref. [1].

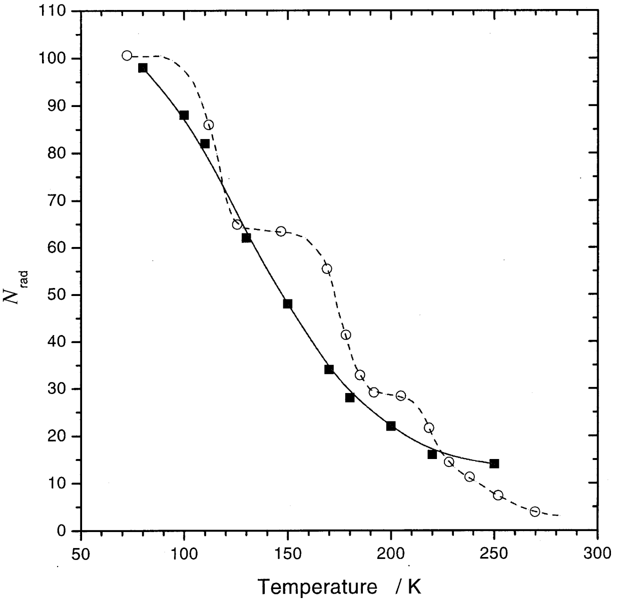

Fig. 4. Decay curve of the free radicals in amorphous PE ($\rho = 0.85$ g cm^{-3}) obtained from MC simulations (■) and the experimental decay curve from irradiated PE with 51% crystalinity (○). The number of radicals (N_{rad}) at the start is 100%.

from this that, at these temperatures, mainly librational motions occurred (Figs. 2, 5(a) and (b)). In addition, from the analysis of the radical decay it appears that mainly radical transfer occurs and not decay. Though the librational motions bring about the transfer of radical centers (Fig. 5(a)), from the number of radicals decayed (Fig. 2), it follows that the transfer has a local character — radical centers do not migrate over large distances. Hence, segmental librations, not the transfer itself, are responsible for the radical decay.

As seen in Fig. 5(b), at higher temperatures, rotational motions occur to a greater extent. The radical centers can migrate and there is a higher probability that the radicals approach each other and vanish. As a result, there is an abrupt decrease of the radical concentration at $T = 150$ K (Fig. 4). Based on these findings, we assume that radicals in amorphous PE are stable at temperatures at which rotational motions of submolecular structures are absent and only librational motions of small amplitude occur, so that the approach of radicals to a distance for their recombination and decay is limited. This is well documented in Fig. 4, in which, for the temperature below 80 K, the concentration of radicals does not vary for both the experimental and the theoretical curves. A change sets in at higher temperatures, where the concentration of radicals decreases. From a theoretical point of view, this is the result of the increasing amplitude of librational motions [7] allowing radicals to approach each other to within a reactive distance. In the temperature range in which rotational and cooperative motions also occur, an abrupt decrease of radical concentration is observed and the vicinity of the T_g is characterized by a complete extinction of alkyl radicals.

Obviously, ESR spectra can also be observed in PE at temperatures of 400 K [10]. These spectra refer to the radicals in the crystalline regions [1].

The results presented here suggest the dependence between free-radical decay and molecular mobility in PE. Though we have used approximations in this theoretical study, the results are in relatively good accord with the experimental decay curve. We can conclude that the chosen model of molecular mobility, which is a function of the temperature, the type of polymer and its density, describe the dynamic processes resulting in the mutual approach of radical centers and the decay of free radicals.

