

Molecular aspects of intramolecular hydrogen abstractions in solid polymers

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In this paper the molecular aspects of 1.2—1.5 intramolecular transfers of the radical centre by hydrogen abstraction are stipulated within the scope of rotation-isomerization model. A set of criteria which enables us to determine the principal allowableness of these transfers depending on phase state of the polymer matrix has been formulated. The obtained results may be used for further analysis on the basis of activation-energy approach. An example of application is demonstrated for polyethylene. It has been revealed that these modes of chemical transport of the radical centre may, in principle, proceed in amorphous zones of the semicrystalline matrix but the estimates of energy barriers when compared with the experimental activation energies for the decay of the alkyl centres show that these modes do not play a dominant role. On the other hand, the migration of free valence along the chain does not proceed in the crystalline phase in conformity with special experiment.

Установлены молекулярные аспекты для 1,2—1,5 интрамолекулярных переносов радикального центра отделением водорода в рамках ротационно-изомеризационной модели макромолекулы и сформулирована совокупность критериев, которая позволяет определить условия для принципиального протекания этих переносов в зависимости от морфологического состояния полимера. Результаты могут быть использованы для анализа с помощью активационно-энергетического подхода. На примере полиэтилена показано, что эти химические миграции могут принципиально протекать в аморфных зонах, но оценки энергетических барьеров показывают на их неглавную роль в миграции центра. В кристаллических зонах миграции алкильного центра не протекают в согласии со специальным экспериментом.

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On the basis of the experimental study of reactivity of macroradicals of the alkyl type carried out for a series of polymers, it has been found that the hydrogen abstraction reaction obeying the scheme



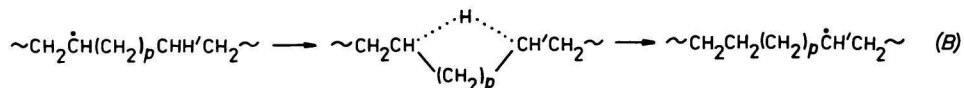
where $\cdot R'$ is a radical equal or different from $\cdot R$, represents a very efficient kind of macroradical transformation and radical centre transfer in their decay process [1–3]. This kind of radical centre transfer was first postulated for polyethylene (PE) [4, 5] and later directly proved by the ESR technique in a number of reactions of this polymer: $\sim\text{CH}_2\dot{\text{C}}\text{H}_2 \rightarrow \sim\text{CH}_2\dot{\text{C}}\text{HCH}_2\sim$ [6], $\text{CH}_3\dot{\text{C}}\text{HCH}_2\sim \rightarrow \sim\text{CH}_2\dot{\text{C}}\text{HCH}_2\sim$ [7], $\sim\text{CH}_2\dot{\text{C}}\text{HCH}_2\sim \rightarrow \sim\text{CH}_2\dot{\text{C}}\text{HCH}=\text{CH}-\text{CH}_2\sim$ [8]. In contrast to these transformations of macroradicals, the process $\sim\text{CH}_2\dot{\text{C}}\text{HCH}_2\sim \rightarrow \sim\text{CH}_2\text{CH}_2\dot{\text{C}}\text{H}_2\sim$ is not detectable because of identity of the spectra of reactants and products but there is no doubt about its course at the present, especially at higher temperatures. This view is supported by such indices as migration of these most stable alkyl centres from crystallites to interface with subsequent decay [1, 9, 10] and catalytic effect of the isotopes of hydrogen on conversion or decay of the $\sim\text{CH}_2\dot{\text{C}}\text{HCH}_2\sim$ centres in PE [11]. In connection with admission of this kind of migration, the question concerning the mechanism arises, *i.e.* whether the intermolecular transfer of hydrogen proceeds between two chains or more distant sections of the same chain or whether the 1.2 up to 1.5 intramolecular migration ways along the chain are in operation. One group of authors [8, 9] suggests that the radical centres of the alkyl type migrate *via* inter-chain abstraction of hydrogen while the second group is inclined for the intramolecular mechanism [7, 12, 13]. In order to determine the dominant type of the transfer reaction, an activity in experimental field has developed recently. The present results achieved by the special method using polyethylene—urea complex indicate only participation of the intermolecular mechanism, at least in the crystalline phase of PE [14, 15]. On the other hand, for the amorphous zones we cannot generally exclude a possible course of some of the intramolecular mechanisms owing to flexibility of the chains in disordered regions of the matrix.

