

THE DECAY OF FREE RADICALS IN POLYMER MEDIA

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ABSTRACT

Kinetic laws and particularities of migration mechanisms of free valence in the processes of decay of free radicals in polymers are dealt with. The basic examples correspond to the results for polyethylene and polymethyl methacrylate. The kinetics of the decay reactions are discussed from the viewpoint of Waite's cage diffusion theory and Levedev's model. From the kinetic data of various authors the cage radius and diffusion coefficient are calculated. With increasing temperature the cage radius in polyethylene increases from 5.3 Å (120°K) to 40–60 Å (360°K) and it has to be looked upon as an effective kinetic parameter. The diffusion coefficient corresponding to free valence displacement at long distances is in the range 10^{-16} to 10^{-18} cm² s⁻¹.

In amorphous polymers at temperatures exceeding the glass temperature diffusion proves to be of major importance for long-distance migration. In a series of other examples, chemical reactions play a more important role, such as hydrogen atom transfer and radical decomposition. Results of measurement of the corresponding elementary reaction compared with the rate constants of decay are mentioned. Under real conditions, migration is affected simultaneously by both diffusion and chemical mechanisms.

The investigation of free radical decay proves to be a complicated problem closely associated with several fields of the chemistry and physics of polymers, reactivity theory and reaction kinetics in the solid state etc. The radicals are formed in chemical, irradiation, mechanical, photochemical and other effects on the polymer. Each of these processes provokes deep changes in the material. Therefore the overall complex of investigations of the laws of decay should consist of a great many phenomena:

The central problem of free radicals in polymers (their structure, conformation, intrinsic mobility, radical reactivity in fundamental kinds of reactions at low temperatures etc.);

The supermolecular structure of polymers (transition and relaxation effects, intrinsic mobility, diffusion and the like);

Radiation and photo chemistry (main types of defects and distortions, radical and ion-molecular reactions, distribution of distortion centres according to their distances and depths of 'traps', structural changes in polymers and so on);

Mechano-chemical and mechano-emission phenomena in polymers (diffusion, amorphization and recrystallization and so forth);

Kinetics of low-temperature reactions in the solid phase (diffusion, activation energy and 'compensation' effect, and oxidation).

From this incomplete array the present lecture will deal briefly with a few laws of kinetic decay and the migration mechanism of the free valence, only.

FORMAL KINETIC LAWS OF THE PROCESS

The investigation of the kinetics of chemical reactions in solids and viscous liquids¹⁻⁴ starts from the cage model. To react with one another the particles should meet in a single cage, i.e. in one elementary structural volume of the solid. The rate of the bimolecular reaction is determined by the correlation between the following parameters:

r_0 —radius of the elementary cell-cage in cm;

D —diffusion coefficient of reacting particles, cm^2/s ;

$S = K_r/K_D$ where K_r is the reaction probability of the particles in the cage, and K_D is the probability of the particle leaving the cage to enter the reaction.

Waite^{1,2} solved the differential equation of the rate of bimolecular reaction for the irregular motion of reacting particles and their random starting distribution in the volume of the system. The general form of the solution is fairly complicated except in extreme limiting cases where individual values may well be neglected.

Thus, at low diffusion rate and a high reaction probability when the formation of each pair of particles in the cage leads to their interaction, i.e. $S \gg 1$, the rate of the process is limited by diffusion:

$$W = -dC/dt = K_D(1 + \tau^{\frac{1}{2}}/t^{\frac{1}{2}})C^2 \quad (1)$$

where $K_D = 4\pi r_0 D$ is the diffusion rate constant at $t \gg \tau$ and $\tau = r_0^2/\pi D$ the lifetime of particles in the cage.

This extreme limiting case is most interesting for analysis of the reaction kinetics of radical decay. The elementary recombination step proceeds here practically without activation energy and the reaction probability in the cage may well be presumed to be very high. For calculation purposes the mechanism of displacement of particles in the volume (diffusion or chemical migration) does not appear to be a decisive one.

Equation 1 is of second order according to concentration but the proportionality coefficient is time-dependent:

$$K_{D,t} = 4\pi r_0 D [1 + \sqrt{(r_0^2/\pi D)} \times 1/\sqrt{t}] \quad (2)$$

The relatively high starting reaction rate is caused by the fact that at $t \ll \tau$ (observation time is comparable with that of transmission of particles from one cage into another), the particles which appeared in pairs due to random distribution, i.e. at distances less than r_0 , react with one another initially.

Another equation form of diffusion kinetics was obtained in quite a simple way by Lebedev:

$$W = -dC/dt = 2K_D \ln(1 - C/r_0^3)C \quad (3)$$

At $C \rightarrow 1/r_0^3$ the rate is relatively high because all the cages are occupied

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by radicals. Provided that $C \ll 1/r_0^3$, the expression 3 can be reduced to the ordinary second order equation.

In coordinates of the second order equation (related to the abscissa axis t/τ , and related to the ordinate axis C_0/C), the kinetic curve of the diffusion-controlled bimolecular reaction in agreement with Waite's and Lebedev's equation will have the form shown in *Figure 1*. The deviation from linearity at low values of t/τ appears to be a characteristic feature of reaction kinetics in the condensed phase. From the shape of the kinetic curve on this section the importance of the parameters r_0 and D may be deduced.

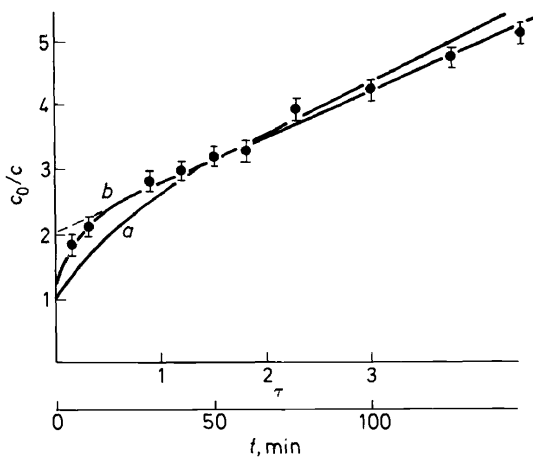


Figure 1. (a) Theoretical curve according to equation 3. (b) Dole's experimental data of allyl radical decay in polyethylene.

