Study of the mechanism of macroradical reactions in solid polymers: 1. Molecular aspects of reactivity and activation energy model of reactions

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A short survey of the problems of post-destruction chemistry is presented from the stand-point of the kinetics and mechanisms of the reactions of macroradicals in solid polymers. Two fundamental hypotheses of mechanism of macroradical decay are discussed in more detail. The philosophy of interpretation of kinetic data is then outlined on the level of activation energy in the terms of a simple kinetic model of decay. In the case of general mechanism of free valence migration, it consists of the physical part which is related to molecular mobility of reactants up to their contact and of the chemical parts which are concerned with redistribution of electron density of reactants on contact. A procedure for calculating the energy barriers of conformational motion in the amorphous phase of a polymer is proposed. Particular contributions are discussed from the molecular point of view in conforming to present knowledge of physical and chemical processes occurring in polymers.

Keywords Macroradical; reactions; mechanism; physical and chemical migration; activation energy model

INTRODUCTION

In the last thirty years, much attention has been paid to the study of reactions of free radicals generated by various methods of destructive action on solid polymers. Aspects of the problems involving destruction and post-destruction chemistry form the topic of several books and reviews[1-11]. The major problems of post-destruction chemistry, studied mainly by the e.p.r.[10] are: (A) chemical and geometrical structure of reactive particles and (B) their reactivity.

Much progress was achieved recently by elaborating algorithms for identifying the reactants observed in the e.s.r. spectra by means of computation techniques[12-15]. However, there are still many problems associated with the study of reactivity. Knowledge of the mechanism of the reactions of free radicals in polymers is of great importance in relation to ageing and modifications of polymers because the required processes and properties of materials could be achieved by controlling the reaction conditions.

The study of mechanisms of macroradical reactions is a complex problem which must be solved in close connection with some branches of the physics and chemistry of polymers (microstructure of chains, morphology, and dynamics of the solid phase), the physics and chemistry of destructive actions on polymers (morphological changes in the solid phase and chemical structure of the products of destruction), reaction kinetics of the solid phase (distribution and transport of reactants) and theory of chemical reactivity.

A characteristic feature of macroradicals in solid polymers is their relatively long life-times when compared with the liquid or gaseous phase. The specific character of the solid phase is reflected in the many phenomena which have no analogy in other phases, i.e. radical pairs[16], 'stepwise' course of reactions[17], and relatively high values of activation energy of the macroradical reactions.

There are two fundamental hypotheses concerning the mechanism of these reactions which can be derived from the present experimental knowledge of structure and reactivity of macroradicals.

(i) Hypothesis of physical migration by which the reactions of reactants are controlled either by mobility of the chains or their parts (segments) with fixed free valence or by diffusion of the low-molecular products of macroradical decomposition, e.g. the so-called radical fragments.

(ii) Hypothesis of chemical migration by which the reactions of reactants are controlled by various reactions of macroradicals or low-molecular fragments.

The first hypothesis was proposed by Ohnishi[18] on the basis of experimental data and the main pieces of evidence supporting this hypothesis are: temperature and activation energy correlation between decay and molecular mobility[18], difference in the decay in the oriented and non-oriented samples[19], non-crosslinked and crosslinked materials[20] and the influence of pressure on decay at higher temperatures[21].

The second hypothesis was put forward by Dole[22] who interpreted his experimental data by using the idea of chemical migration assuming a mechanism of hydrogen abstraction. This hypothesis was later developed by Butjagin[8,23] who pointed out further possibilities of the transport of free valence in the degradation types of polymers, i.e. by depolymerization–polymerization characteristic of the chain- end macroradical and by decomposition of in-chain macroradicals. This hypothesis makes it possible generally to interpret the observations

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concerning the transformation of macroradicals and decay of more distant reactants.

