Study of the mechanism of macroradical reactions in solid polymers: 2. Decay of alkyl macroradicals in linear polyethylene at low temperatures

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Kinetic data on the decay of alkyl macroradicals in polyethylene generated by γ-radiation at 77 K have been interpreted in three temperature regions within the diffusion-controlled reaction model at the activation-energy level. Various possible molecular mechanisms that could account for the approach of the reactive centres have been tested from the viewpoint of chemical and physical migration of radicals. Molecular mechanisms have been proposed for the second and third decay regions. They indicate the participation of segmental conformational motion of chain ends in the second region, and the connection of intermolecular hydrogen abstraction with the mobility of the free ends and inner parts of the chains in the third region in amorphous zones of polymers.

(Keywords: polyethylene; alkyl macroradicals; decay; mechanism)

INTRODUCTION

In our earlier paper[1], we dealt with some molecular aspects of macroradical reactivity in solid polymers and formulated an activation-energy approach to the interpretation of kinetic data on the reactivity of macroradicals in condensed polymer systems. According to this model, the total average activation energy for radical decay is given by the sum of statistically weighted energy barriers for molecular motion, chemical migration and final reaction. A more rigorous approach is based on the formal kinetic treatment of the decay reaction according to the scheme:

$$\dot{R}+\dot{R} \underset{k_{-m}}{\overset{k_m}{\rightleftharpoons}} \dot{R}\dot{R} \xrightarrow{k_d} P \qquad (1)$$

giving, for the effective rate constant,

$$k_{eff}=\frac{k_m k_d}{k_{-m}+k_d} \qquad (2)$$

In the special case of rapid reactions, we may write $k_{eff} \simeq k_m$. Then the general transport mechanism in the presence of physical and chemical components of migration give an equation for the effective activation energy for free-radical decay[2]:

$$E_{eff} \simeq E_m = E_{phm} + E_{chm} \qquad (3)$$

Our original model differs from formula (3) only in a small contribution E_d and also includes special processes controlled by physical or chemical migration only. An alternative model has appeared recently[3]; this, however, will not be applied here because of our confinement to the activation-energy level.

The role of segmental conformational mobility of chains in the transport of free valences has been emphasized in the case of physical migration by molecular motion. In the case of chemical migration, inter- and intramolecular hydrogen abstractions have been reported, but other mechanisms (e.g. β-scission or depolymerization) might be considered as well. The methods for estimation of some contributions to the transfer or transport mechanisms have been described elsewhere[1] and more will be presented in this work.

The aim of this paper is to demonstrate the application of the activation-energy approach to the interpretation of published kinetic parameters on the decay of main-chain alkyl macroradicals in linear polyethylene. For this reason, possible transport mechanisms are systematically tested at the molecular level. The procedure for the selection of suitable types of segmental motion using the criteria defined is described in more detail for physical migration, while some results of a recent study[4] are presented for chemical migration by hydrogen abstractions.

EXPERIMENTAL

The results of another study[5] of alkyl macroradical decay in linear polyethylene (PE) represent the experimental basis of the present work. The samples were evacuated and then γ-irradiated from a ^{60}Co source (total radiation dose 31 kGy) at liquid-nitrogen temperature. Electron spin resonance (e.s.r.) measurements were done on a JEOL JEC-3B spectrometer.

The e.s.r. spectrum of irradiated high-density polyethylene (HDPE) represents a sextet signal over a wide temperature interval between 77 and 294 K. The

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identification of the spectrum using a simulation procedure led to the conclusion that the chemical constitution of the reactants corresponds to the main-chain alkyl macroradicals $\sim CH_2\dot{C}HCH_2\sim$.

The decay curve

$$n(T)/N(77\,\mathrm{K})=f(T)$$

for $\tau = 5$ min shows a stepwise course characterized by three temperature regions of reactivity where the number of macroradicals decreases remarkably: first region (I) at 120 K, second region (II) around 200 K and third region (III) at about 250 K. Other authors have reported similar shapes of decay curves in various types of PE, which provides evidence for some common features in the reactivity of alkyl macroradicals independently of the type of polyethylene[6-9]. The conformations of the alkyl macroradicals that decayed in these reaction regions were found using the Heller–McConnell relation

$$a_i^{\mathrm{H}} = B\cos^2\theta_i$$

The decayed alkyl macroradicals showed $\sim tg^{\mp}\sim$ conformation in region I, while in decay regions II and III it was $\sim tt\sim$ conformation of $\dot{C}_\alpha$–C_β bonds.

Kinetic data on the decay of alkyl macroradicals in the three areas mentioned were evaluated by applying the second-order kinetic model. From temperature variations of rate constants, the activation energies of decay were determined: region I, 1.7 kJ mol^{-1} for 115–125 K; region II, 39.3 kJ mol^{-1} for 190–215 K; and region III, 77.0 kJ mol^{-1} for 243–294 K.

The correlation between the range of the decay in regions I and II and the degree of crystallinity in a series of samples with different content of crystalline fraction, and the correlation between the temperature intervals where the decay takes place in all three regions and the relaxation motions, showed that the decay occurs in the amorphous phases of polymer and is connected with δ, γ and $\beta = \alpha_a$ molecular motions.

Several authors have recently done some special experiments concerned with the reactivity of macroradicals in PE, with the aim of explaining the details of the decay mechanism. The results obtained give supplementary information on the analysis described by Nara *et al.*[5] and confirm their observations. From the point of view of our attempt to interpret theoretically the transport mechanism at the molecular level, four aspects are important.

The first is the problem of the mechanism of the decay reaction of alkyl macroradicals. The general opinion accepted is that the decay proceeds by a radical mechanism including a combination reaction of two reactants leading to the formation of bridges between the chains[10,11].