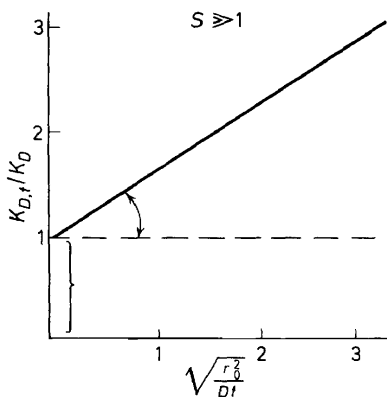


Figure 2. Theoretical curves according to Waite's equation.

Figure 2 illustrates the calculation method used. From the general form of the rate equation 1 it is seen that the proportionality coefficient $K_{D,t}$ given by

$$K_{D,t} = (dC/dt)(1/C^2) \quad (4)$$

has to decrease in the course of reaction to approach the constant K_D value.

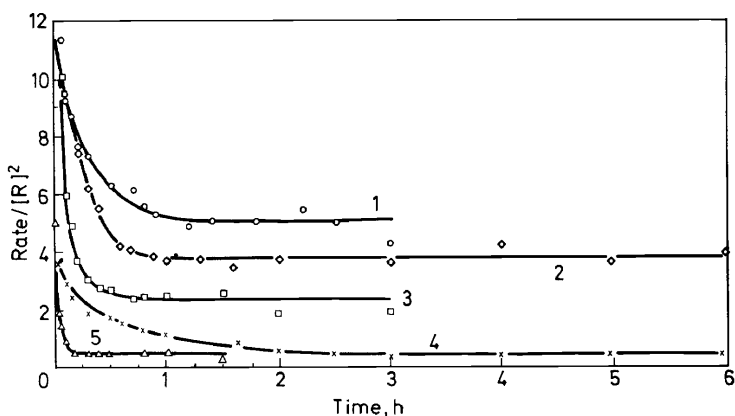


Figure 3. Time-dependent rate constants as a function of time for allyl radical decay in polyethylene⁵.

The dependence of $K_{D,t}(t)$ is shown in Figure 2. At $t/\tau \gg 5$ the proportionality coefficient becomes practically constant with the reaction evidently following a bimolecular law. In the linear section the value $K_{D,t}$ has to be linearly dependent on $1/\sqrt{t}$, whereas from equation 2 it follows that in the figure with coordinates $K_{D,t}$ and $1/\sqrt{t}$ (see Figure 4) the segment cut on the ordinate axis equals $4\pi r_0 D$ and the slope is $4\sqrt{\pi r_0^2/D}$. Thus, by a detailed analysis of the form of the starting section of kinetic curves the radius of the elementary cell as well as the effective diffusion coefficient may well be calculated.

The presumption that radical decay should follow the second order reaction is so persuasive that several authors acquainted with the cage model involuntarily divide the one kinetic curve into two sections ('fast' and 'slow'

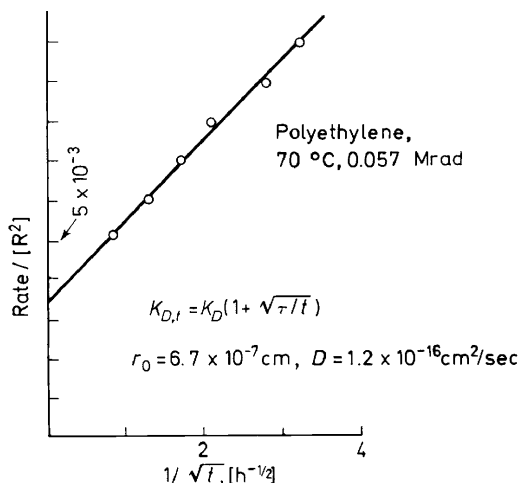


Figure 4. Calculation of the data of ref. 5 according to Waite's equation.

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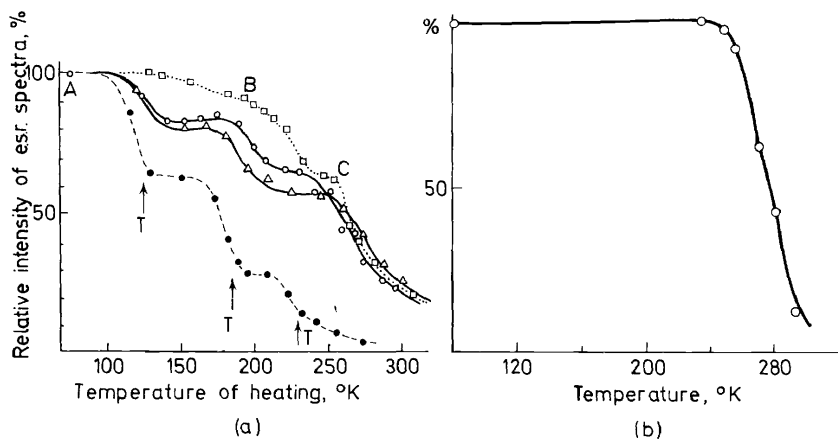


Figure 5. Decay curves of free radicals formed in polyethylene by γ -irradiation (a) and by mechanical degradation (b).

reactions) with their own rate constants. Auerbach⁵ measured the kinetics of allyl radical decay in polyethylene over the temperature range 70° to 135°C. Initial concentrations of radicals are not referred to in the paper, but knowing both the dose and radiation yield they may be evaluated in quite a revealing way. In Figure 3 the kinetic curve of decay is shown in coordinates according to the second order equation. The curve shows the change of coefficient $K_{D,t}$ in the course of the reaction. The shape of the curves on both the figures corresponds to Waite's and Lebedev's equations. In Figure 4 the same data are plotted in the coordinates $K_{D,t}$ and $1/\sqrt{t}$; from the position of the straight line the parameters r_0 , D and τ have been calculated. The results of the calculation are summarized in Table 1.

