A STUDY OF THE MECHANISM OF DECAY OF ALKYL MACRORADICALS IN ISOTACTIC POLYPROPYLENE

Josef BARTOŠ* and Jozef TIŇO

Institute of Polymers, Chemical Research Centre, Slovak Academy of Sciences, 842 36 Bratislava

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The kinetic data of decay of alkyl macroradicals in two temperature regions in isotactic polypropylene exposed to gamma radiation at 77 K were interpreted in terms of the model of diffusion-limited reactions at the activation energy level. The potential molecular mechanisms of transfer of the radical centres were tested from the point of view of their physical and/or chemical migration. Two mechanisms are suggested for the mutual approach of the centres in macroradical decay regions I and II in the amorphous zones of the matrix. Both of them involve the contribution of segmental conformational motions, the mobility of the terminal segments being of importance in region I whereas in region II the mutual nearing of the reactants proceeds in a relay way *via* intermolecular H-abstraction in conjunction with crank and crankshaft motions of the end and inner segments of the chain.

Within the scope of the model of diffusion-limited reactions in solid systems, we have applied the activation energy approach to the study of reactions of radical centres and pointed to some molecular aspects of the macroradical reactivity in polymeric matrices[1]. This approach has been employed with success for the interpretation of the stepwise nature of the temperature dependence of the alkyl macroradical decay in linear polyethylene[2]. Molecular mechanisms of the mutual nearing of macroradicals in two regions of the decay reactivity have been established, and these suggest that the segmental conformational mobility of the chains may play an important part in the transport stages of the decay process.

The aim of this work was to apply the above approach to the interpretation of the mechanism of the mutual approaching of alkyl macroradicals in isotactic polypropylene resulting in their decay in the post-radiation conditions.

RESULTS AND DISCUSSION

Our theoretical analysis is based on the experimental results of the original paper[3] supplemented with additional data obtained by other authors[4-11].

Isotactic polypropylene was irradiated at 77 K and the macroradicals formed were analyzed from the structure and reactivity points of view by the ESR technique[3]. The spectrum scanned

* Present address: Research Institute of Rubber and Plastics Technology, 764 22 Gottwaldov.

at 77 K has an octet nature. The signal is attributed to the alkyl macroradicals $\sim CH_2-\dot{C}(CH_3)-CH_2\sim$, in accordance with the interpretation by other authors[4,5]. The macroradical decay curve, $[\dot{R}](T)/[\dot{R}](77\ K) = f(T)$, exhibits two reactivity regions, one at about 170 K (region I) and the other at about 250 K (region II). The conformation of the decayed alkyl centres in the two decay regions was established by a simulation procedure. The conformations of the $\dot{C}_\alpha-C_\beta$ bonds were found rather distorted as compared with the conformation states of the nonradicalized chain, $\sim tg^{\pm}\sim$, *viz.* $\sim tg^{\pm}_{\pm}\sim$ in region I and $\sim tg^{\pm}\sim$ in region II (the notation of the distorted rotational states is that proposed by Boyd and Breitling[6]). As to the reaction behaviour of the alkyl macroradicals, it was concluded that a temperature correlation exists between the reactivity in region I and the γ-molecular motions, and between the reactivity in region II and the β-molecular mobility[3,7]. Kinetic study in the decay regions using a 2nd order model (taking into account the comment in ref.[7]) afforded the activation energies of the alkyl centre decay of 35·3 kJ . . mol^{-1} in region I (178–213 K) and 81·6 kJ mol^{-1} in region II (249–273 K). Additional aspects of the localization of the radical centres, modification of the matrix polymer on the radiolysis, and the role of the radiolysis products have been summarized in review[7]. Chain cleavage and formation of molecular hydrogen and unsaturated groups are known to occur at 77 K in addition to the formation of macroradicals[7]. At this temperature, macroradicals were found to form predominantly in the disordered zones of semicrystalline polypropylene. Also, not only their formation but also their decay take place in amorphous zones at lower temperatures[9]. Using the radical quencher technique, the chain crosslinking in the post-radiation conditions was found to occur by the radical mechanism by a combination reaction of the thermalized macroradicals at higher temperatures[10]; this is in accordance with the ESR data[3]. The end macroradicals, which are transiently formed during the radiolytic chain cleavage, are highly reactive and they vanish probably by their transformation into the more stable $\sim CH_2-\dot{C}(CH_3)-CH_2\sim$ inner macroradicals as can be inferred from the ESR spectra[3,11].