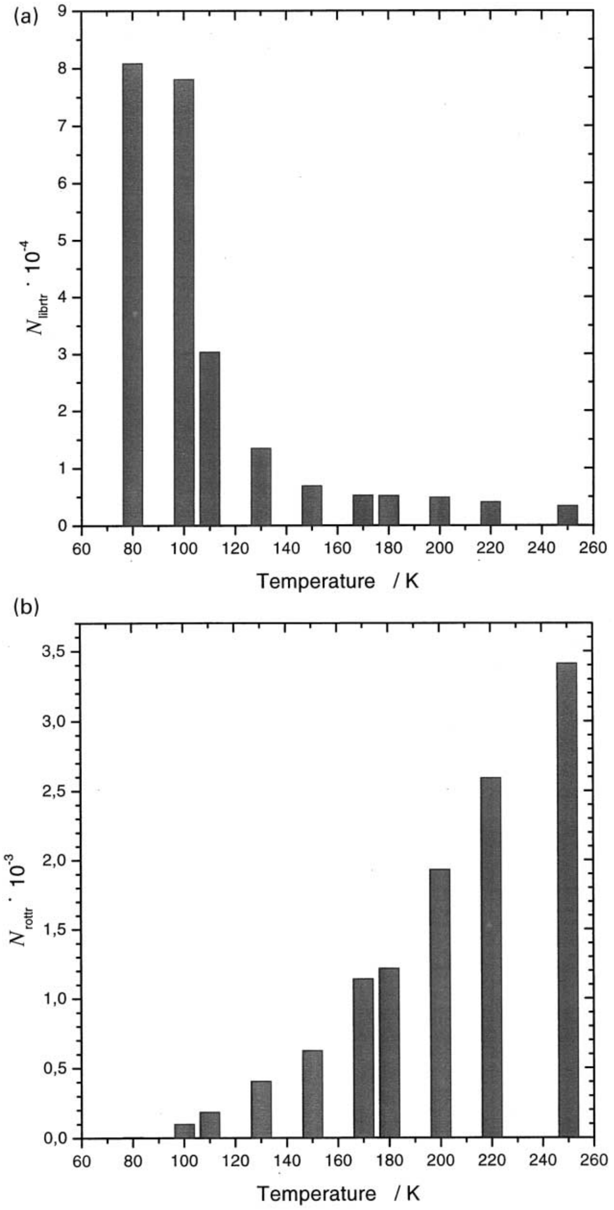

Fig. 5. Number of transferred radical centers in amorphous PE ($\rho = 0.85$ g cm^{-3}) occurring by libration motions N_{librtr} (a) and rotational motions N_{rottr} (b) as a function of temperature. The number of MC trials is 3×10^6.

4. Conclusion

The assumption, of the authors [1] of the experimental measurement of ESR in PE, that molecular mobility accounts for free-radical decay, was confirmed. The MC results show that, at temperatures far below the T_g, only neighboring radicals vanish as a result of librational motions of submolecular structures. With increasing temperature, rotational motions of these structures are realized gradually and, importantly, cooperation between the motions facilitates decay. This occurs at higher temperatures, when the rotating structures have sufficient energy available to stimulate the motion of submolecular structures on adjacent chains in the polymer.

Acknowledgements

This paper was partially supported by the Grant Agency VEGA, project 2/4041/97.

References

[1] Nara S, Shimada S, Kashiwabara H, Sohma J. J Polym Sci A2 1968;6:1435.
[2] Fujimura T, Tamura N. J Phys Chem 1975;79:1859.
[3] Szőcs F, Plaček J, Kotlárik B. J Appl Polym Sci 1977;21:859.
[4] Szőcs F, Plaček J. Eur Polym J 1972;8:525.
[5] Szőcs F, Rostašová O, Tiňo J, Plaček J. Eur Polym J 1974;10:725.
[6] Tiňo J, Urban J, Klimo V. Polymer 1989;30:2136.
[7] Koreň I, Tiňo J, Urban J. Comp Theor Polym Sci 2000;10:491.
[8] Koreň I, Tiňo J. Comp Theor Polym Sci 2001;11:197.
[9] Fujimura T, Arakawa K, Haykawa N, Kuriyama I. J Appl Polym Sci 1982;27:2475.
[10] Hori Y, Kitahara T, Kashiwabara H. Radiat Phys Chem 1982;19:23.
[11] Fujimura T, Hayakawa N, Kuriyama I. J Appl Polym Sci 1982;27:4085.
[12] Shimada S, Hori Y, Kashiwabara H. Polymer 1977;18:25.
[13] Shimada S, Fujiwara A, Kashiwabara H. Radiat Phys Chem 1982;19:33.
[14] Berstein VA, Razguljaeva LG, Galperin VM, Egorov VM, Kolosova TO, Sinani AB. Vysokomol Soedin 1978;20:1885.
[15] Berstein VA, Pertsev NA. Acta Polym 1984;35:575.
[16] Berstein VA, Egorov VM. Vysokomol Soedin 1985;27:2440.
[17] Flory PJ. Science 1975;188:1238.
[18] Brandrup J, Immergut EH, editors. Polymer handbook, vol. 3. New York: Wiley, 1989.
[19] Van Krevelen DW. Properties of polymers, their estimation and correlation with chemical structure. Amsterdam: Elsevier, 1976. p. 129–40.
[20] Tiňo J, Urban J, Klimo V. Polymer 1992;33:3909.
[21] Nunome K, Muto H, Toriyama K, Iwasaki H. Chem Phys Lett 1976;39:542.
[22] Fanconi BM, De Vries KL, Smith RH. Polymer 1982;23:1027.
[23] Rånby B, Rabek JF. ESR spectroscopy in polymer research. Berlin: Springer, 1997.
[24] Shimada S, Hori Y, Kashiwabara H. Polymer 1978;19:763.
[25] Gordy W. Theory and applications of electron spin resonance. New York: Wiley, 1980.