

Study of macroradical reactivity in polystyrene by means of ESR and stochastic models for diffusion-controlled reactions

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Received 8 May 1981

Dedicated to Professor Ing. RNDr. A. Tkáč, DrSc., in honour of his 60th birthday

The macroradicals generated by γ -radiolysis of atactic polystyrene were investigated by means of e.s.r. spectroscopy. The kinetics of decay of alkyl macroradicals in the temperature interval 20–100°C were examined by means of stochastic models for diffusion-controlled reactions. A temperature correlation between kinetic parameters of macroradical transport and molecular motions in an amorphous sample has been found.

При помощи ЭПР исследованы макрорадикалы, полученные при γ -радиолизе атактического полистирола. Кинетика исчезновения алкильных макрорадикалов в интервале температур 20–100°C была исследована при помощи стохастических моделей реакции в диффузионном режиме. Была найдена температурная корреляция между кинетическими параметрами транспорта макрорадикалов и молекулярными движениями в аморфных образцах.

The e.s.r. method is used to advantage not only for identification of the products of polymer destruction but also for investigation of consecutive processes [1, 2]. The structural aspect of the problem of macroradicals in polystyrene (PS) was widely studied [3]. It has been found that radiolysis at low temperatures gives rise to cyclohexadienyl macroradicals [4] while chain alkyl centres predominate at room temperature [5]. The end macroradicals which were generated by mechanical destruction [6] are transformed into chain alkyl centres at –30°C [7]. The decay of macroradicals was investigated by means of usual formal kinetics in mechanically destroyed PS with regard to the influence of the extension of sample in the temperature region 20–100°C [8] as well as in PS subjected to radiolysis with regard to the influence of pressure in the temperature region 80–200°C [9].

In this paper, the reactivity of radical centres in PS is studied by means of kinetic models of diffusion-limited reactions with the aim to obtain a more detailed idea of the mechanism of decay reaction.

Experimental

A plate was made by pressing from polystyrene Vestyron ($\bar{M}_n = 2.7 \times 10^5 \text{ g mol}^{-1}$, Hoechst, GFR). Cylinders ($\varnothing 3 \times 10 \text{ mm}$) were turned out from this plate. The samples were irradiated with γ -radiation of total radiation dose 0.123 MGy at room temperature and afterwards they were stabilized at the temperature of solid CO_2 . The initial spectra were recorded at room temperature with an X-band e.s.r. spectrometer Varian E-4 equipped with a temperature-controlling appliance. After thermal treatment the curves expressing the height of signal as a function of time were recorded in the course of 1–2 h at the temperatures 20–100°C. The concentration of macroradicals was determined by the reference method using the strong-pitch standard Varian.

Theoretical

The kinetic study of decay of alkyl macroradicals in PS was carried out by means of stochastic kinetic models proposed by *Lebedev* [10] and *Waite* [11] for bimolecular diffusion-limited reactions.

The Lebedev cage model of reaction in condensed phase is based on the assumption that the reaction proceeds in two steps, *i.e.* transport of reactants into the reaction cage and reaction of reactants in the cage. For the diffusion-limited reactions of identical reactants in stationary state this model gives the kinetic equation in the form

$$\frac{1}{c} - \frac{1}{c_0} = 2k_m v_0 t \quad (1)$$

where c_0 and c are volume concentrations of reactants (spin cm^{-3}) at the time moment t_0 and t , respectively, k_m is the rate constant of reactant transport, and v_0 is the volume of the reaction cage about reactant ($\text{cm}^3 \text{ spin}^{-1}$).