The aim of this study is to determine the molecular aspects of the 1.2 up to 1.5 intramolecular types of H-abstraction within the scope of the accepted model of macromolecule and to formulate the criteria which allow to ascertain the conditions for principal course of these migrations in amorphous and crystalline zones of the matrix. In the part concerned with application, an example of this approach is demonstrated for polyethylene. After all, the results obtained by this analysis have been used for the calculation of energy barriers of the 1.2 and 1.3 migrations of hydrogen by means of the extended version of the BEBO method [16]. Their values are in the scope of the hypothesis of chemical migration of radical centres confronted with experimental data about the decay of alkyl centres in PE [8–10]

from the point of view of evaluation of their incidental participation in the transport stage of the decay process.

Molecular aspects of the intramolecular transfer of hydrogen

The most important types of intramolecular migration ways may be represented in summarized form for the polyethylene chain as follows



where $p = 0, 1, 2, 3$ for 1.2, 1.3, 1.4, and 1.5 H-transfer, respectively. From the intuitive point of view, the necessary condition for the course of arbitrary of these transfers is the creation of convenient geometrical prerequisite, *i.e.* the existence of the optimum cyclic state in the reaction section of chain which exhibits maximum approaching of the reaction centres $\cdot\text{C}$ and H or H' . Provided the model of rotation-isomerization states of the bonds in the chain molecules [17] is accepted, it results that a certain sequence of the q bonds in skeleton (where $q = p + 1$) is consistent with a certain conformation sequence of these bonds. If the bonds can come into rotational states in the proximity of the *trans* and *gauche* \pm local minima, there are altogether 3^q combinations of states of the q bonds. Each conformational combination is characterized at least by one distance $d_{\text{C}\cdots\text{H}}$ between the carbon atom where the radical centre decays and the hydrogen atom on the second up to fifth carbon atom where the centre is transferred. For the choice of the optimum initial configuration in cyclic state, we may formulate the so-called geometrical-energy criterion according to which the most convenient conformational sequence of the q bonds is that which exhibits the maximum bending of the reaction section of chain and results from the maximum approaching of the C_{sp^2} and H or H' atoms. For more exact specification of this postulate, we may put the condition that the reaction centres must be approached to each other in the distance which is nearly equal to the sum of their van der Waals radii or to the contact distance, *i.e.* the minimum distance between the atoms in given bonding states in the solid phase [18]. In our case of hydrocarbon polymers of the vinyl and vinylidene type, it is $d_{\text{C}\cdots\text{H}, \text{w}} = 0.275$ nm or $d_{\text{C}\cdots\text{H}, \text{cont}} = 0.27$ nm. In relation with this criterion, special attention must be paid to the effect of excluded volume, *i.e.* steric interactions which show themselves by overlapping of atoms [17]. As for short cycles, the pentane interference, *i.e.* the elimination of those conformational sequences which involve the $\sim g^\pm g^\pm \sim$ pairs of rotational states of bonds comes into consideration.

Further requirements which are contained in the morphological and radical criterion must be added to the geometrical-energy criterion.

The morphological criterion comprises the postulate that the conformational sequence of cycles must be consistent with the conformational microstructure of the chains in the pertinent phase region of polymer. While the occurrence of every conformational sequence allowed from the energy point of view may be, in principle, expected in the amorphous phase, this criterion is of particular importance for the crystalline phase. This aspect shall be illustrated in more detail in the part dealing with applications.