In summary, the experimental data[3–11] indicate that the decay of the alkyl centres in the two temperature regions proceeds by their combination reaction in the amorphous phase of semicrystalline polypropylene and it is sensitive to the γ- and β-molecular mobility within the disordered regions of the matrix[12,13].

Chemical Migration Concept

For the inner alkyl macroradicals, there are two possibilities of the free valency transfer by a chemical reaction, namely, by β-scission or by migration *via* abstraction of hydrogen.

In the former case, the slowest reaction that should control the displacement of the radical centres is the β-scission

$$\sim CH_2-C(CH_3)CH_2-CH(CH_3)CH_2\sim \underset{E_{ad}}{\overset{E_{sc}}{\rightleftharpoons}} \sim CH_2\underset{\underset{CH_3}{|}}{C}{=}CH_2 + \underset{\underset{CH_3}{|}}{\dot{C}H}-CH_2\sim . \quad (A)$$

The activation energy estimate by the Vojevodsky method (see ref.[2]) is 124·8 kJ mol^{-1}, exceeding considerably the experimental activation energies of the decay in reactivity regions I and II. This implies that this mechanism can contribute to the mutual nearing of the reaction centres at low temperatures to a negligible extent.

The second group of chemical ways of migration are intramolecular and intermolecular migrations of a hydrogen atom. The intermolecular migration by the pathway

$$\begin{array}{ccc} \sim CH_2\dot{C}(CH_3)CH_2\sim & & \sim CH_2CH(CH_3)CH_2\sim \\ + & \rightarrow & + \\ \sim CH_2CH(CH_3)CH_2\sim & & \sim CH_2\dot{C}(CH_3)CH_2\sim \end{array} \qquad (B)$$

was examined by the BEBO and ZAV/3 methods[2] which gave the energy barriers 43·1 and 43·9 kJ mol^{-1}, respectively. These values are higher than the activation energy of decay in region I, hence, the possibility of participation of migration of this kind at low temperatures is again low. For reactivity region II, however, the participation of the intermolecular transfer is not impossible. This case is analyzed in detail later.

Of the intramolecular H-abstractions, only the odd types, *viz.* the 1·3 and 1·5 migrations,

$$\sim CH_2\dot{C}(CH_3)CH_2CH(CH_3)CH_2CH(CH_3)CH_2\sim$$

come into consideration due to their consistency with the constant shape of the spectra during the decay.

Adopting the concept of the rotation-isomerization states of the chain bonds, the conformations of the corresponding skeletal bond cycles could be analyzed by the geometry-energy and radical criterion[2]. It follows from the analysis that for the 1·3 H-migration, the $\sim g^{\pm}(tg^{\pm})t\sim$ sequence is the optimum conformation sequence for the cycle bonds (the parentheses bound the rotational state of the two skeletal bonds of the four-membered ring). This is consistent with the preferential helix conformation of the chains in isotactic polypropylene[6]. However, the ensuing calculation of the energy barrier of this reaction by the E-BEBO method[14] gave a comparatively high value of 139·7 kJ mol^{-1}, indicating a high energy demand of the process. Since this values exceeds greatly the activation energies for both decay regions I and II, this transport mechanism can be securely ruled out.