At present, there is a lack of suitable ideas that could lead to a real understanding of the mechanisms of the reactions of macroradicals on a molecular level. This situation is due to the character of the reaction system (usually a coexistence of several reactants and simultaneous occurrence of several reactions) as well as to the complexity of structural–dynamic relations in solid polymers which is determined by the character of the polymer itself and by the preparation of the sample. It is clear that these aspects of the problem are related, e.g. the decay of macroradicals by combination results in the formation of bridges between chains resulting in changes in the possibility of motion of the polymer matrix. Nevertheless, we may attempt to interpret some special cases of relatively well defined reactions of macroradicals on a molecular level. Moreover, the results of theoretical study of model processes (motions and reactions) may help to solve some problems which concern the reactivity of macroradicals in solid polymers.

The aim of this work is to discuss some molecular aspects of the reactions of macroradicals in solid polymers and to propose a model of the level of activation energy for these reactions. We apply this model to special cases of macroradical reactions controlled by molecular motion as well as reactions which are limited by the chemical transport of free valence due to hydrogen abstraction.

MODEL

Information about the mechanism of reactions in solid polymers has been mainly obtained by application of the methods of formal kinetics as well as some more special kinetic models, e.g. diffusion-controlled reactions. Kinetic experiments enable us to easily find out the rate coefficients. By using the Arrhenius representation, we may thus determine the pre-exponential factors and activation energies. From the theoretical point of view, the activation energy is the most accessible quantity for interpretation. For this reason, the basic idea of our model is established on the use of activation energy as the main parameter of the reaction which has physical sense and may be interpreted in terms of potential barriers.

The most general reaction of macroradicals in solid polymers is their decay which manifests itself by a decrease in the number of reactants with time. It is assumed intuitively that every reaction of two reaction centres comprises two elementary acts:

(a) mutual approach of reactants up to contact, with probability p_m; by consideration of the general mechanism of free valence motion in a physical way by means of mechanical transfer of the chain in space and the chemical way consisting of redistribution of electron density, e.g. in hydrogen abstraction by a macroradical, the above mentioned hypotheses lead to

$$p_m = p_{phm} \cdot p_{chm}$$

(b) decay of reactants at their contact, the probability being p_d.

For simultaneous events, the mean total activation energy is:

$$\bar{E}_{tot} = \bar{E}_{phm} + \bar{E}_{chm} + \bar{E}_d \qquad (1)$$

where $\bar{E}_{phm}$ is the statistically weighted activation energy of the transfer of free valences by different kinds of motion of the chains. $\bar{E}_{chm}$ stands for the weighted activation energy of the chemical migration by e.g. abstraction of hydrogen involving the transfer of free valences by redistribution of electron density between macroradical **R**· and macromolecule RH, and $\bar{E}_d$ is the mean activation energy of the decay macroradicals at their contact by combination or disproportionation.

Equation (1) may be used as a criterion for classifying the decay reactions into reactions controlled by physical migration ($\bar{E}_{chm} = 0$ and $\bar{E}_{tot} = \bar{E}_{phm} + \bar{E}_d$ and reactions controlled by chemical migration ($\bar{E}_{ph} = 0$ and $\bar{E}_{tot} = \bar{E}_{chm} + \bar{E}_d$). Moreover, it also comprises the special case of transformation reactions ($\bar{E}_d = 0$ and $\bar{E}_{tot} = E_{phm} + \bar{E}_{chm}$).

Contribution of physical migration $\bar{\mathrm{E}}_{phm}$

A close relationship between the reactivity of macroradicals and mobility of polymer matrix results from many experimental findings[8,9] and the temperature correlation between the decay of macroradicals and the thermodynamic transitions (T_m, T_g) as well as numerous dynamic transitions ($T < T_g$, $T < T_m$)[24–27]. The contribution of physical migration represents a portion of total activation energy in all reactions in the solid phase because it is evident that the motion in arbitrary form plays an important role in reactivity (approaching and mutual orientation of reactants).