The kinetic equation for the reactions of identical reactants resulting from the Waite model on the assumption of their initial homogeneous distribution and chaotic motion obeying the Smoluchowski boundary condition has the form

$$\frac{1}{c} - \frac{1}{c_0} = 4\pi r^* D \left(1 + \frac{2r^*}{\sqrt{\pi Dt}} \right) t \quad (2)$$

where r^* is the capture radius, *i.e.* the distance to which the reactants must approach in order that the irreversible reaction may take place, D is the coefficient of the relative transport of reactants for which it may be written $D = 2D'$. The coefficient D' characterizes the motion of reactant. It is evident from the structure of the rate constant in eqn (2) that it describes not only the initial nonstationary but also the subsequent stationary stage of reaction.

Results and discussion

Interpretation of ESR spectra

The e.s.r. spectrum of irradiated PS recorded immediately after generation of macroradicals at room temperature is represented in Fig. 1A. It contains two

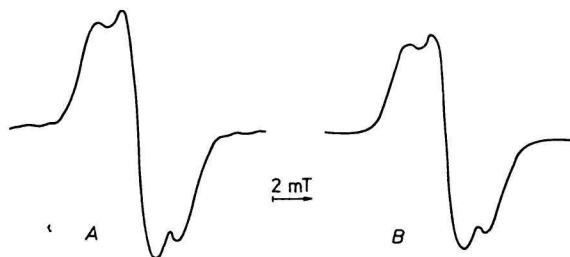
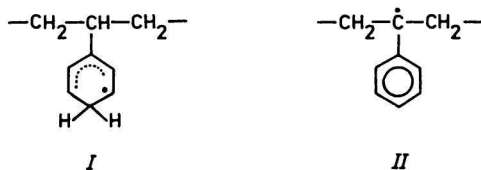


Fig. 1. ESR spectrum of polystyrene irradiated by γ -radiation at room temperature. A. Recorded at 20°C; B. After 15 min thermal treatment at 85°C, recorded at 20°C.

signals with the constants of hyperfine splitting $a_H = 4.5$ mT (weak triplet with additional triplet structure which brings about side peaks) and $a_H = 1.9$ mT (distinct triplet in the centre of spectrum). The interpretation of these signals was carried out by comparison with literature data. The broad triplet was assigned to cyclohexadienyl macroradical (I) by *Ohnishi* [4]. This assignment was confirmed by theoretical interpretation of the spectrum according to *Fessenden* [12].



The predominant narrow triplet corresponds to the chain alkyl macroradical (II) according to *Abraham* [5]. The nonpaired electron interacts with two β protons while the contribution of other β protons brings about only a broadening of lines. A small value of the constant of hyperfine interaction is, according to theoretical interpretation of *Milevskaya* [13], due to the delocalization of nonpaired electron which accompanies parallel orientation of the plane of the phenyl group with respect to the plane of the section of chain to which this side group is attached.

Kinetics of decay of alkyl macroradicals

The fundamental postulate of applied kinetic models is the presence of one kind of macroradicals. Because of different relative stability of macroradicals *I* and *II* this postulate was fulfilled by heating the samples. Fig. 1B shows a narrow triplet obtained after thermal treatment. The form of spectrum of alkyl macroradicals does not principally change with temperature and time during the decay reaction. The second assumption requiring homogeneous distribution of reactants in the sample may be regarded as fulfilled because of amorphous character of atactic PS and isotropic arrangement of the source of γ -radiation.

The reactivity of alkyl macroradicals was studied in the temperature interval 20–100°C. It has been found that the radical centres are relatively stable at 20°C because the decrease in volume concentration was about 3% in the course of 1 h. On the other hand, a mass decay takes place in the course of 1/2 h at 100°C, which is due to the transition of polymer from glass to high-elastic state ($T_g = 100^\circ\text{C}$). An orientation study of the decay of alkyl macroradicals is represented in Fig. 2. The