The last, so-called radical criterion results directly from the idea of intramolecular migration of free valence. If this process is limiting in approaching of the reaction centres in the transformation or decay reaction, the observed constancy of shape of the ESR spectrum gives evidence that the conformation of macroradicals in the transport stage of reaction has been preserved. This fact leads to the conclusion that the $\cdot C_{\alpha}-C_{\beta}$ bonds of macroradical are the end bonds of cycles and thus the conformation of the end skeleton bonds of cycles must be identical with the conformation of the $\cdot C_{\alpha}-C_{\beta}$ bonds of macroradical ascertained by the structural analysis of spectral parameters.

If we take all criteria into account, we can reduce the original great number of combinations of rotational states of the bonds of cycles and select the most suitable of them for further activation-energy analysis. This analysis based on a set of criteria gives theoretical arguments for determining principal possibility of the occurrence of intramolecular mechanisms in the amorphous and crystalline phase of polymer. Of course, the final decision concerning the participation or nonparticipation of different types of intramolecular mechanism may be made after forming the estimate of energy barriers of model reactions by using some theoretical approach, e.g. E-BEBO or a quantum chemical method.

Application

The greatest amount of information about the structure and reactivity of macroradicals has been obtained in the radiation chemistry of macromolecular substances for the chemically simplest polymer, *i.e.* polyethylene. For this reason, we illustrate the application of our approach in the analysis of possible intramolecular migrations of the alkyl macroradicals $\sim\text{CH}_2\dot{\text{C}}\text{HCH}_2\sim$ in this polymer.

Amorphous phase of polyethylene

All possible combinations of rotational states of the skeleton bonds of cycles may, in principle, occur in the disordered regions of PE owing to relatively high flexibility of chains. Thus, it is sufficient to respect the geometrical-energy and radical criterion. The results are listed in Table 1. The following molecular-structu-

Table 1

Analysis of principal allowableness of intramolecular transfer of the alkyl centre in polyethylene

N	Type of intramigration	Conformational sequence of q bonds in cycle	Interatomic distances $d_{C...H, H'}$ nm	Geometrical-energy criterion	Radical criterion	Morphological criterion			
						Amorphous phase		Crystalline phase	
						Defect aspect	Total	Defect aspect	Total
1	1.2	t	0.213; 0.213	+	+	+	+	+	+
2		g^{\pm}	0.213; 0.213	+	-	+	-	+ ^{a, b}	-
1	1.3	tt	0.276; 0.276	+	+	+	+	+	+
2		tg^{\pm}	0.276; 3.345	+	-	+	-	+ ^{a, b}	-
3		$g^{\pm}t$	0.276; 0.276	+	-	+	-	+ ^a	-
4		$g^{\pm}g^{\pm}$	0.276; 0.345	+	-	+	-	+ ^b	-
5		$g^{\pm}g^{\mp}$	0.345; 0.276	-	-	+	-	-	-
1	1.4	ttt	0.419; 0.419	-	+	+	-	+	-
2		$g^{\pm}tt$	0.419; 0.419	-	-	+	-	+ ^{a, b}	-
3		$tg^{\pm}t$	0.338; 0.268	+	+	+	+	+ ^a	-
4		ttg^{\pm}	0.467; 0.419	-	-	+	-	+ ^a	-
5		$g^{\pm}g^{\pm}t$	0.338; 0.268	+	-	+	-	+ ^b	-
6		$g^{\pm}tg^{\pm}$	0.467; 0.419	-	-	+	-	-	-
7		$tg^{\pm}g^{\pm}$	0.399; 0.268	+	-	+	-	+ ^b	-
8		$g^{\pm}g^{\mp}t$	0.268; 0.378	-	-	+	-	-	-
9		$g^{\pm}tg^{\mp}$	0.419; 0.467	-	-	+	-	+ ^{a, b}	-
10		$tg^{\pm}g^{\mp}$	0.338; 0.399	-	-	+	-	-	-
11		$g^{\pm}g^{\pm}g^{\mp}$	0.399; 0.338	-	-	+	-	-	-
12		$g^{\pm}g^{\mp}g^{\pm}$	0.399; 0.338	-	-	+	-	-	-
13		$g^{\mp}g^{\pm}g^{\pm}$	0.399; 0.268	-	-	+	-	-	-
14		$g^{\pm}g^{\pm}g^{\pm}$	0.399; 0.268	+	-	+	-	+ ^b	-