The second problem, closely connected with the preceding one, consists of the question of the localization of the crosslinking reaction in semicrystalline PE. A detailed analysis of all direct and indirect proofs in a review[12] has shown that at small doses the combination of macroradicals proceeds in disordered, amorphous zones of PE.

The third aspect is concerned with the localization of the combination reaction in the amorphous phase and encompasses the problem of alkyl macroradicals in the crystalline phase. In order to clarify the situation when decay takes place in the amorphous phase, whereas alkyl macroradicals are (especially at higher temperatures) preferentially located in the crystalline regions of PE, the migration of radicals from crystallites on the phase boundary[13,14] has been postulated on the basis of the concept of migration of hydrogen abstraction[15]. We have to know the threshold temperature below which this phenomenon does not occur to be able to ascribe the decay to processes and reactions realized in the amorphous phase of PE. A recent paper[16] shows that alkyl centres are incorporated in crystallites up to 275 K.

The last aspect that has to be considered in an investigation of the transport mechanism of free valences is known from radiation chemistry of PE. During radiolysis at 77 K, apart from the formation of macroradicals $\dot{R}$ and H_2, vinylene double bonds are formed[17,18] and skeleton bonds[19] are ruptured. At higher temperatures, vinyl unsaturation vanishes and crosslinking elements of H and Y type[20] are created, i.e. when the temperature is raised, a modification of the amorphous phase occurs because of the formation of H bridges and Y branches. But because of the low radiation dose, which does not reach the gel point for low-pressure PE[21] and does not lead to the destruction of the crystalline phase, we can use the first approximation of a slightly perturbed matrix[22]. On the other hand, H_2 shows catalytic effects on the decay of alkyl centres in PE[23], i.e. it lowers the activation energy of macroradical decay[24]. According to other authors[25], radiolytic hydrogen starts to diffuse from the matrix at 150 K and forms a H_2 atmosphere above the sample. However, as will be seen in another paper[26], the detailed testing of the possibility of the participation of H_2 in the transport of alkyl radicals gives negative results for all reactivity regions. Finally, the end alkyl macroradicals $\sim CH_2\dot{C}H_2$ are stable up to 140 K[27], i.e. they overlap decay region I. This region will not be studied because of the complication of the coexistence of $\sim CH_2\dot{C}HCH_2\sim$ and $\sim CH_2\dot{C}H_2$ macroradicals at about 120 K.

RESULTS AND DISCUSSION

The main conclusion of the above analysis is that decay of alkyl macroradicals in decay regions II and III of γ-irradiated PE proceeds in the amorphous phase. To determine the decay mechanism, i.e. the character of the transport process that ensures the approach of radicals, some possible alternatives have to be tested. For a better understanding of the situation, we first examine the mechanisms on the hypothesis of chemical migration, and then the molecular mechanisms for individual decay regions will be proposed.

Hypothesis of chemical migration

For alkyl macroradicals, there are two possibilities for the transport of free valences proceeding by chemical reaction: β-scission and migration of hydrogen abstraction.

In the first place we examined the possibility that β-scission is the slowest reaction that could control the transport of free valences:

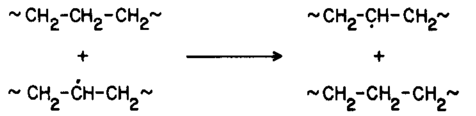
$$\sim CH_2\dot{C}HCH_2CH_2CH_2\sim \xrightleftharpoons[E_{ad}]{E_{\beta sc}} \sim CH_2{-}CH{=}CH_2 + \dot{C}H_2{-}CH_2\sim$$

According to this scheme, the end macroradical $\dot{C}H_2CH_2\sim$ would be formed temporarily. This is not only very reactive but also very mobile, as follows from the fact that it disappears at 140 K[27] and decays by an abstraction reaction, thus re-establishing an alkyl macroradical in another place in the matrix. The activation energy for β-scission, $E_{\beta sc}$, was estimated using the Vojevodskii method[28] according to the relation:

$$E_{\beta sc} = E_{ad} + \Delta H_r \tag{4}$$

Here E_{ad} is the activation energy for addition of an end macroradical to the end vinyl group of the chain and ΔH_r is the enthalpy of this reaction. The individual contributions were estimated as follows. The first contribution was approximated by the activation energy of an analogous addition reaction in low-molecular-weight compounds[29]; the second one, representing the dissociation energy of a C_β–C_γ bond in the macroradical, was calculated by employing a thermodynamic cycle of reactions[28] and additive methods of group contributions of thermodynamic functions[30]. The value of the activation energy for β-scission of alkyl macroradicals is 126.0 kJ mol^{-1} and is much higher than the activation energies determined for free-radical decay in reactivity regions II and III. This mechanism is thus ineffective in a process of approaching free valences at low temperatures.

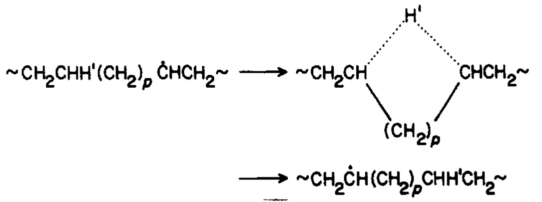
The next possibility investigated was inter- or intramolecular hydrogen-atom migration. First, we examine intermolecular migration. Here the migration of free valence should proceed by transfer of hydrogen between chains according to the scheme:



$$\begin{matrix} \sim CH_2\text{-}CH_2\text{-}CH_2\sim & & \sim CH_2\text{-}\dot{C}H\text{-}CH_2\sim \\ + & \longrightarrow & + \\ \sim CH_2\text{-}\dot{C}H\text{-}CH_2\sim & & \sim CH_2\text{-}CH_2\text{-}CH_2\sim \end{matrix}$$

The values of activation energy were calculated by two methods: BEBO[31] and ZAV/3[32]. These have been successfully applied to the interpretation of kinetic data of hydrogen abstractions in a whole series of reactants[33]. The energy barrier, according to the first procedure, is $E_{chm}^{inter} = 46.1\,kJ\,mol^{-1}$ and, according to the second procedure, it is 48.3 kJ mol^{-1}. A comparison of activation energies for alkyl macroradical decay in both regions shows that, while the mechanism may be eliminated in the region II, it is not possible in region III. The latter case will be discussed below.