For the 1·5 H-migration, the analogous procedure leads to the optimum sequence of four skeletal bonds in the six-membered ring of $\sim g^{\pm}(tg^{\pm}g^{\pm}t)g^{\pm}\sim$. However, no estimate of the energy barrier for this isomerization by some of the adequate theoretical methods is available. To our knowledge, no activation energy values have been reported for an analogous low-molecular reaction either. Still, a rather convincing argument against the participation of the 1·5 intramolecular migration in the transport stage of the decay can be deduced from the conformation analysis, namely that if the mutual nearing of the centres in the amorphous phase occurred *via* this mechanism, then the segments of the chain where this process operates

should form only by linking of the optimum sequences of the skeletal bonds of the rings; the probability of this phenomenon is actually very low indeed. It can be thus concluded that neither 1·3 nor 1·5 migration represents the dominating ways of mutual approach of the radical centres.

Decay Region I

The above results give evidence that no chemical mechanism of mutual approach of the macroradicals operates in this low-temperature region. Therefore, it is appropriate to consider the molecular mobility within the concept of physical migration.

A temperature correlation has been found[3] between decay region I and the γ-molecular motion. On the other hand, the activation energy of the decay (35·3 kJ mol^{-1}) and the activation energy of the γ-motions (54·4 kJ mol^{-1}, ref.[12]) are far from agreement. This indicates that these processes are only related indirectly; the γ-motions do not control the mutual nearing of the macroradicals but they affect it in some way. As to the mechanism of the γ-motions, there is consensus that these motions concern a small number of structure units of the chain in the amorphous phase[13,15]. The only suggested proposal at a molecular level[16] postulates the participation of minimal crankshaft motions with the nonrigid mobile part of the segment,

$$Ps_n(tg^{\pm}t)\, s_{n+4}Q \;\rightarrow\; Ps'_n(tg^{\mp}t)^x\, s'_{n+4}Q\,.$$

This concept, which is consistent with the preferential conformation of isotactic polypropylene, has not been so far tested from the point of view of the energy barrier in order to prove or disprove its participation in the γ-mobility.

It follows from a topological analysis of the chains in the amorphous phase of the semicrystalline polymer that the kinetic motion units can be the end and/or the inner segments of the macromolecules[2].

For the inner segment, the application of the mobility, energy, and radical critetion[2] leads to the choice of segmental conformation motions of the minimal crankshaft segments with a rigid mobile part:

$$Ps_n(tg^{\pm}\, tg^{\pm}\, t)\, s_{n+6}Q \;\rightarrow\; Ps'_n(tg^{\pm}\, tg^{\pm}\, t)^x\, s'_{n+6}Q\,.$$

This result is in agreement with the preferential conformational microstructure of the polypropylene chains, formed by right-hand and left-hand helices[6], and also with the established conformation of the alkyl macroradicals[3]. The kinetic energetics for twelve physically different modes of crankshaft motions of five-bond segments are summarized in Table I; the method of calculation of the energy barriers for the segmental conformation motions and the meaning of the terms are given in refs[1,2].

TABLE I

Kinetic energetics of the minimal crankshaft motions $Ps_n(tg^{\pm}\ tg^{\pm}\ t)\ s_{n+6}Q \rightarrow Ps'_n(tg^{\pm}\ tg^{\pm}\ t)^{x}\ s'_{n+6}Q$ in isotactic polypropylene, in kJ mol^{-1}; $\bar{T}_1 = 195{\cdot}5$ K, $\bar{T}_2 = 261{\cdot}0$ K