Table 1 (Continued)

N	Type of intra-migration	Conformational sequence of q bonds in cycle	Interatomic distances $d_{C...H, H'}$ — nm	Geometrical-energy criterion	Radical criterion	Morphological criterion			
						Amorphous phase		Crystalline phase	
						Defect aspect	Total	Defect aspect	Total
1	1.5	tttt	0.520; 0.520	—	+	+	—	+	—
2		g^+ttt	0.520; 0.520	—	—	+	—	+ ^{a, b}	—
3		tg^+tt	0.458; 0.520	—	+	+	—	+ ^a	—
4		ttg^+t	0.458; 0.409	—	+	+	—	+ ^a	—
5		$tttg^+$	0.596; 0.520	—	—	+	—	+ ^a	—
6		g^+g^+tt	0.503; 0.459	—	—	+	—	+ ^b	—
7		g^+tg^+t	0.458; 0.409	—	—	+	—	—	—
8		g^+ttg^+	0.596; 0.520	—	—	+	—	—	—
9		tg^+g^+t	0.316; 0.433	+	+	+	+	—	—
10		tg^+tg^+	0.503; 0.503	—	—	+	—	—	—
11		ttg^+g^+	0.545; 0.409	—	—	+	—	+ ^b	—
12		g^+g^+tt	0.503; 0.459	—	—	+	—	—	—
13		g^+tg^+t	0.458; 0.409	—	—	+	—	+ ^{a, b}	—
14		g^+ttg^+	0.520; 0.596	—	—	+	—	+ ^a	—
15		g^+g^+tt	0.503; 0.459	—	—	+	—	—	—
16		tg^+g^+t	0.289; 0.197	—	+	+	—	—	—
17		tg^+tg^+	0.459; 0.503	—	—	+	—	+ ^{a, b}	—
18		g^+tg^+t	0.458; 0.409	—	—	+	—	+ ^a	—
19		tg^+g^+t	0.197; 0.189	—	+	+	—	—	—
20		ttg^+g^+	0.545; 0.458	—	—	+	—	—	—
21		g^+ttg^+	0.596; 0.520	—	—	+	—	—	—
22		tg^+tg^+	0.503; 0.459	—	—	+	—	+ ^{a, b}	—
23		ttg^+g^+	0.458; 0.545	—	—	—	+	—	—
24		$g^+g^+g^+t$	0.433; 0.316	+	—	+	—	+ ^b	—

Table 1 (Continued)

N	Type of intra-migration	Conformational sequence of q bonds in cycle	Interatomic distances $d_{C...H...H}$ nm	Geometrical-energy criterion	Radical criterion	Morphological criterion			
						Amorphous phase		Crystalline phase	
						Defect aspect	Total	Defect aspect	Total
25		$g^+g^+tg^+$	0.503; 0.503	-	-	+	-	-	-
26		$g^+tg^+g^+$	0.409; 0.545	-	-	+	-	-	-
27		$tg^+g^+g^+$	0.316; 0.437	+	-	+	-	+	-
28		$g^+g^+g^+t$	0.289; 0.197	-	-	+	-	-	-
29		$g^+g^+tg^+$	0.503; 0.459	-	-	+	-	+	-
30		$g^+tg^+g^+$	0.545; 0.458	-	-	+	-	-	-
31		$g^+g^+g^+t$	0.197; 0.289	-	-	+	-	-	-
32		$g^+g^+tg^+$	0.459; 0.503	-	-	+	-	-	-
33		$g^+tg^+g^+$	0.545; 0.458	-	-	+	-	-	-
34		$g^+g^+g^+t$	0.433; 0.316	-	-	+	-	-	-
35		$tg^+g^+g^+$	0.433; 0.437	-	-	+	-	-	-
36		$g^+g^+tg^+$	0.503; 0.503	-	-	+	-	-	-
37		$tg^+g^+g^+$	0.289; 0.363	-	-	+	-	-	-
38		$g^+tg^+g^+$	0.545; 0.408	-	-	+	-	+	-
39		$tg^+g^+g^+$	0.363; 0.197	-	-	+	-	-	-
40		$g^+g^+g^+g^+$	0.437; 0.316	+	-	+	-	-	-
41		$g^+g^+g^+g^+$	0.433; 0.437	-	-	+	-	-	-
42		$g^+g^+g^+g^+$	0.363; 0.289	-	+	+	-	-	-
43		$g^+g^+g^+g^+$	0.197; 0.363	-	-	+	-	-	-
44		$g^+g^+g^+g^+$	0.437; 0.316	-	-	+	-	-	-
45		$g^+g^+g^+g^+$	0.363; 0.197	-	-	+	-	-	-
46		$g^+g^+g^+g^+$	0.363; 0.289	-	-	+	-	-	-
47		$g^+g^+g^+g^+$	0.437; 0.433	-	-	+	-	-	-
48		$g^+g^+g^+g^+$	0.437; 0.433	-	-	+	-	-	-