Two extreme types of relationship between the reactivity of macroradicals and the mobility of a polymer system can occur under particular conditions in our problem. The first is characterized by the fact that the reaction is directly controlled by the pertinent molecular motion which dominates in a given temperature region. This relation could lead to temperature correlation between decay and molecular motion on the so-called decay curve $c = f(T)$ for a certain reaction time[28] and to correlation between the activation energies of macroradical decay and molecular motions[28]. In the second case, an indirect relationship may exist because we may imagine a mechanism of indirect influence of mobility on the reactivity of reactants, for instance, high-energetic motion ensures the necessary free-volume conditions for the occurrence of some low-energetic motion or its combination with chemical processes which may be effective in the decay reaction. In this case, the temperature region of reactivity occurs in the temperature domain of molecular motion, but the activation energies of the processes are different.

For these aspects, the statistically weighted activation energy can be defined in the general form as follows

$$\bar{E}_{phm} = \sum_a C_a E_{phm}{}^{(a)} \qquad (2)$$

where c_a is the contribution of motion of the a-th mechanism in the transfer of free valences and $E_{phm}{}^{(a)}$ is the energy barrier for the a-th mechanism of motion.

There now arises a problem concering the kinds of motion, their selection, and determination of the terms of summation. In general, there are two fundamental groups of kinetic units of motion: the motion of the main chains of macromolecules and the motion of the sidegroups bonded to the chain of the macromolecule. Since a reaction necessitates shifts in the reaction centres which are localized on the main chain, we confine ourselves to chain motion only in this paper. There are two views on the nature of chain motions which have a common feature, arising from the deformation abilities of structural–molecular parameters (bond lengths, bond angles and torsional angles)[29] that the rotational angles are the most liable to deformation so that the chain motions are connected with change in torsional bond angles. In the first approach of the so-called local modes[30], the torsional oscillations of the chain segments in the vicinity of local equilibrium configurations are regarded as local motions. In the second group of approaches which were proposed by several authors[31–35] it is assumed, in terms of the rotation–isomerization approximation[36], that the chain motions of the skeleton consist of conformational transitions of the chain segments realized by bond-transitions over the rotational barriers. Both approaches are principally applicable to the calculation of $\bar{E}_{\text{phm}}$ because they provide the instruction for calculation. In this paper we confine ourselves to the second and more useful approach because we may expect that these kinds of motion will more effectively contribute to the approaching of the reaction pairs macroradical–macroradical and macroradical–macromolecule. The classification of conformational transitions[37] according to the basic criterion, for which the influence of these transitions on the chain tails is used, distinguishes two classes of transitions:

(1) Conformational motions which are accompanied by rotational or translational motion of the rest of the chain, e.g. crank-motion[34], creation, inversion and annihilation of a *gauche*-pair (the so-called 2 g 1 kink-sequence[33]), *gauche* migration, etc.

(2) Conformational motion without any motion of the rest of the chain, e.g. crankshaft-motions with a conformationally rigid or non-rigid mobile section of segment[31,32,34,35].

The real selection of the possible kinds of motion which may be responsible for the reactions of macroradicals is based on e.s.r. experiments which allow determination of the chemical and geometrical structure of the reactants. These facts are completed by some logical requirements, e.g. problem of localization of reaction centre on the kinetic unit of motion, problem of local free-volume, etc. The details will be presented in a following paper dealing with a special class of macroradical reactions which are controlled by molecular mobility.

The calculation of the energy barrier to a given motion in certain environments may be, in principle, performed by various methods, for instance quantum mechanics and molecular mechanics. In practice, these techniques can be used for special cases of reactions in the crystalline phase. As the detailed morphology of the amorphous phase is not known, it is advisable to formulate some simplified approaches which make possible at least an approximate estimate of the kinetic energetics of motions in this phase.