Table 1. Parameters r_0 , D and τ of the decay reaction of allyl radicals in polyethylene at 70°C (evaluations according to ref. 5)

Dose Mrad	$C_0 \times 10^{-18}$ cm^{-3}	$l \sim C_0^{-1/2}$ Å	r_0 Å	D cm^2s^{-1}	τ s
0.057	0.3	150	67	1×10^{-16}	130
27.4	8	50	43	2×10^{-18}	2600

Thus, in polyethylene, the effective kinetic cage radius in the premelting region appears to be quite high and reaches 40 to 60 Å. At the same time, the initial concentration of radicals results in the average distance between them amounting to between 50 and 150 Å respectively, which is comparable with the cage radius. The comparison of the values l and r_0 clearly illustrates the role of radical recombination in the cage.

Equation 1, on the basis of which the values of r_0 have been calculated, corresponds to the limiting case when $S \gg 1$. Consequently, the effective cage

radius may be determined as some distance between the radicals where the probability of recombination is considerably higher when compared with the probability of their separation without any interaction. For this reason, the kinetic radius of the cage cannot always be identified with such parameters as the principal dimension of the elementary cell of a crystal or, for instance, the average distance between adjacent chains.

PECULIARITIES OF VARIOUS METHODS OF RADICAL GENERATION

From the viewpoint of the cage model the kinetic analysis of decay of radicals exhibits some peculiarities. In real systems the requirement of a random particle distribution in the volume of the system is not always satisfied and the actual or local radical concentration frequently does not correspond to the average concentration measured, for example, by integration of the line of the e.s.r. absorption spectrum.

The character of particle distribution in the volume depends on the method of radical generation and on the supermolecular structure of the polymer. In the action of low-energy particles (e.g. in the treatment of films by a high-frequency charge), bombardment by hydrogen atoms and by other chemically active particles, ultra-violet irradiation of massive specimens and grinding crystals or glasses, the radicals get concentrated, particularly in the thickest surface layers. In individual cases the thickness of the layer in which the radicals are formed amounts to several hundred Ångstrom units (bombardment by hydrogen atoms⁶, grinding particles⁷, treatment by gas discharge⁸) and consequently, in the case of a specific material surface about $1 \text{ m}^2/\text{cm}^3$ (characteristic particle dimension $\sim 5 \times 10^{-4} \text{ cm}$) the local concentration of radicals exceeds the average one by a hundredfold and the effective rate constant of decay differs from the actual one by a hundredfold also.

The volume distribution by mechanical radical generation depends on the character of the forces acting. The stretching tensions in amorphous crystalline polymers are localized in amorphous intermediate layers where the radicals also concentrate. The treatment of powders in mills is accompanied by intensive amorphization even to complete loss of crystallinity. The tension provoking both the displacement of chains and amorphization activates the diffusion. The curve of radical accumulation exhibits a limit, whereas the coefficient of forced diffusion which may be calculated from this curve is comparatively high equalling $10^{-18} \text{ cm}^2/\text{s}$. Thus, in long-term milling the polymer may be expected to be amorphous and the radical distribution random.

The decay rate and its dependence on temperature are related to the kind of particle distribution in the volume given by the method of radical generation. In *Figure 5*¹⁰ curves of alkyl radical ($-\text{CH}_2\dot{\text{C}}\text{HCH}_2-$) concentration in polyethylene as a function of temperature are shown. Each temperature was maintained for five to ten minutes. The left-hand curve has been obtained after irradiation of the specimen with a dose of 3 Mrad (the initial radical concentration being $3 \times 10^{19} \text{ cm}^{-3}$), after treatment in a vibration mill ($C_0 = 1 \times 10^{18} \text{ cm}^{-3}$). In the milled amorphized polyethylene the decay of

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radicals takes place over a relatively narrow temperature range between 240° and 300°K. In the γ -irradiated polymer three temperature regions may well be differentiated: 120°, 190° and 240°K.

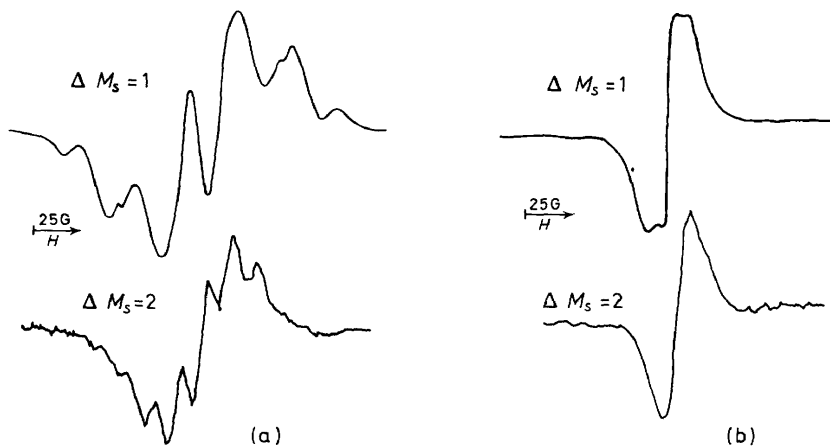


Figure 6. The e.s.r. spectra of individual radicals (1,3) and pairs (2,4) in (a) polyethylene (1,2) and (b) polyoxy ethylene (3,4) taken from ref. 11.