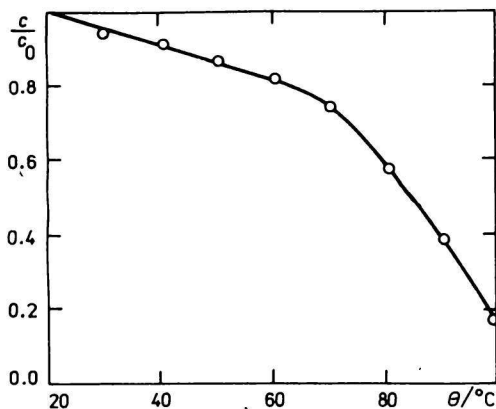
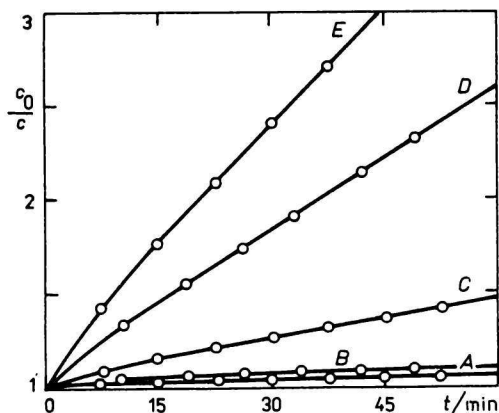


Fig. 2. Heating curve of polystyrene subjected to radiolysis obtained from the intensities of spectra after successive 15 min thermostatings at given temperatures.

heating curve shows two regions of different reactivity, the first one in the region 20–75°C and the second one in the region 75–100°C. Identical course also appears in Fig. 3 which describes the variation of concentration with time in relative coordinates of a common bimolecular reaction $c_0/c = f(t)$. It is obvious that a deviation from linearity is to be observed at higher temperatures (70–90°C) in the initial stage of reaction which indicates nonstationary progress of reaction.

It results from the Lebedev equation (1) that the rate constant of the second-order reaction has the form $k_{II} = 2k_m v_0$ owing to which the values of k_m may be calculated for convenient choice of the magnitude of reaction cage. The estimation is to be performed on the assumption of spherical approximation of the cage by

Fig. 3. Kinetics of the decay of alkyl macroradicals in relative coordinates of a second-order reaction.
 A. 30°C; B. 50°C; C. 70°C; D. 80°C;
 E. 90°C.

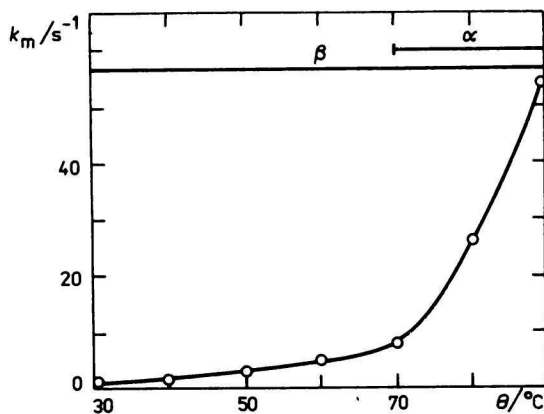


means of a simple physical model according to which the reactants react at approaching provided their distance is smaller than the contact distance, *i.e.* the minimum distance in nonbonding interaction in the solid phase. Then we may write for a decay reaction of two macroradicals which may proceed as a combination or disproportionation

$$r_0 = \frac{1}{2} (r_{C.C} + r_{C.H})$$

where $r_{C.C}$ and $r_{C.H}$ are contact distances between the carbon atoms in combination reaction and between the atoms of carbon and hydrogen in disproportionation reaction, respectively. Their values are 0.29 and 0.27 nm [14]. Fig. 4 represents the

Fig. 4. Temperature dependence of the rate constant of transport of alkyl macroradicals according to the Lebedev model.



rate constant of macroradical transport as a function of temperature as found from the stationary linear sections of the curves in Fig. 3. It can be seen that a rapid acceleration of the transfer of radical centres in polymer takes place in the temperature region over 75°C.