a	initial Conformation state	Conformation motion	final Conformation state	E_{intra}	$E^{(a)}_{phm}$ $\bar{T}_1$	$E^{(a)}_{phm}$ $\bar{T}_2$	p_i, % $\bar{T}_1$	p_i, % $\bar{T}_2$	c_a, % $\bar{T}_1$	c_a, % $\bar{T}_2$
1	Ptt(t...t) ttQ	↗	Ptg$^+$(t...t)^x g$^-$tQ	23·5[a]	53·7	53·1	0·014	0·127	0·04223	0·29338
2		↘	Ptg$^-$(t...t)^x g$^+$tQ	23·5	53·7	53·1	0·014	0·127	0·04223	0·29338
3	Ptt(t...t) g$^+$tQ	↗	Ptg$^+$(t...t)^x ttQ	18·0	48·2	47·6	1·192	3·457	99·46796	97·95697
4		↘	Ptg$^-$(t...t)^x g$^-$tQ	41·5	71·7	71·7	1·192	3·457	0·00005	0·00199
5	Ptt(t...t) g$^-$tQ	↗	Ptg$^+$(t...t)^x g$^+$tQ	23·5	53·7	53·1	0·082	0·084	0·24135	0·19302
6		↘	Ptg$^-$(t...t)^x ttQ	33·9	64·1	63·5	0·082	0·084	0·00038	0·00155
7	Ptg$^+$(t...t) g$^+$tQ	↗	Ptg$^-$(t...t)^x ttQ	36·8	67·0	66·4	98·025	94·002	0·07571	0·45198
8		↘	Ptt(t...t)^x g$^-$tQ	36·8	67·0	66·4	98·025	94·002	0·07571	0·45198
9	Ptg$^+$(t...t) g$^-$tQ	↗	Ptg$^-$(t...t)^x g$^+$tQ	41·5	71·7	71·7	0·682	2·275	0·00003	0·00131
10		↘	Ptt(t...t)^x ttQ	29·3	59·5	58·9	0·682	2·275	0·05431	0·35240
11	Ptg$^-$(t...t) g$^-$tQ	↗	Ptt(t...t)^x g$^+$tQ	33·9	64·1	63·5	0·005	0·055	0·00002	0·00102
12		↘	Ptg$^+$(t...t)^x ttQ	33·9	64·1	53·5	0·005	0·055	0·00002	0·00102

[a] E_{inter}: $\bar{T}_1$: 30·2, $\bar{T}_2$: 29·6.

In the calculation of the energy barrier of the a-th mode, the intramolecular contribution was estimated from the rotational energy diagram of a model compound for isotactic polypropylene, *viz.* 2,4,6-trimethylpentane[6], and the intermolecular contribution was calculated from the cohesive energy increments taken from ref.[17]. The statistically averaged energy barrier for all the crankshaft motions of the five-bond segments, 48·6 kJ mol^{-1}, approaches the activation energy of the γ-molecular motions (54·4 kJ mol^{-1}) but it exceeds somewhat the activation energy of the alkyl centre decay in reactivity zone I (35·3 kJ mol^{-1}).

Attention was therefore paid to the end segments. This is warranted by the fact[7] that chain cleavage occurs on the gamma radiolysis at 77 K. Clearly, the cage effect will hinder the process of separation of the chain ends to a considerably lesser extent in the amorphous zone than in the crystalline domains. With respect to the mobility, energy, radical, and free volume criterion, the participation of the minimal four-bond terminal segments $CH_2{=}CH{-}CH_2{-}\dot{C}(CH_3)CH_2{-}CH(CH_3)P$ and $CH_3{-}CH_2{-}CH_2{-}\dot{C}(CH_3)CH_2{-}CH(CH_3)P$ in the crank type mobility

$$Ps_nQ \rightarrow Ps'_nQ^x$$

is feasible.

The kinetic energetics of the crank motions for the two types of end segments are summarized in Tables II and III. The averaged energy barrier for the crank motions of the four-bond segments with a vinyl terminal group is 33·1 kJ mol^{-1} and with a methyl terminal group, 38·1 kJ mol^{-1}. Both values agree well with the activation energy of the decay, 35·3 kJ mol^{-1}. Tables II and III show that the 1st mode and the 3rd mode take part in the free valency displacement to the greatest extent (63 and 36%, respectively) which is related with the maximum population of the initial rotational state of the 5th bond undergoing the conformation transition with the lowest energy barrier.