Close to 120°K the temperature coefficient of the decay rate appears to be very small (less than 1 kcal/mole) and it may well be presumed to correspond to the activation energy of the elementary recombination step of radicals located one beside the other, i.e. the radical pairs.

The pairs, i.e. the radicals located at a distance of a few Ångstrom units from one another, have been found in some organic crystals and polymers^{11,12} following irradiation (γ or u.v.) at 77°K. The e.s.r. spectra of radical pairs in polymers are shown in Figure 6¹¹. The unpaired electron interacts with

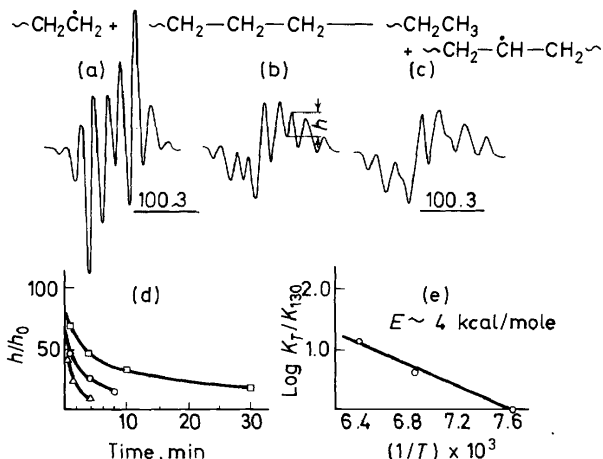


Figure 7. Transformation of $\sim\text{CH}_2\dot{\text{C}}\text{H}_2$ radicals into $\sim\text{CH}_2\text{---}\dot{\text{C}}\text{H}\text{---}\text{CH}_2$ radicals in polyethylene: 1—130°K; 2—146°K; 3—157°K (taken from ref. 13).

the protons of both the radicals; as a result the value of the hyperfine splitting decreases and the number of hyperfine system components increases. According to qualitative evaluations the concentration of pairs may reach a tenth of the overall radical concentration. In agreement with these data¹² the distance between the radicals in pairs, decaying in a low temperature region, equals 5.3 Å. This value may evidently be accepted as the cage dimension in polyethylene at 120°K. when the defrosting of the inner motions of the chain is just starting.

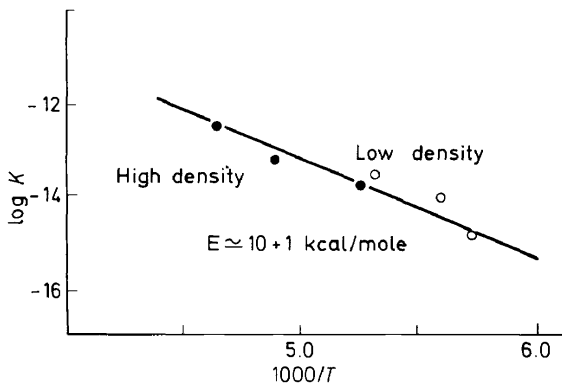


Figure 8. Alkyl radical decay in polyethylene (170°–215°K). Calculation of the data of ref. 10.

Over the same temperature range in polyethylene also another reaction, i.e. the transformation of end radicals into inner ones which may quite as well be denoted as a cage reaction, has been observed. The kinetic reaction curves are shown in Figure 7¹³. The activation energy of 4 kcal/mole well characterizes the elementary process of hydrogen atom transfer.

The next step of radical concentration decrease is in the region of 190°K. In the irradiated polymer the average distances among radicals and among vinyl groups do not exceed 20 to 30 Å and for their interaction there is no need of gradual displacement of the free valence to longer distances (chemical migration or diffusion). The partial radical decay in the region of 190°K is associated, first of all, with a further increase of cage radius as a result of the defrosting of inner motions. The corresponding decrease of alkyl radical concentration is due to the cage reactions, i.e. recombination or interaction with weak C—H bonds around vinyl groups (transformation of alkyl radicals into allyl ones¹⁴).

The effective activation energy of decay in this range is close to 10 kcal/mole. The dependence of the rate constant on temperature is shown in Figure 8; the data on the amorphous and crystalline polyethylene specimens are taken from Figures 2 and 3 in reference 10.

The elucidation of the steps of decay at 190°K by the increase of the effective cage radius (presumably up to 10 to 20 Å) is confirmed by comparison of the curves taken from Figure 5a and 5b. In milled amorphized polyethylene

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(Figure 5b) the starting radical concentration equals $1 \times 10^{18} \text{ cm}^{-3}$ and the average distance among them is $\sim 100\text{\AA}$. The decay starts over the temperature range 230° to 240°K . (i.e. at a temperature corresponding to the last decrease of the curves shown in Figure 5a) with the temperature dependence lacking any steps whatsoever.

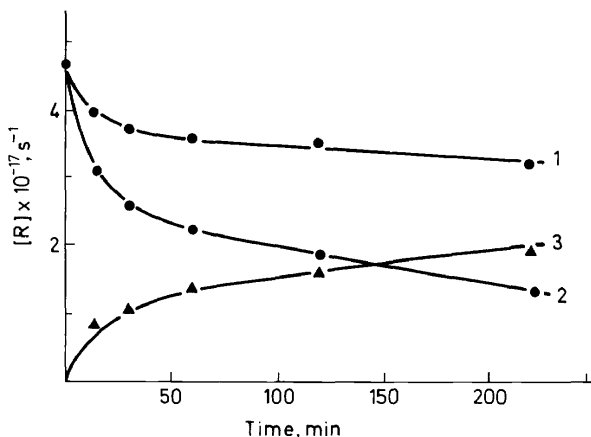


Figure 9. Decay of peroxy radicals in polymethyl methacrylate at high vacuum and 0°C . Concentrations of radicals $\{[\text{ROO}^\bullet] + [\text{R}^\bullet]\}$ —1, $[\text{ROO}^\bullet]$ —2 and $[\text{R}^\bullet]$ —3 from ref. 20.