Table 1 (Continued)

N	Type of intra-migration	Conformational sequence of q bonds in cycle	Interatomic distances $d_{C...H, H'}$ nm	Geometrical-energy criterion	Radical criterion	Morphological criterion			
						Amorphous phase		Crystalline phase	
						Defect aspect	Total	Defect aspect	Total
49		$g^{\mp}g^{\pm}g^{\mp}g^{\pm}$	0.289; 0.363	—	—	+	—	—	—
50		$g^{\pm}g^{\mp}g^{\pm}g^{\mp}$	0.198; 0.363	—	—	+	—	—	—

a) A part of cycle of skeleton bonds is formed by 2g1 kink-defect $\sim g^{\pm}tg^{\mp} \sim$.

b) A part of cycle of skeleton bonds is formed by twist-defects $\sim g^{\mp}tg^{\pm}g^{\pm}g^{\mp} \sim$ and $\sim g^{\mp}tg^{\pm}g^{\mp}g^{\pm} \sim$.

ral parameters of polyethylene in the solid state were used for calculating the interatomic distances [19]: $l_{C-C} = 0.1532$ nm, $l_{C-H} = 0.1058$ nm, $\vartheta_{CCC} = 112^\circ$, and $\vartheta_{HCH} = 109.5^\circ$. If a certain combination satisfies the competent criterion, it is denoted by the sign + and in the opposite case by the sign -. The use of Table 1 may be demonstrated by the example of the 1.3 transfer. We may select six physically different combinations (tt, tg^\pm , g^+g^- , $g^\pm g^\pm$) from the number $3^2 = 9$ of formal combinations of rotational states (t, g^\pm) of two skeleton bonds by taking regard to the symmetry of some of them. By calculating the interatomic distances $d_{C\dots H, H'}$ and comparing them with the critical value $d = 0.275$ nm (the deviation being, let us say, ± 0.05 nm) we may deduce that all combinations could be effective in hydrogen abstraction. Of course, after taking the steric effect which leads to elimination of the $\sim g^+g^- \sim$ combination into account, there are only five possibilities left. As a matter of fact, the radical criterion which respects the experimentally observed $\sim tt \sim$ sequence of both $\cdot C_\alpha - C_\beta$ bonds in the alkyl $\sim CH_2 - \dot{C}H - CH_2 \sim$ [1, 20] indicates further reduction of allowed combinations only for one case, i.e. $\sim (tt) \sim$. Moreover, the fact that one $\cdot C_\alpha - C_\beta$ bond is a constituent of cycle not only before but also after the transfer of the centre leads to the conclusion that the reaction region of chain must possess the $\sim t(tt)t \sim$ conformational sequence.