The second type of hydrogen transfer reaction is represented by intramolecular migration. The most important types can be summarized as follows:



where $p = 0, 1, 2, 3$ for cases of 1–2, 1–3, 1–4 and 1–5 H transfers. The higher types show features of intermolecular migration[1]. The molecular aspects of these transport channels have been analysed in detail elsewhere[4]. Here we briefly summarize only the most important results. A basic condition for realizing 1–2 to 1–5 H transfers is the presence of a favourable geometry for free valence transfer, i.e. maximum approach of the respective $\dot{C}$ and H (H′) atoms. After accepting the model of rotation-isomeric states of chain bonds, this means that a certain conformational sequence of the cyclic state corresponds to a certain configuration of q bonds (where $q = p + 1$) in the cycle. If the bonds have rotation states near t and $g^\pm$ positions, there are 3^q combinations of the bond states in a cycle. Each of the sequences for PE is characterized by two distances, $d_{C\ldots H,H'}$. The conformational sequence of q bonds characterized by the greatest bending of part of the macromolecule is considered to be the optimum conformation of the initial cycle. This leads to maximum mutual approach of C_{sp^2} and H(H′) atoms. Thus the geometry–energy criterion is a condition for maximum approach to the reaction centres. It is also necessary to consider the so-called morphological and radical criteria.

The morphological criterion requires compatibility of the conformational sequence of the cyclic state with the conformational microstructure of macromolecules in the corresponding phase region of the polymer. This criterion is not relevant in our case because the existence of all possible combinations of bond rotational states can be admitted in the amorphous phase.

Under the radical criterion we understand that the end bonds should be in the conformational state that agrees with the state of $\dot{C}_\alpha$–C_β bonds. This follows directly from the idea of intramolecular hydrogen migration, i.e. if the assumption of a dominant intramolecular mechanism in the transport of radical centres is accepted, then the observed constant shape of the e.s.r. spectra confirms that the conformation of macroradicals does not vary in the approach process. The result of this analysis for PE is a set of optimum conformational sequences of bonds in the cycle for the respective types of intramolecular transfers of alkyl macroradical: 1–2, $\sim t(t)t\sim$; 1–3, $\sim t(tt)t\sim$; 1–4, $\sim t(tg^\pm t)t\sim$; and 1–5, $\sim t(tg^\pm g^\pm t)t\sim$.

Estimates of energy barriers for the first two cases were made by employing a recently formulated E-BEBO method[34]. The value of 145.4 kJ mol^{-1} was found for 1–2 H transfer, and for 1–3 intramigration it was 146.9 kJ mol^{-1}. Analogous reactions of low-molecular-weight radicals in the gaseous phase are the 1–2 isomerization of 2-pentyl radical and approximately 1–3 isomerization of 1-pentyl radical, which show activation energies[35] of 138.1 kJ mol^{-1} and 129.8 ± 4.1 kJ mol^{-1}. The estimated values have to be understood as lower limits, because they can be expected to increase as a result of the existence of inertial and viscous effects in the solid polymer matrix. These transport mechanisms of alkyl radical centres can obviously be eliminated. On the other hand, in the case of higher isomerizations, the activation energies for the decay in regions II and III can be compared only with the activation energies of 1–4 and 1–5 isomerizations of low-molecular-weight analogues, since there is no theoretical method able to describe them. The experimental values of 1–4 isomerization of 4-octyl to 2-octyl radical and 1–5 isomerization of 2-octyl to 3-octyl radical are 92.1 and 46.1 kJ mol^{-1} respectively[36]. An increase of these values in going from gaseous to condensed phase occurs, and therefore the 1–4 H transfer can also be eliminated. As for the 1–5 H transfer through a relatively unstrained transition state, its value can correspond to the activation energy for the third region of free-radical decay even though an increase in energy barrier is taken into account. But according to the results of conformational analysis, this mechanism will not appreciably affect the approach of alkyl centres. This is because the probability that the chains in the amorphous phase would have only the optimum conformational sequence necessary for 1–5 migration is very low, practially negligible.

Recapitulation of the analysis described shows that there is no chemical mechanism in temperature region II, but participation of the intermolecular type of H abstraction can be expected in region III. These partial results may be used to test other possible transport mechanisms of alkyl centres on the hypothesis of physical migration or physicochemical migration. It is appropriate to divide this problem according to the reactivity regions.