Evidently, starting from 240°K , in both the polyethylene specimens the motion of free valence becomes possible over relatively long distances. At a constant temperature the kinetic reaction law depends on whether the recombination (equation 1) or the reactions with 'weak' C—H bonds appear to be prevailing.

Thus, at the temperature increase the effective kinetic cage radius increases from a few Ångstrom units (120°K) to tens of Ångström units (pre-melting region, $r_0 \approx 40$ to 60 \AA).

POSSIBLE MECHANISMS OF FREE VALENCE MIGRATION

Thermal kinetic analysis of the decay reaction dealt with above is in fact based on the presumption that active centres participate in two types of motions:

- (1) Inner motions of macromolecular chain segments; the comparatively intense motion in a cage volume appears to be a distant analogy of rotation diffusion in low molecular compounds;
- (2) Displacements in polymer volume at relatively long distances (translation diffusion or chemical migration).

Reasonable division of the motion into two parts is, of course, possible in the cases when the frequencies of both the motion forms differ considerably from one another ($\nu_{\text{rot}} \nu_{\text{tz}}$). The kinetic (effective) cage radius depends, to a great extent, on the correlation of the frequency and amplitude of the two motion forms.

In many systems, marked with great local concentrations of active centres and intense inner segmental motion the decay processes may be elucidated by the course of reactions in the cage without the need to apply the conception of long-distance free valence migration.

In another extreme case, when the inner motions are hindered (crystalline phase, low temperature) the effective cage radius decreases up to the geometric dimension of the elementary crystalline cell, the basic role in the decay processes then being played by free valence migration.

Table 2. Temperature of decay of polymer radicals

Polymer	T_g , °K	Stability temperature, °K			ROO'
		R— $\dot{C}H_2$	R—CXY	inner radicals	
Polyethylene	188	120–140	—	260–280	260–280
Polypropylene	256	< 90	120–140	250–290	300
Polyisobutylene	200	< 90	200–220	200–220	300–340 200–220
Polystyrene	370	120–140	330–350	—	260–280
Polymethyl methacrylate	380–390	< 90	330–350	250–270	260–280
Polyvinyl alcohol	358	120–140	—	330–360	200–220
Polyformaldehyde	250	250–270	—	350–370	200–220
Polycaprolactam	320	120	—	280–290	

In most of the intermediate cases, the contribution of both motion types may be expected to be comparable and the laws of decay not to be attributed to any single mechanism of free valence displacement.

The long-distance free valence migration may be associated with both diffusion and chemical reactions. The migration mechanism depends on many factors, namely on radical reactivity, structure and chemical properties of macromolecules, supermolecular polymer structure, medium properties etc. The first image on the nature of the processes of free valence displacements is presented by analysis of the conditions of various types of radical decay in the given polymer. The simplest criterion is the comparison of the temperature of structural transition in the given polymer with the temperature range in which the radical decay proceeds at a measurable rate. In Table 2¹⁵ the temperature ranges of the registration of decay reaction for two types of end, inner and peroxy radicals in various polymers are shown; here, fifteen authors' data are summarized.

Diffusion

Alkyl and peroxy radicals in polyisobutylene have been generated by the method of mechanical dispersion at 80°K in a vacuum. The initial concentration is about 10^{18} cm⁻³. Three types of radical decay over the narrow temperature range from 200° to 220°K coincide with the glass transition temperature of polyisobutylene (200°K). On this basis diffusion may well be presumed to be the fundamental mechanism of free valence migration.

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The rate constant of peroxy radical decay in polyisobutylene in air depends on the temperature according to the equation

$$K_D = 3.2 \times 10^{-4} \exp(-18000/RT) \text{ cm}^3 \text{ s}^{-1}$$

In the diffusion mechanism $K_D = 4\pi r_0 D$ and provided that $r_0 \sim 10^{-7}$ cm, we obtain

$$D \approx 0.3 \times 10^3 \exp(-18000/RT) \text{ cm}^2 \text{ s}^{-1} \quad (5)$$

In polyisobutylene the coefficients of diffusion of hydrocarbons of paraffinic order C_{22} to C_{25} have been measured¹⁶ and for them we obtain

$$D = 3 \times 10^3 \exp(-18000/RT) \text{ cm}^2 \text{ s}^{-1} \quad (6)$$

With regard to the discrepancy between the dimensions of the segment in polyisobutylene and that in the hydrocarbons C_{22} to C_{25} as well as the possibility of the molecular weight effect on the diffusion coefficient, the coincidence of equation 5 and 6 may be found quite satisfactory. Similar evaluations confirm the presumption of the prevalence of the diffusion mechanism of radical decay in polyisobutylene.

Both lower and upper limits of diffusion rate assuring measurable rates of macroradical decay may be evaluated by very general considerations. In the measurement of decay kinetics, the radical concentration is usually $10^{18 \pm 1} \text{ cm}^{-3}$ and the duration of the reaction observation is 10^3 to 10^4 s. Provided that during the observation period the radical concentration decreases by twofold, then

$$\tau_{\frac{1}{2}} \approx 1/K_D C_0 \approx 1/4\pi r_0 D C_0 \text{ s}$$

Provided that $r_0 \sim 10^{-7}$ cm

$$D \approx 10^7/10 \times 10^{3.5 \pm 0.5} \times 10^{18 \pm 1} \approx \text{between } 10^{-15} \text{ and } 10^{-18} \text{ cm}^2 \text{ s}^{-1}$$

Should the diffusion coefficient be less than 10^{-18} , the process may last some tens of hours and should it exceed 10^{-15} , the reaction will terminate within one minute, i.e. at the moment of establishment of thermal equilibrium.

Table 3. The diffusion coefficient, cm^2/sec .