The deviations from linearity in Fig. 3 in the region of higher temperatures suggest the application of the Waite equation (2) which contains the rate constant dependent on time. The evaluation of kinetic data in the coordinates $(1/c - 1/c_0)/\sqrt{t} = f(1/\sqrt{t})$ enables us to determine the kinetic parameters of reaction $D(\Theta)$ and $r^*(\Theta)$. These values are listed in Table 1. They are in harmony with the estimate of

Table 1

Values of the kinetic parameters r^* and D according to the Waite model

$\Theta/^\circ\text{C}$	$D \cdot 10^{16}/\text{cm}^2 \text{ s}^{-1}$	r^*/nm
70	2.02	1.91
75	2.70	1.85
80	6.00	1.71
85	10.10	1.49
90	13.50	1.26

these parameters for other polymers [15]. They make possible to demonstrate the applicability of eqn (2) on the basis of the relationship between relative concentration change and time (Fig. 5). It results from the graph that this kinetic model is able to describe even a time stepwise decay of macroradicals at discontinuous temperature rise. The temperature dependences of the kinetic parameters D and r^* represented in Figs. 6 and 7 indicate that the mobility of centres increases with

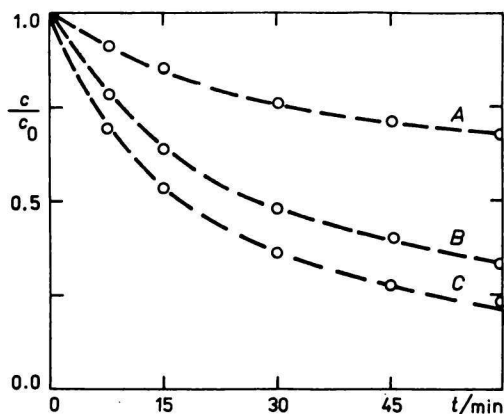


Fig. 5. Variation of the relative concentration with time.

○ Experimental values; --- values calculated according to eqn (2) with parameters listed in Table 1.

A. 70°C; B. 80°C; C. 90°C.

Fig. 6. Temperature dependence of the coefficient of relative transport of reactants D .

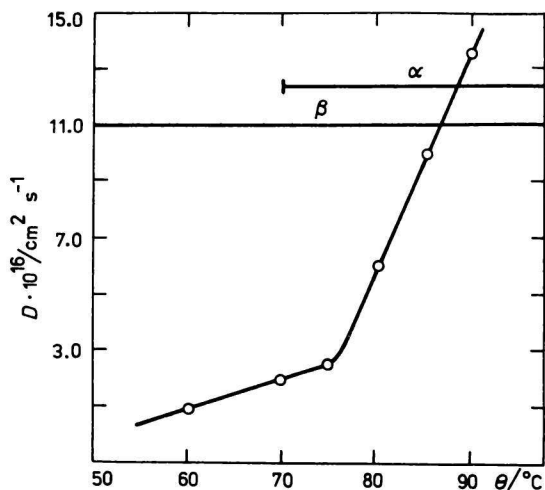
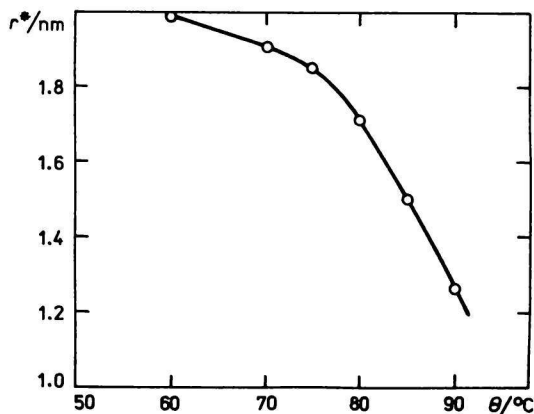


Fig. 7. Dependence of the capture distance on temperature.



temperature. The increased intensity of motion cuts down the distance to which the reactants must approach in order to undergo decay reaction. In the region of about 75°C we may observe a great acceleration of motion of centres which results in a considerable decrease in concentration of reactants. Moreover, a linear relation between the capture distance and transport coefficient of reactants has been ascertained (Fig. 8). This fact is in good agreement with inverse proportionality of r^* and D as derived on the basis of the general reaction scheme according to which a diffusion-controlled reaction involves a sequence of two steps, *i.e.* a) transport up to the contact of reactants and b) reaction of particles in the contact [16].