By using an analogous procedure, we may obtain the optimum sequence for the bonds of cycles and further types of the intra H-abstraction: 1.2: $\sim t(t)t \sim$, 1.3: $\sim t(tt)t \sim$, 1.4: $\sim t(tg^\pm)t \sim$, and 1.5: $\sim t(tg^\pm g^\pm)t \sim$. The presence of isolated *gauche* bonds and pairs of *gauche* bonds surrounded by the bonds in *trans* states in the amorphous phase of PE was evidenced on the basis of infrared spectroscopy by some authors [21, 22]. The different forms of sequence for the bonds of cycles are represented in Fig. 1 where the potential reaction interactions between the C_{sp^2} and H(H') atoms are also outlined.

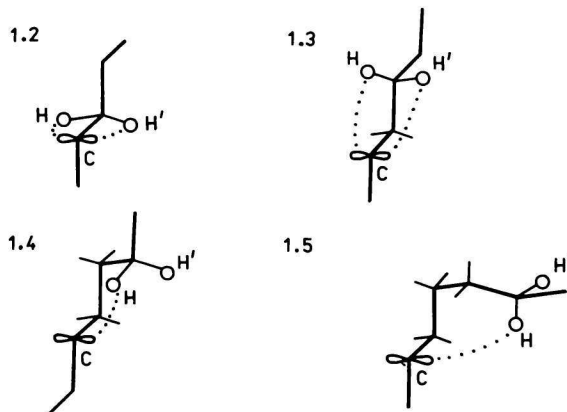


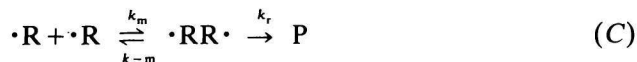
Fig. 1. Optimum starting conformation of cyclic states of sections of chain for the 1.2 up to 1.5 H-transfer.

Crystalline phase of polyethylene

The statement of principal allowableness of intramolecular transfer in the ordered zones of PE may be given after taking all three criteria into account. The morphological criterion is of special importance. It has resulted from X-ray diffraction measurements that the chains in the orthorhombic lattice of PE are in the most stable all *trans* conformation [23]. Besides this basic conformational microstructure, certain conformational defects may be built in the ordered regions. These deviations from the most stable sequence must, however, be compatible with the orthorhombic lattice [24], e.g. kink-defects [25] or twist-defects [26]. Then the morphological criterion requires that the conformational state of skeleton bonds of cycles should be either identical with the most stable microstructure of chain or representing a whole or partial constituent of conformational defects. The results of analysis are summarized in Table 1. As for 1.2 migration, the skeleton bond of the triplet cycle may be in the (t) or (g^\pm) state while the second possibility is admissible only if this bond is a constituent of kink-defects, e.g. of the 2g1 type: $\sim ttt^+tg^-ttt\sim$ or localized twist-defects: $\sim ttt^+tg^+g^+g^+ttt\sim$ or $\sim ttt^+tg^+g^+g^+ttt\sim$. These defects respect the steric limitation imposed by adjacent chains in the crystalline lattice. But the subsequent consideration of the radical criterion, i.e. the necessity of the $\sim t(t)t\sim$ sequence of rotational states of bonds indicates that the course of the 1.2 intra H-abstraction in the defect regions of chain is not possible. It results from this fact that the 1.2 transfer is principally allowed only in a conformationally undisturbed chain. Analogously, all criteria under equal conditions are fulfilled for the 1.3 H-transfer. On the other hand, it has been found that the higher types of transfer are not, even in principle, possible because the adjacent chains in the lattice prevent sufficient bending and approaching of the reaction centres of chain in the ordered zones of PE.