If we accept the above-mentioned concept of conformational motions, we can, on general lines, outline a simple method of calculation for the energy barrier of the a-th motion of the part of chain, called a segment. It is a system of N bonds among $(N+1)$ atoms of chain skeleton which is in motion. This motion is independent of rest of the chain and is due to transition of the rotational bond angles from one local conformational state into another. Assuming the energy barrier of the a-th motion can be separated and comprised in the intramolecular contribution which represents the situation in an isolated state and respecting the intermolecular contribution which comprises the influence of environment, we may write:

$$E_{\text{phm}}^{(a)} = E_{\text{intra}}^{(a)} + E_{\text{inter}}^{(a)} \tag{3}$$

The individual contributions are defined as follows. The intramolecular contribution for the so-called correlated bond transitions involving a simultaneous traversing of energy barriers by n-bonds has the form:

$$E_{\text{intra}}^{(a)} = \sum_{n} E_n(s,s') \tag{4}$$

where $E_n(s,s')$ is the energy barrier of rotational transition of the n-th bond from s-th local conformational state into s'-th potential well, while $(s,s' = t,g^{\pm})$.

The intermolecular contribution may be expressed to a first approximation by means of the principle of additivity in the form:

$$E_{\text{inter}}^{(a)} = \sum_{m} r_m \Delta\varepsilon_m \tag{5}$$

where r_m is the number of structural groups of the m-th kind (e.g. $-\text{CH}_2-$) in the mobile part of the segment which changes its position and $\Delta\varepsilon_m$ is the difference between the intermolecular potentials of a kinetic unit of motion on the top of barrier ε_m^{+} and in the initial state ε_m^{0}. In the special case of local conformational motions, we can, owing to sufficient local free volume and short-range character of intermolecular forces, write approximately $\varepsilon_m^{+} \simeq 0$ and thus $\Delta\varepsilon_m \simeq \varepsilon_m^{0}$.

The values of $E_n(s,s')$ may be approximated by the use of rotational-energy diagrams of model compounds of polymers while all bonds which change their rotational state are comprised within the summation.

The values of ε_m^{0} may be approximated for the amorphous state by the corresponding increment of cohesion energy at a given average temperature $\bar{T}$ because these contributions are principally dependent on temperature. The summation involves all structurally different functional groups of the mobile part of the segment.

In some cases, the energy barriers of different kinds of motion may be close to each other so that their simultaneous participation in the process of physical migration have to be presumed. Therefore we can use the following expression for c_a in equation (2):

$$c_a = \frac{p_a \mathrm{e}^{-E_{\text{phm}}^{(a)}/R\bar{T}}}{\sum_{a} p_a \mathrm{e}^{-E_{\text{phm}}^{(a)}/R\bar{T}}} \tag{6}$$

where p_a is the probability of occurrence of the initial state of the bonds which are subject to changes in their rotational state[38] and $\bar{T}$ is the mean temperature in the temperature interval where the kinetic measurements were carried out and the experimental activation energies were determined. The coefficients c_a fulfil the normalization condition:

$$\sum_{a} c_a = 1$$

for which the summation comprises all the types of motion mechanisms involved.

Contribution of chemical migration $\bar{E}_{chm}$

One of possible types of chemical migration is migration of free valence due to hydrogen abstraction. There are two groups of abstraction mechanisms. (i) Intermolecular process where the hydrogen exchange takes place between different macromolecules. (ii) Intramolecular mechanisms by means of 1.2-, 1.3-, 1.4- and 1.5-migration through three- to six-membered cyclic states inside the same macromolecule. In the second case, we may distinguish two sub-groups according to the ratio l/d where l is the distance traversed by hydrogen atom between reacting atoms and d is the distance between these atoms along the chain. The types of migration mentioned belong to the first sub-group characterized by $l/d \leqslant 1$ whereas the second sub-group with $l/d \ll 1$ shows features of an intermolecular mechanism.

Experimentally, there is much activity in trying to discover the type of abstraction which manifests itself in special experiments, especially for PE, which could indicate which of the mechanisms is preferred. Recent results confirm the occurrence of the intermolecular mechanism only in the crystalline phase[39,40].

Alternatively, the second group of mechanisms is also interesting because the presence of these mechanisms cannot be excluded in the amorphous phase owing to high flexibility of macromolecules in disordered regions of the polymer. From the geometrical point of view it is clear that the optimum configuration of the cyclic state corresponds to a certain conformational sequence of bonds in the cycle of the framework of rotation–isomerization approximation. There are other factors which contribute to this purely geometrical aspect and result in a reduction of a great number of possible conformational sequences of cycle bonds. They are: steric criteria, such as the so-called pentane interference[36], radical criteria, i.e. a certain conformational state C_α–C_β of macroradical bonds and the morphological criteria, i.e. possible occurrence of given sequences of cycle bonds in the amorphous or crystalline phase[41].