Mechanism of macroradical decay in region II

It follows from what has been said above that for this decay region we have to look for a mechanism of approaching radicals within the hypothesis of physical migration. In their original experimental paper, Nara *et al.*[5] found a correlation between the decay of alkyl macroradicals and γ-relaxation motions, thus indicating a connection between these phenomena. There are two types of mutual relation[1]: (a) direct correlation, i.e. molecular motion starting in the given temperature region and leading to approach of the reaction centres; (b) indirect correlation, i.e. molecular motion dominating in the given temperature region and forming conditions for processes that cause decay of radicals. If the first relation is valid, not only temperature but also activation-energy correlation between both phenomena should exist, but the second relation ought to be characterized only by temperature correlation. A comparison of the activation energy for decay of alkyls in region II ($E_d^{II} = 39.3$ kJ mol^{-1}) with activation energies for γ-molecular motion determined by mechanical and dielectric methods[37] ($E_\gamma = 46.2$–63.0 kJ mol^{-1}) indicates an indirect connection between the reactivity of macroradicals and the mobility of chains in the amorphous regions of PE. This implication is also supported by the results of a detailed study of the molecular mechanism of γ-molecular motions in the amorphous regions of PE[38]: the localized motion of five-bond crankshaft segments of $Ps_n(tg^{\pm}t)s_{n+4}Q \rightleftharpoons Ps'_n(tg^{\mp}t)^x s'_{n+4}Q$ type, mainly a special mode of motion including diffusion motion of $2g1$ kink sequence: $Ptg^{+}(tg^{-}t)ttQ \rightleftharpoons Ptt(tg^{+}t)g^{-}tQ$. This interpretation of γ-molecular motion agrees with recent results of computations of the lineshapes in ^{2}H n.m.r. spectra of PE[39]. An alternative or complementary proposal for the mechanism is based on the idea of *gauche* migration $Pg^{\pm}ttQ \rightleftharpoons P'ttg^{\pm}Q'$ with a weak motion of chain tails leading in a glassy matrix to deformation of the structural molecular parameters[40]. γ-Molecular motions cannot directly contribute to the approach of radical centres because the mobile parts of their segments do not contain the $\sim tt \sim$ sequence of $\dot{C}_\alpha$–C_β bonds of alkyl macroradicals.

The actual motion type based on segmental conformational motions that could secure the transfer of $\sim\dot{C}H\sim$ centres in decay region II may be determined from analysis of topological chain structures in amorphous zones of semicrystalline PE. According to present ideas[41], the disordered regions with lamellar structure of crystallites are realized by (a) free chain ends, part of the macromolecule being built in the crystallite; (b) bridges between lamellae of crystallites; (c) tight or loose folds of chains incorporated in the lamella; (d) free chains, i.e. macromolecules that are not part of crystallites. The inner segments can evidently occur in all the structures, while the end segments occur only in structures (a) and (d). As has already been said, γ-molecular motion includes only motion of inner five-bond segments. For this reason, the end segments appear to be right for segmental conformational mobility.

According to the type of catalyst[42], the chains of linear polyethylene can end in a saturated, methyl, group (titanium catalysts) and/or in unsaturated, vinyl, group (chromium catalysts). Since the type of catalyst was not specified in the original paper[5], we investigated both types of end segment. There are also other facts favouring chain end segments. First, 90–98%[43,44] of chain ends are localized outside the crystalline region of PE, at least for the vinyl chain end. Secondly, during radiolysis of PE at 77 K, alkyl macroradicals and H_2 are formed[18] and chain scission[19] occurs. We expect that the end macroradicals decay either by geminal recombination under the conditions of a cage effect (crystalline phase) or by transformation to alkyl macroradicals $\sim CH_2\dot{C}HCH_2\sim$ in less tight surroundings in amorphous regions of the matrix, leading to methyl endings. Thirdly, by heating the sample from 77 K to the corresponding temperature from the given interval, alkyl centres decay partially due to the combination reaction, yielding H bridges, and vinyl groups[45] decay slightly, probably giving Y branches[20,46]. Alkyl centres trapped near these vertex points are almost immobile at low temperatures, so that they can be excluded from participation in transfer in the matrix.

The choice of the proper mobility type of end and inner segments in segmental conformational mobility depends on the following criteria:

(1) Mobility criterion, i.e. the demand for minimum motion of chain 'tails' following from an argument recognizing the existence of inertial and viscous effects in the condensed phase. This condition involves independence of segment motions on other parts of a macromolecule and leads to the concept of correlation of transitions including simultaneous crossing of two or more barriers.

(2) Radical criterion, i.e. the assumption that the mobile part of the segment that changes its position within the matrix includes the respective conformational sequence of $\dot{C}_\alpha$–C_β bonds obtainable from the known relation between the geometry of macroradicals and hyperfine splitting constants.

(3) Energy criterion, i.e. the conditions of minimal intramolecular energy of the mobile part of the segment. This concerns the so-called pentane interference, including strong repulsion interaction in the sequence $\sim g^{+}g^{-}\sim$ and conditions their negligible probability of occurrence.

(4) Free-volume criterion, i.e. from the set of several possible segments of a given mobility type, such a segment is selected that requires the smallest so-called minimal local free volume for its motion. This is estimated on the basis of the cylindrical approximation, according to which it has the form of a cylindrical section or a set of

concentric cylindrical sections:

$$V_f^{\min}=\tfrac{1}{3}V_c=\tfrac{1}{3}\sum R_i^2 L_i \qquad (5)$$

where V_c is the volume of the formation created by complete free rotation around the given bond or bonds, and R_i and L_i are the radii and lengths of partial cylinders, which may be determined from the known structural-molecular parameters. The coefficient $\frac{1}{3}$ stems from the fact that, within the approximation of a simple jump, the conformational transition represents a change by ±120°.