Polymer	M	$T^\circ\text{K}$	$D \frac{\text{cm}^2}{\text{sec}}$	Ref.
Natural rubber	1×10^4	220	4.5×10^{-17}	17 (Bresler)
Butylstyrene rubber	3×10^5 1×10^4	220 220	2.4×10^{-17} 5.0×10^{-15}	17 (Bresler)
Ethylene-propylene (1:1) rubber	2×10^5 1×10^4	220 220	4.2×10^{-17} 5.0×10^{-15}	18 (Skewis)

Table 4. The rate constants (l./mol. sec) of the reaction
 $R'_0 + RH \rightarrow R_0H + R'$

compound	radical	—CH(C ₆ H ₅)ĊH ₂	ROO'
C ₆ H ₅ CH ₂ —H		10 ⁻⁶	—
C ₆ H ₅ > CH—H		7 × 10 ⁻⁶	—
H ₃ C			
C ₆ H ₅ NH—H		10 ⁻⁶	10 ⁻⁶ to 10 ⁻⁵
C ₆ H ₅ S—H		≥ 10 ⁻⁴	≥ 10 ⁻⁴

The diffusion rates have been measured by direct methods in some elastomers, such as natural and butadiene–styrene rubbers, and ethylene–propylene copolymer. In Table 3 values of diffusion coefficients extrapolated to the temperature range of radical decay are shown. In all cases the D values are in the mentioned ranges. Consequently, in these elastomers as well as in polyisobutylene the diffusion rate proves to be quite sufficient for the elucidation of the laws of radical decay.

Evidently, in amorphous samples of many polymers at temperatures close to the glass temperature, the diffusion decay mechanism prevails and the measurement of macroradical kinetics may under these conditions be considered as a method of measuring diffusion coefficients. It has to be stated that chemical migration does not play any role here.

The reaction of hydrogen atom transfer

For many polymer radicals the possibility of hydrogen atom transfer at low temperatures starting with room temperature or less has now been established. The corresponding experimental results are summarized in Tables 4 and 5 respectively.

In Table 4¹⁹ the values of the rate constant of the reaction of end [$-\text{CH}(\text{C}_6\text{H}_5)-\dot{\text{C}}\text{H}_2$] and peroxy (ROO[•]) radicals of polystyrene with some aromatic compounds in frozen solutions at 100°K are shown. In all cases

Table 5. The reaction ROO[•] → R' in some polymers (the radicals have been produced by grinding)

Polymer	T°C	Time of reaction, sec
Polyethylene	273	~ 10 ⁴
Polypropylene	273	10 ⁴ to 10 ⁵
Polycaprolactam	250	10 ³ to 10 ⁴
Polyacrylonitrile	273	10 ⁴
Polystyrene	273	~ 5 × 10 ³
Polymethyl methacrylate	250–350	$K = 10^{6 \pm 1} \exp\left(-\frac{12000}{RT}\right) \left(\frac{\text{l.}}{\text{mol. sec.}}\right)$

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as well as in that of toluene, the reaction of hydrogen atom abstraction proceeds at a measurable rate.

Analogous reactions have also been found in solid polymers when the radical abstracts the hydrogen atom from the adjacent macromolecule (*Table 6*). In polyethylene, the transformation of end radicals into inner ones at 120°K has been mentioned¹³. The activation energy of this reaction is 4 kcal/mole and generally half that of the analogous reaction of low molecular radicals in the gas phase. In just the same way, the end radicals in polyformaldehyde and polypropylene change into inner ones. The interaction of the inner radicals with adjacent macromolecules has only been proved in polyethylene where, at room temperature, alkyl radicals are transformed into allyl radicals.

The reactions of peroxy radicals with macromolecules have been observed in many polymers (*Table 5*). Only in capron, end products of the reaction $ROO^{\bullet} \rightarrow R^{\bullet}$ are alkyl radicals with a free valence inside the chain²⁰. In polyethylene allyl radicals¹⁴ and in polymethyl methacrylate the end radicals²⁰ are formed. Evidently, in the latter case abstraction of the hydrogen atom is succeeded by further transformation of inner radicals including decomposition reactions.

Table 6. The reaction $\dot{R}_0 + HR \rightarrow RH + \dot{R}$ in polyolefins

Polymer	T°K	Time of reaction, sec
$\sim \dot{C}H_2 \rightarrow \sim \dot{C}H \sim$ (polyethylene)	120	10 to 100 ($E = 4$ kcal/mol) (Radtzig)
$\sim \dot{C}H(CH_3) \rightarrow \sim \dot{C}(CH_3) \sim$ (polypropylene)	140	10^2 to 10^3 (Radtzig)
$\sim \dot{C}H \sim \rightarrow \sim HC-CH=CH \sim$ (polyethylene)	297	1×10^5 (Waterman, Dole)

The reaction of hydrogen atom transfer (*Table 6*) is always accompanied by a marked decrease of the total concentration of radicals. The corresponding kinetic curves for the reaction $ROO^{\bullet} \rightarrow R^{\bullet}$ in polymethyl methacrylate are plotted in *Figure 9*²⁰.

From the viewpoint of the cage model the single hydrogen atom transfer appears to be a simple model of the elementary process of transition of the free valence from one cage to another. It is evident that the radicals occurring in one cage following such a transition, recombine. The fraction of radicals decaying in the single free valence transfer

$$\omega = (C_0 - C)/C_0 \quad (7)$$

should be dependent on both the cage dimensions and radical concentration. The ω values for some reactions of free valence transfer are shown in *Table 7*²⁰. These values are preliminary, because both the kinetics and mechanism of corresponding reactions have not been investigated completely.