Physically the experimental activation energy of decay in zone I can be interpreted so that in this region the relatively close centres vanish by their mutual combination in the amorphous zones, the reactants coming to mutual vicinity by the crank motion of the relatively mobile chain ends. This agrees well with the presence of radical pairs withing the temperature range in question[18]. The temperature correlation of the decay with the γ-molecular mobility, presumably of crankshaft type, indicates that the motion of the inner segments affects the mobility of the chain ends indirectly *via* fluctuations of the local free volume. In this respect, the decay of alkyls in polypropylene resembles that in polyethylene[2].

Decay Region II

Consider first this alkyl centre reactivity region from the point of view of the physical migration concept. In the original work[3] a temperature correlation was observed

TABLE II

Kinetic energetics (in kJ mol^{-1}) of the mininal crank motions $Ps_nQ \rightarrow Ps'_nQ^x$ for the vinyl termination of the chain in isotactic polypropylene

a	initial Conformation state	Conformation motion	final	E_{intra}	E_{inter} (298 K)	$E^{(a)}_{phm}$	$P_i(\bar{T}_1)$ %	$c_a(\bar{T}_1)$ %
1	$Ptg^+(tg^\pm s_1)$	↗	$Ptt(tg^+ s_1)^x$	12·5		35·3	98·124	63·22
2		↘	$Ptg^-(tg^+ s_1)^x$	24·2		47·0		0·04
3	$Ptt(tg^\pm s_1)$	↗	$Ptg^+(tg^\pm s_1)^x$	6·3	22·8	30·5	1·193	46·62
4		↘	$Ptg^-(tg^\pm s_1)^x$	17·2		40·0		0·04
5	$Ptg^-(tg^\pm s_1)$	↗	$Ptg^+(tg^\pm s_1)^x$	16·7		39·5	0·683	0·03
6		↘	$Ptt(tg^\pm s_1)^x$	17·2		40·0		0·02

TABLE III

Kinetic energetics (in kJ mol^{-1}) of the minimal crank motions $Ps_nQ \rightarrow Ps'_nQ^x$ in isotactic polypropylene for the methyl termination of the chain

a	initial Conformation state	Conformation motion	final Conformation state	E_{intra}	E_{inter} (298 K)	$E^{(a)}_{phm}$	$p_i(\bar{T}_1)$ %	$c_a(\bar{T}_1)$ %
1	$Ptg^+(tg^\pm s_1)$	↗	$Ptt(tg^\pm s_1)^x$	12·5		40·6	98·1241	63·23
2		↘	$Ptg^-(tg^\pm s_1)^x$	24·2		52·3		0·05
3	$Ptt(tg^\pm s_1)$	↗	$Ptg^+(tg^\pm s_1)^x$	6·3	28·1	34·4	1·1934	36·62
4		↘	$Ptg^-(tg^\pm s_1)^x$	17·2		45·3		0·05
5	$Ptg^-(tg^\pm s_1)$	↗	$Ptg^+(tg^\pm s_1)^x$	16·7		44·8	0·6825	0·03
6		↘	$Ptt(tg^\pm s_1)^x$	17·2		45·2		0·02

between the decay and the $\beta \equiv \alpha_a$ molecular motions within the glassy state–elastic state transition region of the amorphous polypropylene phase. The nonexistence of an activation-energy correlation, however, implies that the molecular mobility on its own, which is associated with the change in the physical state of the matrix, does not contribute to the mutual nearing of the centres. As to the molecular mechanism of the mobility within this temperature range, identical concepts have been suggested by several authors[16]; the β-molecular motion is assumed to be due to crankshaft motions $Ps_n(tg^{\pm}\ tg^{\pm}\ t)\ s_{n+6}Q \rightarrow Ps'_n(tg^{\pm}\ tg^{\pm}\ t)^x\ s'_{n+6}Q$. In contrast to the analogous concept for the γ-region, however, the process is rather a localized one at lower temperatures, taking place in certain parts of the chain, while crankshaft motions of segments of several chains in concert take place at higher temperatures[16].