As has already been said, macromolecules may be terminated by methyl or vinyl groups. The mobility criterion shows that crank motions might be a suitable type of chain-end segment. They involve a transfer of the rigid mobile part of the segment comprising the radical centre through rotational transition of a specific bond located near the chain end while the rest of the macromolecule is rigid. Acceptance of the radical criterion leads to the conclusion that the minimal segment for a chain terminated by methyl involves four bonds, while in the case of vinyl termination it contains five bonds. When the free-volume criterion is considered, we see that the segments mentioned need the least free space, the estimated values for $V_f^{\min}$ being 0.133 nm^3 and 0.145 nm^3 respectively. For estimation we used the group approximation and the known parameters of bond lengths, bond angles, and van der Waals radii[47]. The values of dihedral angles agreed with $\sim tt \sim$ sequence of the radical region: for CH_3– ending, $\phi_1=\phi_2=180°$; and for CH_2=CH– ending, $\phi_2=\phi_3=180°$ and $\phi_1=180°$. The existence of free spaces of the values given is supported by the result (0.204 nm^3) found for bulk film PE by measurement of the solubility of hydrogen isotopes[48]. In addition, γ-molecular motion leads to fluctuation in the positions of chain atoms in the amorphous phase. The fluctuation results in migration of free volume, leading to redistribution of free spaces in the matrix, which may create conditions for the occurrence of minimal local free volume in the vicinity of the end segments. This may be one of the reasons for the indirect connection between reactivity of macroradicals and chain mobility in the matrix. The concept of motion of relatively more mobile chain ends is also supported by the partial disappearance of vinyl groups when heating the radiolysed PE from 77 K to higher temperatures[45] preceeding by their reaction with alkyl centres (during their transfer), as has recently been confirmed, at least at room temperature[20].

Consideration of the above criteria for inner segments leads to the conclusion that the crankshaft mobility type is of thirteen-bond segments. But these are characterized by great energy demands and thus will not be realized in reactivity region II.

The mechanisms of crank motion of end segments in PE are shown in *Figure 1*. Their energies were estimated using a procedure described in part 1[1] (see also *Tables 1* and *2*). Within the simple jump concept, six physically different modes of crank motion are described in both cases, in agreement with the Helfand notation for conformational transitions[49]. A limitation has been accepted that both bonds adjacent to the bond that changes its rotation state are in *trans* states because the bond fraction in this state considerably exceeds the portion of bonds in $g^{\pm}$ states. Intramolecular contributions to the total energy barrier were approximated by values from the rotation-energy diagram of the central bond of an appropriate model compound for PE (n-hexane obtained by molecular-mechanical method[50]): $E(t \rightarrow g^{\pm})=11.3$ kJ mol^{-1}, $E(g^{\pm} \rightarrow t)=8.8$ kJ mol^{-1} and $E(g^{\pm} \rightarrow g^{\mp})=17.2$ kJ mol^{-1}. The intermolecular part consists of group contributions of methyl and methylene groups and CH_2=, =CH– and –CH_2– groups[51] for $T=298$ K. The temperature correction for $\bar{T}=\frac{1}{2}(T_{\min}+T_{\max})=202.5$ K represents a slight increase by about 1 kJ mol^{-1}. The probabilities of occurrence of the bonds in one of three possible rotation states were calculated according to the Boltzmann relationship, $p=e^{-\Delta E/RT}$, where ΔE is the energy difference between *gauche* and *trans* states from the rotation diagram of n-hexane[50] (2.45 kJ mol^{-1}), which agrees well with experiment[52,53] (2.51 ± 0.42 kJ mol^{-1}). Then the statistically weighted values for the energy barriers of crank motion are: for methyl ending, $\bar{E}_{\mathrm{fm,methyl}}=28.1$ kJ mol^{-1}; and for vinyl ending, 27.1 kJ mol^{-1}. After considering the relationship between the activation energy and the energy barrier, the values obtained for activation energies are 29.8 and 28.8 kJ mol^{-1} respectively. These values are very close and indicate almost the same mobility independently of the type of chain termination. *Tables 1* and *2* show that the largest and almost the same proportion belongs to crank motions connected with $t \rightleftharpoons g^{\pm}$ transitions, while the participation of the highly energetic $g^{\pm} \rightleftharpoons g^{\mp}$ transition through the *cis* state is almost negligible.

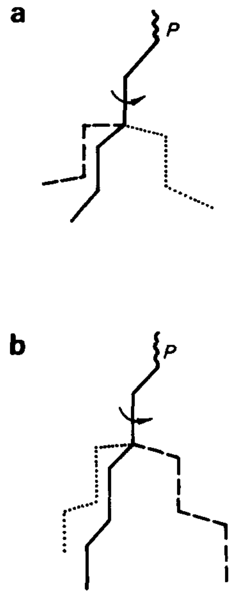


Figure 1 Scheme of the mechanism of crank motion of minimal end segments in PE: (a) methyl, (b) vinyl ending

To complete the analysis of the decay mechanism, we have to mention the final, i.e. combination, stage of decay at contact. Until recently, the concept of combination reactions of low-molecular-weight radicals[54] without an activation energy has been accepted. Although the activation energy has lately been experimentally estimated, the error in determining such energy often reaches values comparable with very low values of activation energy itself[55] (about 5 kJ mol^{-1}). Since the combination of radical centres is a strongly localized process, we assume that the combination of macroradicals may be approximated by the combination of low-molecular-weight analogues. Thus the combination of alkyl macroradicals is approximated by the

Table 1 Kinetic energies (kJ mol^{-1}) of crank motions of minimal end segments with methyl ending in PE: $Ps_nQ \rightarrow Ps'_nQ^x$

	Conformational motion						
a	Initial	Final state	$E_{\mathrm{intra}}^{(a)}$	$E_{\mathrm{inter}}^{(298\,\mathrm{K})}$	$E_{\mathrm{fm}}^{(a)}$	$p_i^{(a)}(\bar{T})$	$c_a(\bar{T})$
1	$Ptt(tt)$	$Ptg^+(tt)^x$	11.3		29.3	0.682	0.245
2	$Ptt(tt)$	$Ptg^-(tt)^x$	11.3		29.3	0.682	0.245
3	$Ptg^+(tt)$	$Ptt(tt)^x$	8.8	18.0	26.8	0.159	0.253
4	$Ptg^+(tt)$	$Ptg^-(tt)^x$	17.2		35.2	0.159	0.002
5	$Ptg^-(tt)$	$Ptt^+(tt)^x$	8.8		26.8	0.159	0.253
6	$Ptg^-(tt)$	$Ptg^+(tt)^x$	17.2		35.2	0.159	0.002