Activation-energy analysis

According to the kinetic model of the reactions of radical centres in condensed media obeying the reaction scheme



it is valid in the diffusion limit for the effective rate constant of decay $k_{ef} \doteq k_m$, where k_m is the rate constant of migration of centre. Thus it holds for the effective activation energy of decay reaction and general migration mechanism which comprises both physical and chemical component of transport

$$E_{ef} \doteq E_m = E_{phm} + E_{chm} \quad (1)$$

where E_{phm} and E_{chm} are energy barriers of molecular motion and chemical reaction. Then for the special case of intramolecular migration, we may put $E_{\text{phm}} = 0$ and $E_{\text{ef}} \doteq E_{\text{chm}}$. It means in connection with the above reasoning about the principal allowableness of individual modes of the intra H-abstractions in reference with the phase state of matrix that the final conclusions in favour or disfavour of a given type of migration are feasible after comparing the experimental effective activation energies of transformation or decay with the values of energy barriers of model reactions or activation energies of analogous isomerization reactions in low-molecular analogues. In this case, we estimated the energy barriers of the 1.2 and 1.3 transfers by using the BEBO method modified for abstraction reactions proceeding through cyclic planar transition states [16]. This version reflects with satisfactory accuracy the experimental activation energies of isomerization in low-molecular radicals [16].

According to the E-BEBO method, the total potential energy of the reaction region comprising the skeleton atoms between which the hydrogen exchange takes place and the atoms inside skeleton is given by the equation

$$E = E_{\text{b}} + E_{\text{tripl}} + E_{\text{def}} + E_{\text{nb}} \quad (2)$$

where E_{b} is the bonding contribution due to transformation of the original bond into activated bonds, E_{tripl} is the antibonding contribution respecting the repulsive interaction of the C_i and $C_{i+(p+1)}$ atoms, E_{def} is the contribution including the energy necessary for the deformation of bond angles from equilibrium state to transition state, and E_{nb} is the contribution of nonbonding interactions between the transferred hydrogen and the atoms of cycle (only for 1.3 migration). The actual expressions for individual contributions depend on the type of intramolecular transfer because it qualifies the character of transition state. The details are given in paper [16]. The values of energy barriers and individual contributions for the 1.2 and 1.3 transfer in a polymethylene sequence are quoted in Table 2. It results from these values that the dominant component of barriers is the antibonding contribution of the atoms with parallel electron spins which exchange the hydrogen atom. The estimated barriers may be compared either with the available activation energies of low-molecular radical in gaseous phase or, at least approximately, with

Table 2

Energy barriers and their particular contributions of the 1.2 and 1.3 H-transfers in polymethylene sequence calculated by the E-BEBO method ($E_i/(\text{kJ mol}^{-1})$)

Model reaction	E_{b}	E_{tripl}	E_{def}	E_{nb}	E_{chm}
$\sim\text{CH}_2\overset{\curvearrowright}{\text{C}}\text{HCH}_2\text{CH}_2\sim$	28.81	107.64	8.86	—	145.4
$\sim\text{CH}_2\overset{\curvearrowright}{\text{C}}\text{HCH}_2\text{CH}_2\text{CH}_2\sim$	28.63	85.62	11.28	21.40	146.9

the effective activation energies of the decay of alkyl macroradicals in PE. As for the first comparison, the course of the 1.2 isomerization of the 2-pentyl to 3-pentyl radical requires the activation energy of $138.2 \text{ kJ mol}^{-1}$ [27] which is in good agreement with the barrier of the 1.2 transfer $145.4 \text{ kJ mol}^{-1}$. As for the 1.3 transfer, there is not available in literature any activation energy of an analogous reaction except for a rather approximate isomerization reaction of 1-pentyl to 3-pentyl radical for which it holds $E_{\text{act}} = (129.8 \pm 4.1) \text{ kJ mol}^{-1}$ [27]. A comparison with the 1.2 transfer shows that this is energetically only a little more exacting than the 1.3 migration. On the other hand, the values of energy barriers for 1.2 and 1.3 migrations obtained by calculation are considerably near. For appreciating the E-BEBO method, it would be necessary to have data about the experimental activation energy of the 1.3 isomerization at least of 2-pentyl to 4-pentyl radical or in longer n-alkyl radicals with free valence on internal and not external carbon atoms.