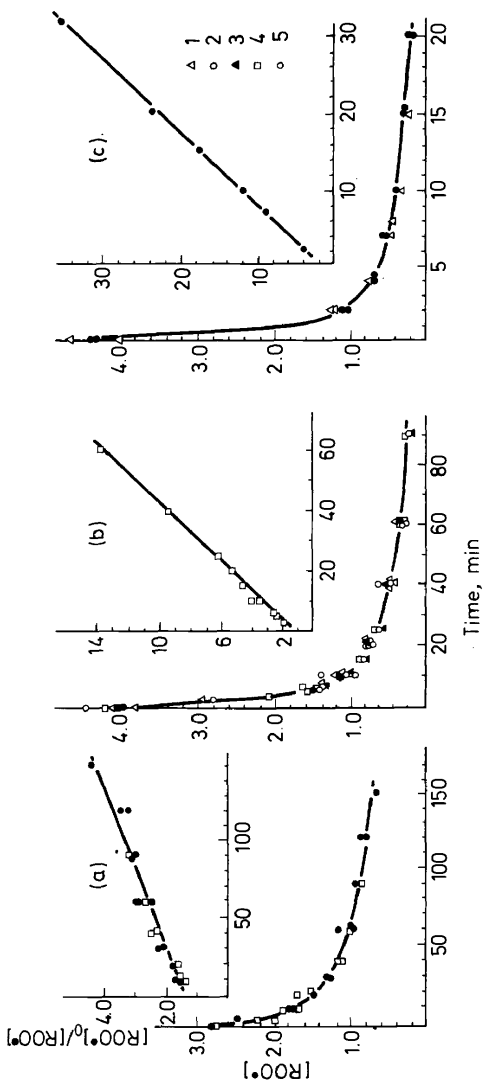


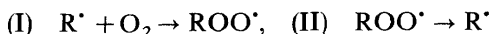
Figure 10. Decay of peroxy radicals in polymethyl methacrylate: (a)— 22°C ; (b)— 0°C ; (c)— 15°C . The oxygen pressure was: 10 torr—1; air—2; 3 atm—3; 4 atm—4 and 10 atm—5 [ref. 20].

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Table 7. The values of $\omega = (C_0 - C)/C_0$ (reaction $\text{ROO}^* \rightarrow \text{R}^*$)

Polymer	$T^\circ\text{C}$	ω
Polycaprolactam	-20	0.7
Polystyrene	0	0.4
Polyacrylonitrile	0	0.75
Polyethylene	0	0.96
Polymethyl methacrylate	-22	0.4 to 0.6

Thus, for the active end radicals as well as for peroxy radicals in a vacuum, the decay process terminates in just a single free-valence transfer into the adjacent cage, which is accompanied by the formation of radicals more stable at the given temperature and by partial recombination. For long-distance free valence displacement due to the mechanism of hydrogen atom transfer, the development of the chain reaction is to be admitted. This migration course has been postulated by several authors for polyethylene (see e.g. ref. 21), though it has strictly been proved only in the case of radical decay in the presence of oxygen. Quite an important characteristic of the chain process consisting in the alternation of reactions



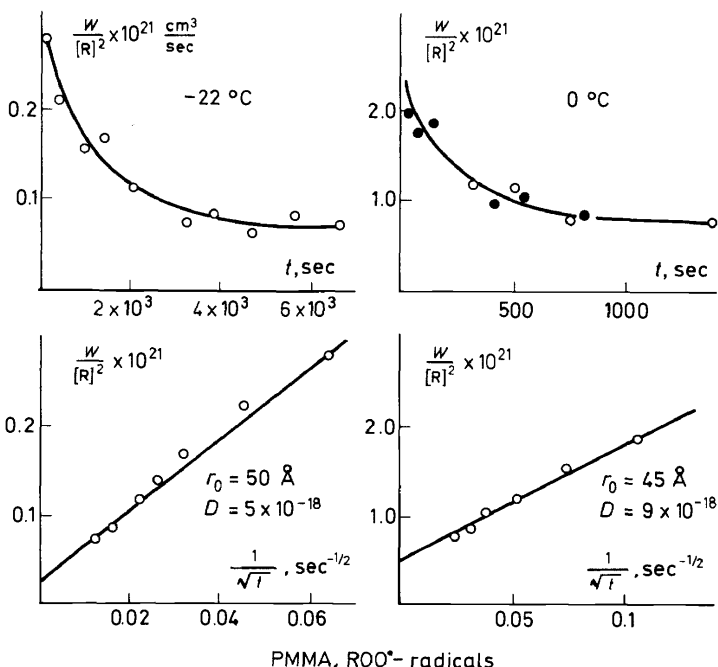
proves to be the chain length which may be determined by measurement of the oxygen consumption or of the fraction of recombining radicals in one step of the chain growth. Actually, should ω not change considerably in the course of the process, following the first cycle of the reactions I and II in polymer, the sequence $(1 - \omega)$ following to the second, $(1 - \omega)^2$, following to the third, $(1 - \omega)^3$ etc. of radicals is preserved. Consequently, the chain length equals

$$v = [\text{O}_2]/C_0 = (1 - \omega) + (1 - \omega)^2 + (1 - \omega)^3 + \dots = (1 - \omega)/\omega$$

The results of chain length measurement in peroxy radical decay in air are shown in Table 8. In all cases, the chain length is relatively small not exceeding a few units. This is in agreement with the notion requiring a comparatively large cage radius. The kinetic curves of peroxy radical decay in polymethyl methacrylate in air at 0° and -22°C respectively are shown in Figure 10²⁰.

Table 8. The length of chain during the decay of peroxy radicals

Polymer	Chain length	Ref.
Polyethylene	5 to 12	Lawton
Polypropylene	3 to 6	Fischer
Polyvinylchloride	3 to 7	Loy
Polymethyl methacrylate	1.5	



PMMA, ROO^\bullet radicals
 Figure 11. Calculation of data taken from Figure 10 according to Waite's equation.