Table 2 Kinetic energies (kJ mol^{-1}) of crank motions of minimal end segments with vinyl ending in PE: $Ps_nQ \rightarrow Ps'_nQ^x$

	Conformational motion						
a	Initial state	Final state	$E_{\mathrm{intra}}^{(a)}$	$E_{\mathrm{inter}}^{(298\,\mathrm{K})}$	$E_{\mathrm{fm}}^{(a)}$	$p_i^{(a)}(\bar{T})$	$c_a(\bar{T})$
1	$Ptt(ttt)$	$Ptg^+(ttt)^x$	11.3		28.3	0.682	0.246
2	$Ptt(ttt)$	$Ptg^-(ttt)^x$	11.3		28.3	0.682	0.246
3	$Ptg^+(ttt)$	$Ptt(ttt)^x$	8.8	17.0	25.8	0.159	0.252
4	$Ptg^+(ttt)$	$Ptg^-(ttt)^x$	17.2		34.2	0.159	0.002
5	$Ptg^-(ttt)$	$Ptt(ttt)^x$	8.8		25.8	0.159	0.252
6	$Ptg^-(ttt)$	$Ptg^+(ttt)^x$	17.2		34.2	0.159	0.002

combination of 2-propyl radicals, where an activation energy of 5.4 kJ mol^{-1} was found[55]. The theoretical estimate by the method of thermochemical kinetics according to the relation $E_{\mathrm{comb}} = E_{\mathrm{dis}} - \Delta H_{\mathrm{r}}$ (E_{dis} being the activation energy of dissociation of the product of combination, equal to 318.2 kJ mol^{-1}, and ΔH_{r} the reaction enthalpy determined by the group method) gives[54] 5.9 kJ mol^{-1}.

Since the activation energy of the final stage is very low and lies within the limits of error of the activation energy of alkyl macroradical combination (it is not reported in the original paper, but it is usually $\pm$5–8 kJ mol^{-1}), a model of diffusion-limited reaction may be used to a good approximation. Then the estimated energy barrier of minimal crank motions is almost consistent with the experimental activation energy of the decay of alkyl centres in decay region II of PE. The value of $\bar{E}_{\mathrm{fm}}$, which is slightly lower than E_{eff}, can be understood in the light of the approximate nature of the method of estimation of the energy barrier of physical migration and strictly, for the rate constants at the diffusion limit, it holds that $k_{\mathrm{eff}} \leqslant k_{\mathrm{m}}$ so that $E_{\mathrm{eff}} \geqslant E_{\mathrm{m}} = \bar{E}_{\mathrm{fm}}$.

On the basis of the relatively good agreement, we may outline the decay mechanism of alkyl centres in region II of the reactivity as follows: the reaction of a certain fraction of alkyl centres proceeds by their mutual combination, the approach of reactants being partially caused by crank motions of chain-end segments in the amorphous phase. Then two cases are possible: (a) motion of one chain end carrying the radical centre towards the neighbouring centre attached to the neighbouring rigid chain and/or (b) motion of two end radical segments of macromolecules.

The proposed correlation of free-radical decay in region II is consistent with some literature data. The first concern the character of the motion of macromolecules in the region examined. Detailed analysis of all data on mobility in semicrystalline polymers led to the concept of a double glass transition[56]. The low glass transition $T_{\mathrm{g(L)}}$ of PE lies at 195 $\pm$ 10 K and the upper glass transition $T_{\mathrm{g(U)}}$ at 240 $\pm$ 20 K. Model calculations[57] that try to describe the topological character of the moving units showed that $T_{\mathrm{g(L)}}$ is caused by motion of macromolecular chains, so-called cilia. (On the other hand, $T_{\mathrm{g(U)}}$ depends on the degree of crystallinity and is assigned to motion of very loose bridges and folds of macromolesules in amorphous zones.)

The second fact concerns the space distribution of reactants. It follows from the proposed molecular correlation that, in this temperature region, reaction of relatively close radical centres should take place. It is interesting to compare this conclusion with experimental findings in a similar type of linear PE (Sholex 6050 with $\chi_{\mathrm{c}} = 83\%$), where the e.s.r. spectra of the $\Delta M_{\mathrm{s}} = 1$ transition from 'isolated' macroradicals and the $\Delta M_{\mathrm{s}} = 2$ transition from radical pairs were recorded[9]. Decay curves of both signals are of stepwise character very close to that in Sholex 6000. Moreover, there is a very good temperature correlation between the decay of macroradicals and their specific space-distribution forms – radical pairs in decay regions I and II – indicating that the decay of at least part of the macroradicals is due to reaction of radical pairs of intermolecular type. An approximate estimate of distances between radical centres over the studied temperature region may be done as follows. The minimal interspin distance between radical pairs in PE at 77 K is[58] $L_{\mathrm{min}} = 0.50 \pm 0.02$ nm. On the other hand, the average interspin distance in various forms of PE and n-alkanes at the same temperature is[59,60] 0.53 nm and is independent of the physical state of the matrix, i.e. the stability of radical pairs with a certain interspin distance depends only on temperaure[61]. In a special experiment[61] with polycrystalline n-decane, which can be regarded as a model compound for PE[9], the graphical dependence of minimum interspin distance on temperature $L_{\mathrm{min}} = f(T)$ was determined. The plot shows that radical pairs with $L_{\mathrm{min}} \simeq 0.73$ nm are present in the matrix in our temperature region. If making a simple estimate of interspin distances from crank motion, then in the case of one reactant only moving towards the other we obtain $L = 0.66$ nm while when both reactants move $L = 0.86$ nm and 0.90 nm. These values are of the same order as the given L_{min}.