In spite of these facts, we may assume that these data enable us to have a practical discussion about the participation of the 1.2 and 1.3 migration in the transport stage of alkyl decay in PE. First of all, it must be remarked that the above values are to be regarded as lower limits of the corresponding reactions leading to the condensed state of the polymer matrix. It is obvious that the reaction region where the transfer reaction accompanied with a change in molecular-structural parameters takes place is in interaction not only with other sections of the own chain but also with adjacent chains. Owing to these inertial and viscous effects, we may expect a certain rise in energy barriers. The effective activation energy for the decay of alkyl centres in the amorphous phase of PE in the temperature interval $-30 \text{ }^{\circ}\text{C}—+60 \text{ }^{\circ}\text{C}$ is $(70.1 \pm 2.0) \text{ kJ mol}^{-1}$ [10, 20, 28] and for the migration of alkyls from the crystalline phase to phase interface of PE in the temperature interval $0 \text{ }^{\circ}\text{C}—+60 \text{ }^{\circ}\text{C}$, it is $(73.2 \pm 2.0) \text{ kJ mol}^{-1}$ [8—10, 28]. A comparison of these values with the estimated energy barriers unambiguously discloses that neither the 1.2 nor 1.3 intramolecular transfer contributes to the transport of the alkyl centres not only in the amorphous but also crystalline phase. This conclusion based on the results of analysis obtained by a set of criteria and calculations of energy barriers is in good agreement with the results of study concerning the preference of inter- or intramolecular migrations of alkyls in PE [14, 15]. In this study we investigated the decay behaviour of alkyls in isolated chains of PE in all *trans* conformation in the so-called urea—PE complex. It has been found that alkyls are stable up to the temperature of complex decomposition so that their decay does not proceed by approaching along the chain giving rise to unsaturated groups. Thus it has been deduced that the migration of alkyls takes place at least in the crystalline phase solely by intermolecular way.

As for the 1.4 and 1.5 migrations which are principally allowed in the amorphous phase, we may compare the effective activation energies of decay with the

activation energies of the 1.4 and 1.5 transfers in low-molecular radicals because, at present time, there are no data obtained by theoretical methods in literature. The experimental activation energy of the 1.4 transfer of 4-octyl to 2-octyl radical is 92.1 kJ mol^{-1} and the activation energy of the 1.5 isomerization of 2-octyl to 3-octyl radical is 46.1 kJ mol^{-1} [29]. The statement of the increase in these values accompanying the transition from gaseous to solid polymer phase is valid in these cases as well, owing to which we may reliably rule out the 1.4 transfer through five-membered cycle. In spite of the relatively unstrained six-membered cycle, we may expect a certain increase in barrier for the 1.5 H-abstraction. This increase might be sufficient for reaching the value of the observed activation energy of decay in the amorphous phase (70.1 kJ mol^{-1}). It results from Table 1 that the optimum conformational sequence of cycle is represented by the $\sim(\text{tg}^{\pm}\text{g}^{\pm}\text{t})\text{t}\sim$ bonds. But irrespective of the presence of these *gauche* pairs of chain in disordered zones [21, 22], we may put forward a quite convincing statistical argument which gives evidence against the dominating participation of this mechanism in the transport stage of decay. Its essence consists in the condition that this type of transfer necessitates for the chains in the amorphous phase to be formed solely by arrangement of the optimum sequences $\sim\text{t}[(\text{tg}^{\pm}\text{g}^{\pm}\text{t})]_n\text{t}\sim$. It is obvious that the probability of occurrence of the chains in the amorphous phase exhibiting only this microstructure is very small. It seems that the situation is not improved even by the course of occasional conformational transitions of bonds in chains in the amorphous phase in elastic state ($T > T_g = 243 \text{ K}$) [30, 31]. It may be deduced from this fact that the 1.5 intra H-abstraction does not proceed in significant extent and is not a dominant process in the transport stage of alkyl decay in the amorphous phase of PE. The alternative mechanism admits a dominant role of intermolecular migration in connection with the conformational motion of chains [32].

Our approach is of general character and may be used for testing the incidental participation of intramolecular transfer of radical centre in other polymers.

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