On the other hand, these results concerning the molecular mobility in reactivity zone II are of importance in conjunction with the results of analysis of the chemical ways of the centre transport, in particular, intermolecular hydrogen transfer. Thus we suggest within the concept of the physico-chemical migration that the mutual nearing of the radical centres proceeds *via* intermolecular migration of the free valency, the nearing of the R and RH reactants being provided by the crankshaft motions of the inner chain segments. It has been mentioned that this concept of the motion mechanism is consistent with the mobility, energy, and radical criterion[2]. The averaged effective energy barrier E_{eff} is given by the contributions from the chemical migration, E_{chm}, and the physical migration, $\bar{E}_{phm}$:

$$E_{eff} = \bar{E}_m = E_{chm}^{inter} + \bar{E}_{phm} =$$
$$= 43{\cdot}5\ \text{kJ mol}^{-1} + 47{\cdot}7\ \text{kJ mol}^{-1} = 91{\cdot}2\ \text{kJ mol}^{-1}$$

The statistically averaged barrier of the crankshaft motions was calculated from the data of Table I for $\bar{T}_2 = (T_{min} + T_{max})/2 = (249 + 273)\ \text{K}/2 = 261\ \text{K}$ according to refs[1,2]. A reasonable agreement is obtained with the activation energy for decay region II ($81{\cdot}6\ \text{kJ mol}^{-1}$). The slightly higher value of the barrier estimate can be partly accounted for by the approximate nature of the method of calculation of the kinetic energetics for the segmental conformation motions. Another cause of the deviation can be in the conformation of the macroradicals departing somewhat from the initial geometry of the chemically undisturbed chain[6]. It is clear that as the radical centre is localized at the mobile part of the segment, the distortion will spread over to the neighbouring structure-molecular parameters (the rotational angles in particular). This can lead to a deflection of the starting rotational states of the rotating bonds of the segment from their minimum positions, whereupon a slight change appears in the intramolecular part of the energy barriers for the individual modes of the crankshaft motions. Table I shows that of the twelve crankshaft motion modes, the 3rd mode is dominating owing to its lowest barrier. The other modes contribute

to the overall energetics to a lesser extent; the most significant of them is the 6th mode, realizing from the most stable initial state of the chain. It can be inferred that enhanced crankshaft mobility should occur in the "breaks" of the helices in the amorphous phase of semicrystalline polypropylene.

An alternative mechanism of the mutual approaching of the radical centres involves the above-mentioned crank motions of the end segments within the physical stage of the intermolecular migration. The energy barrier estimates for the crank motions of the minimal segment are 33·2 kJ mol^{-1} for terminal vinyl and 38·2 kJ mol^{-1} for terminal methyl. The total barriers then are 76·1 and 81·7 kJ mol^{-1}, respectively, approaching well the activation energy of the decay within reactivity region II (81·6 kJ mol^{-1}).

It is difficult to choose from the motion mechanism concepts suggested. It can be assumed that since a fraction of the end segments participates in reactivity region I, the crankshaft motion type will play a major role in the mutual approach of R and RH and ultimately R and R macroradicals. Still, it is reasonable to conclude that within decay region II, intermolecular migration of free valencies occurs in accord with crankshaft and/or crank motions of the chain segments in the amorphous polypropylene zones. This conclusion is consistent with the nonexistence of RR radical pairs within this temperature region[18] which points to the participation of the chemical mechanism in the nearing of distant reactants. This is also borne out by the fact that allyl centres, which can only form by a transformation reaction from alkyls[19], begin to appear in this temperature region.

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