On the basis of the above arguments, we may conclude that in region II the decay of alkyl centres proceeds by mutual combination, approach of $\sim\dot{C}H\sim$ centres being controlled by physical migration in the presence of crank motions of macromolecular end segments.

Mechanism of macroradical decay in region III

Approach of centres within this temperature region may be due to physical migration and/or chemical migration in the form of intermolecular migration in connection with a certain chain motion.

First, we examine the hypothesis of physical migration. The original paper[5] reports that the third reaction region lies within $\beta=\alpha_a$ of the molecular motions, i.e. within the region of the glass transition in PE. The analysis of the glass phenomenon in a series of PE showed that, for linear PE, the related relaxation peak in dynamic-mechanical spectra was observed only occasionally, namely after special processing by the so-called quenching technique[62]. This indicated that β-molecular mechanism involves motions of relatively loose bridges and folds in amorphous zones among crystallites[57]. From recent detailed ^2H n.m.r. study of PE isothermally crystallized from the melt with $K_c=77\pm5\%$, it is obvious that changes in the shape of spectra with temperature may be interpreted in terms of localized segmental conformational motions[39]. The ^2H n.m.r. data in the temperature interval between 230 and 300 K were evaluated by superposition of crankshaft motions with a non-rigid mobile five-bond segment part and with a rigid mobile segment part (preferably minimal seven-bond segment).

According to our topological analysis associated with mobility, energy and radical criteria show that the minimal segmental conformational motion also incorporates the mechanism of crankshaft type[63] but the segments contain thirteen bonds in all four-topological structures. The conformational sequences of eleven-bond mobile parts are given in *Table 3* in order according to the number of g bonds and minimal free volume. The first three sequences show minimal free-volume requirements, the first having lowest intramolecular energy. *Figure 2* shows a scheme of crankshaft motions of this segment. The energies of the three segments were estimated by the procedure described in ref. 1. The procedure is demonstrated on the first segment in *Table 4*. The intramolecular contribution is given by an additive scheme. The intermolecular part consists of contributions due to cohesive energy of five basic structural units, $\sim CH_2–CH_2\sim$, which are 8.80 kJ mol^{-1} for the average temperature of kinetic measurements, $\bar{T}=\frac{1}{2}(T_{min}+T_{max})=258$ K. The value involves a correction for the temperature dependence of the molar cohesion energy[51] obtained from the empirical relation between molar cohesion energy and molar volume[64] and a model of thermal expansion of polymer[65] together with the concept of double glass transition of semicrystalline polymers[56]. The statistically weighted energy barrier of

Table 3 Summary of conformational sequences of crankshaft segments satisfying a set of criteria

k	Conformational sequence of the mobile part of the segment	n_g	V_f^{min} (nm^3)
1	$(tg^+tttg^+tttg^+t)$	3	0.220
2	$(tg^+tttg^+tg^+tg^-t)$	4	0.220
3	$(tg^+tg^-tg^-tttg^-t)$	4	0.220
4	$(tg^+tttg^-tg^-ttt)$	3	0.258
5	$(tttg^+tg^+tttg^-t)$	3	0.258
6	$(tg^+tg^-tg^+tg^+ttt)$	4	0.258
7	$(tttg^+tg^+tg^-tg^+t)$	4	0.258
8	$(tttg^+tttg^+ttt)$	2	0.287

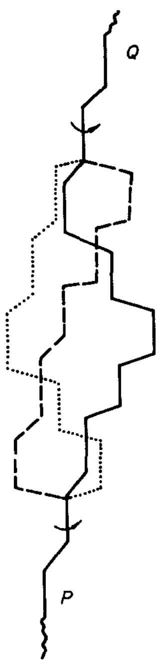


Figure 2 Scheme of individual modes $a=1$ and 2 of motion of crankshaft segment from *Table 4*

Table 4 Kinetic energies (kJ mol^{-1}) of crankshaft motions ot the type $Pts_n(tg^+tttg^+tttg^+t)s_{n+12}tQ \rightarrow Pts'_n(tg^+tttg^+tttg^+t)^x s'_{n+12}tQ$ in PE

	Conformational motion						
a	Initial state	Final state	$E^{(a)}_{intra}$	$E_{inter}(\bar{T})$	$E^{(a)}_{fm}$	$p_i^{(a)}(\bar{T})$	$c_a(\bar{T})$
1	$Ptt(t\ldots t)ttQ)$	$Ptg^+(t\ldots t)^x g^-tQ$	22.6		66.6	0.515	0.19168
2	$Ptt(t\ldots t)ttQ)$	$Ptg^-(t\ldots t)^x g^+tQ$	22.6		66.6	0.515	0.19168
3	$Ptt(t\ldots t)g^+tQ$	$Ptg^+(t\ldots t)^x ttQ$	20.1		64.1	0.164	0.19591
4	$Ptt(t\ldots t)g^+tQ$	$Ptg^-(t\ldots t)^x g^-tQ$	28.5		72.5	0.164	0.00390
5	$Ptt(t\ldots t)g^-tQ$	$Ptg^+(t\ldots t)^x g^+tQ$	28.5		72.5	0.164	0.00390
6	$Ptt(t\ldots t)g^-tQ$	$Ptg^-(t\ldots t)^x ttQ$	20.1	44.0	64.1	0.164	0.19591
7	$Ptg^+(t\ldots t)g^+tQ$	$Ptg^-(t\ldots t)^x ttQ$	25.9		69.9	0.052	0.00418
8	$Ptg^+(t\ldots t)g^+tQ$	$Ptt(t\ldots t)^x g^-tQ$	25.9		69.9	0.052	0.00418
9	$Ptg^+(t\ldots t)g^-tQ$	$Ptg^-(t\ldots t)^x g^+tQ$	34.3		78.3	0.052	0.00008
10	$Ptg^+(t\ldots t)g^-tQ$	$Ptt(t\ldots t)^x ttQ$	17.6		61.6	0.052	0.20023
11	$Ptg^-(t\ldots t)g^-tQ$	$Ptt(t\ldots t)^x g^+tQ$	25.9		69.9	0.052	0.00418
12	$Ptg^-(t\ldots t)g^-tQ$	$Ptg^+(t\ldots t)^x ttQ$	25.9		69.9	0.052	0.00418