Analogously to the preceding case (2) we may write for $\bar{E}_{\rm chm}$:

$$\bar{E}_{\rm chm}=\sum_b c_b E^{(b)}_{\rm chm} \qquad (7)$$

where c_b is the contribution of the b-th type of mechanism of hydrogen abstraction in the transfer of free valence with the activation barrier $E^{(b)}_{\rm chm}$. The numerical calculations of energetic barriers for model reactions may be carried out by means of the pertinent methods of quantum chemistry or various semiempirical methods, e.g. BEBO[42], ZAV/3[43], and EBEBO[44]. The coefficients expressing the extent of participation of a certain type of migration are to be calculated according to equation (6) by replacing $E_{\rm phm}$ by $E_{\rm chm}$, where p_a expresses the relative probability of occurrence of a given conformational sequence of bonds in the cyclic state. We assume the validity of the normalization condition in this case, also.

Contribution of decay reaction $\bar{E}_d$

The decay of macroradicals may follow two mechanisms: combination or disproportionation. It follows that

$$\bar{E}_d=\sum_c c_c E^{(c)}_d \qquad (8)$$

where c_c is the contribution of individual types of decay mechanism with the corresponding energetic barrier $E^{(c)}_d$. For this stage, there is the problem concerning the determination of these contributions, but different physico-chemical manifestations and changes in properties of the polymers subjected to destroying effects, i.e. mainly crosslinking, point to the dominant role of the combination mechanism which gives rise to the formation of bridges in the amorphous regions of the polymer[45,46]. It has been assumed, on the basis of the recent interpretations of the kinetic data concerning the decay of macroradicals in polymers obtained mainly by the use of kinetic models of diffusion limited reactions[8,9], that this final act is a process without activation energy which is in agreement with analogous combinations of low-molecular radicals in the gaseous phase[47]. Nevertheless, the modem and more sensitive methods used for studying the reactivity of radicals indicate the existence of a certain but small energy barrier[48]. As combination is a localized process dependent on the nearness of reacting atoms, we can assume that the combination of macroradicals is to be approximated by the combination of low-molecular analogues. In this case, we can theoretically estimate that $\bar{E}_d = E_{\rm comb}$ by the method thermochemical kinetics[49] using the experimental values of dissociation energy of the products of combination $E_{\rm dis}$ and the concept of additivity of group contributions to the thermodynamic functions of reactants and products of the combination $E_{\rm comb}=E_{\rm dis}-\Delta H_r(T)$, where $\Delta H_r(T)$ is the reaction enthalpy of the combination reaction at the temperature T. The agreement between the values of activation energy obtained by experiment and theory is good, though it seems that somewhat higher values due to steric effects of macromolecules should be expected for macroradicals. However, we suppose that it is an acceptable approximation for the purpose of estimation.

CONCLUSION

In this paper, some molecular aspects of reactivity of macroradicals in matrices of polymers under post-destruction conditions are analysed. In agreement with the kinetic theory of matter, the role of motions, in particular, conformational mobility in transformation and decay reactions of free valences on macromolecules is analysed. This model is limited to the level of activation energy and does not enable us to estimate the rate coefficients. This limitation is given by the very complicated structural–dynamic–reaction relations in the reaction system. In the amorphous phase, the possibility of a simultaneous effect of several types of motion and reactions must be considered. However, the application of the model may, in some cases, bring about problems concerning the inputs into equations (2) and (7) because it will be necessary to test several types of motion and migration mechanisms. However, by considering similar conditions following from experiments we may reduce a number of actual motions and reactions. Therefore, we may expect that the proposed interpretation scheme may give a more detailed insight into the mechanism of macroradical reactions in solid polymers.

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