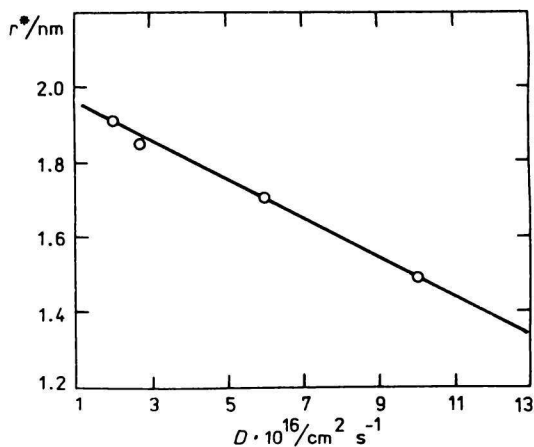


Fig. 8. Experimental relationship between the capture distance and diffusion coefficient of alkyl macroradicals.

Correlation between the kinetics of decay and mobility of macromolecules

According to the hypothesis of molecular motion, the transport of radical centres proceeds *via* conformational transformations of macromolecules while the hypothesis of chemical migration takes it for a consequence of a chemical reaction involving the migration of a hydrogen atom and/or decomposition of macroradicals.

The heating curve (Fig. 2) as well as the temperature dependences of the kinetic parameters of reactant transport k_m and D (Figs. 4 and 6) reveals an acceleration of the motion of alkyl macroradicals in the region of about 75°C. The observed breaks on these plots characterize the change in mechanism of the limiting process.

These results may be confronted with the facts obtained by studying the relaxation properties of atactic polystyrene by the use of dynamic-mechanical method and $^1\text{H-n.m.r.}$ method. It has been disclosed [17] that a-PS exhibits a few relaxation regions. The γ -relaxation maximum is to be observed in the region of -120°C. The β -relaxation region manifests itself by a broad peak with the maximum in the region of 20°C. The α -relaxation region begins over 70°C and reaches the maximum in the proximity of $T_g = 100^\circ\text{C}$.

A comparison of the temperature regions of initial release of the α -relaxation and acceleration of macroradical transport indicates the relationship between the kinetic parameters of decay and molecular motion. A conspicuous temperature correlation reveals the predominating influence of molecular motion on the decay of alkyl macroradicals in PS. In the region 20–75°C the transfer of free valences is ensured by the β -molecular motion. At higher temperatures the decay is controlled mainly by the α -molecular motion. Thus a change in mechanism of the limiting process is related with a change in character of the molecular motions in atactic sample. According to the hypothesis of molecular motion, we may principally

compare the measured values of the kinetic parameters k_m and D' with the values of the frequencies of molecular motions (ν) or the coefficients of self-diffusion of macromolecules in PS (D_{self}). In the first case, we found a good quantitative agreement of the determined values of k_m with the values of ν obtained experimentally from the relaxation map of PS according to [18]. In the second case, neither direct nor qualitative comparison with the measured values of the coefficient of macroradical transport D' was possible because experimental data concerning the self-diffusion of macromolecules in PS in the glass and high-elastic state were lacking.

Nevertheless, the ascertained temperature correlations between the kinetic parameters of reaction and kinetic parameters of mobility inspire the idea of predominating role of molecular motions in the decay of alkyl macroradicals in polystyrene in the investigated temperature interval.

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Translated by R. Domanský