crankshaft motions is $E_{\mathrm{fm}} = 64.7\ \mathrm{kJ\ mol^{-1}}$, giving, after correction, an activation energy of $66.9\ \mathrm{kJ\ mol^{-1}}$; this is a little lower than the experimental activation energy for free-radical decay ($77.0\ \mathrm{kJ\ mol^{-1}}$). If crankshaft motions of this type ensure the transport of $\sim\dot{\mathrm{C}}\mathrm{H}\sim$ centres, then the highest portion according to *Table 4* should be the tenth mode, followed by the third, sixth, first and second modes respectively.

The second possibility of interpretation of the mechanism of approach of reactants in decay region III is based on the above-mentioned possible participation of intermolecular H migration in connection with some motion according to the hypothesis of physicochemical migration. The analysis of topological structures of the amorphous phase and examination of a set of criteria lead to the conclusion that crank motions of end segments localized almost completely in disordered regions[42,43] (and therefore relatively very mobile) may be an actual motion type. The energies were estimated in a way similar to that in region II but the corresponding probabilities were calculated for $\bar{T} = 258\ \mathrm{K}$. Then the average activation energy of crank motions of minimal end segments $\bar{E}_{\mathrm{fm}}$ is $30.8\ \mathrm{kJ\ mol^{-1}}$ for methyl ending and $29.8\ \mathrm{kJ\ mol^{-1}}$ for chains with vinyl at the end. The energy barrier of intermolecular migration is $E_{\mathrm{chm}}^{\mathrm{inter}} = 47.2\ \mathrm{kJ\ mol^{-1}}$, which is the arithmetic mean of BEBO and ZAV/3 values. Then $\bar{E}_{\mathrm{m}} = 77.0$–$78.0\ \mathrm{kJ\ mol^{-1}}$, a value very close to experiment.

Now we evaluate both alternatives, i.e. we try to explain any preference. The second alternative is preferred because it provides results in better agreement with experiment. This is supported by several arguments. The disadvantage of the first mechanism is that the probability of occurrence of conformational sequences of the mobile parts is relatively very low[63], and it is further lowered after considering radical, energy and free-volume criteria. Apart from this, the proposed transport mechanism indicates the approach of relatively close centres (~ 0.66 nm distance) in the case of the motion of one segment or 0.86–0.90 nm for the motion of two segments. Though these values lie within the limits of interspin distances of radical pairs (0.3–1.0 nm), the experiment with analogous LPE showed[9] that the upper temperature of detectability of radical pairs characterized by maximum interspin distance 0.8–1.0 nm was little higher than 250 K, i.e. close to the lower limit of the interval of kinetic measurements (243–273 K). On the other hand, we can say in favour of the second migration mechanism that the existence of more distant reactants indicates the presence of a chemical mechanism, the most probable being migration of free valence by hydrogen abstraction. This is in good agreement with the fact[9] that, at temperatures above 250 K, allyl macroradicals appear, which may be formed from alkyl macroradicals only by means of a H abstraction mechanism. A relatively good accord of activation energies, when crank motions of end segments occur, indicates that they are effective in relay type of free valence migration. But after considering the concentration argument, i.e. material balance of chain ends (initial concentration + additional concentration caused by scission and transformation during γ-radiolysis + partial loss caused by their partial participation in decay region II) we see that motions of the residual ends are probably not the only possible motions participating in the transport stage. We have therefore to admit the participation of some other conformational motions of inner parts of chains, probably *gauche* migration and/or kink motions, especially creation and annihilation of 2*g*1 kink defect[66]. These motion types are accompanied by slight deformation of structure-molecular parameters of attached chain tails, which results in approach of the reaction centres RH and $\dot{\mathrm{R}}$. A rough estimate of the energy of these motions performed by a simplified model[1] yields energy barriers for *gauche* migration of $Pg^{\pm}ttQ \rightleftharpoons P^{x}ttg^{\pm}Q^{x}$ equal to $28.5\ \mathrm{kJ\ mol^{-1}}$ and for creation and annihilation of kink sequences $PtttQ \rightleftharpoons P^{x}g^{\pm}tg^{\mp}Q^{x}$ equal to 31.0 and $26.0\ \mathrm{kJ\ mol^{-1}}$ respectively. After addition of $E_{\mathrm{chm}}^{\mathrm{inter}}$ we obtain E_{m} between 73.2 and $78.2\ \mathrm{kJ\ mol^{-1}}$, which is close to $E_{\mathrm{eff}} = 77.0\ \mathrm{kJ\ mol^{-1}}$. It is reasonable to conclude that alkyl centres decay in reactivity region III by mutual combination; approach proceeds by a mechanism of relay type through intermolecular migration in connection with conformational motions of end segments and inner parts of macromolecules.

CONCLUSION

We have proposed molecular mechanisms for transport stages for the decay of alkyl macroradicals in linear polyethylene in an attempt to explain a very interesting phenomenon of stepwise reactivity. Application of the activation-energy approach to effective activation energies has enabled us to discuss transport mechanisms in terms of segment conformational mobility. Approach of reactants in decay region II is controlled by conformational motions of chain ends and, in region III, intermolecular migration proceeds in connection with conformational motions of both end and inner parts of chains in the amorphous phase of polyethylene.

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