By elaboration of these results in agreement with equations 1 and 2 (Figure 11) the values $r_0 \sim 40\text{--}50 \text{ \AA}$ and $D \sim 10^{-16}$ to $5 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$ have been obtained. Therefrom, at 0°C the value $\tau = r_0^2/\pi D$ or the time of free valence transition from one cage to another equals 650 s. When transition from one cage to another takes place due as a reaction to hydrogen atom transfer, the characteristic reaction time should be comparable with the value of τ .

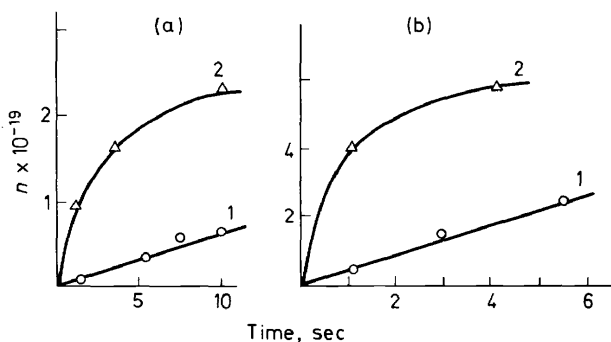


Figure 12. Formation of low molecular products in polyvinyl acetate (a) and polystyrene (b) according to ref. 20.

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In polymethyl methacrylate, as mentioned above, the rate constant of reaction $\text{ROO}^* \rightarrow \text{R}^*$ is ²⁰

$$K_{\text{ROO}^* \rightarrow \text{R}^*} = 10^{6 \pm 1} \exp [-(12000 \pm 1000)/RT] \text{ l. mole}^{-1} \text{ s}^{-1}$$

and the characteristic reaction time at 0°

$$\tau_{\text{ROO}^* \rightarrow \text{R}^*} \approx 1/K_{\text{ROO}^* \rightarrow \text{R}^*} [\text{RH}] \approx 10^{-7} \exp(12000/RT) \approx 10^{2.5} \text{ s}$$

(in the calculation the value $[\text{RH}] \approx 10 \text{ mole l}^{-1}$ has been assumed). The characteristic reaction time ($\tau_{\text{ROO}^* \rightarrow \text{R}^*}$) is of the same order of magnitude as the previously obtained time of free valence transition from one cage to another (650 s).

It should be stated that in calculating the decay rate irrespective of large cage radius, i.e. presuming every reaction step $\text{ROO}^* \rightarrow \text{R}^*$ to lead to free valence displacement only at 'inter-chain' distances (3 to 5 Å), the decay rate would appear to be less by a hundred times and the expected chain length more (and oxygen consumption) by ten to a hundredfold, which does not correspond with experimental data available.

The above reaction of peroxy radical decay in air is quite a good example of migration from one cage to another as well as of intensive inner motions within the cage itself. Thus, every reaction step leads to long-distance free valence displacement (up to 50 Å), the chain length being small. The nature of 'inner' motions leading to such a high value of an effective cage radius will be discussed below.

The fact of long-distance chemical migration in alkyl radicals in the absence of air has so far not been unambiguously proved because there does not appear to be any experimental idea confirming the $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$ radical transformation within the chain. There are some supporting grounds for assuming this^{14, 21, 22}.

- (1) The reaction rate of hydrogen atom transfer evaluated by extrapolation of the results referring to gas-phase reactions to room temperature is quite sufficient to account for the kinetic laws of alkyl radical decay in polyethylene;
- (2) The decay is accelerated in the atmosphere of hydrogen and methane being accompanied by H-D exchange;
- (3) The reaction of radical decomposition in polyethylene at room temperature does not take place.

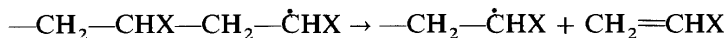
The major 'negative' ground lies in the fact that all the measurements of decay kinetics have been carried out with samples containing up to $2-3 \times 10^{19} \text{ cm}^{-3}$ 'weak' C—H bonds (around vinyl and other groups). The average distance between the mobile hydrogen atoms amounts altogether to $1/\sqrt[3]{(3 \times 10^{19})} \approx 30 \text{ Å}$, i.e. may be comparable with the cage radius. The quantitative transformation of alkyl radicals into allyl ones, i.e. abstraction of mobile hydrogen atoms, has been demonstrated sufficiently¹⁴.

Thus, the nature of free valence migration in polyethylene has so far not been established.

Reactions of radical decomposition

The strength of individual chemical bonds in radicals is markedly lower than in molecules and the decomposition appears to be quite a widespread group of radical reactions.

The activation energy of end radical decomposition according to the depolymerization scheme



equals the sum of the heat and the activation energies of polymerization. For the end radicals of polyethylene

$$E_a = 22.3 + 5.5 \approx 28 \text{ kcal mole}^{-1}$$

and for those of polymethyl methacrylate

$$E_a = 13.0 + 4.7 \approx 18 \text{ kcal mole}^{-1}$$

The end radicals in polymethyl methacrylate decay at a measurable rate at 50° to 60°C and higher. At these temperatures the rate constant of depolymerization is

$$K = 10^{12} \exp(-18000/RT) \approx 1 \text{ s}^{-1}$$

At a single depolymerization step the free valence displaces to one chain element (i.e. irrespective of inner motions) distant 3 to 4 Å. The diffusion coefficient $D = (1/6)l^2 (dn/dt) \approx 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ corresponds to the displacement rate of 3 Å/s, i.e. end radical decay may under these conditions be elucidated by free valence migration according to the depolymerization-polymerization mechanism. Actually, radical decay in polymethyl methacrylate is always accompanied by monomer release, whereas in a vacuum a few tens of molecules for each pair of radicals decayed may be found. The decomposition rate of inner radicals should not differ substantially from the depolymerization rate. Random heat motion of segments in amorphous samples may provoke the increase of the probability of decomposition reactions accompanied by the formation of low molecular compounds. The analysis of light low molecular products in the process of radical decay appears to be quite a simple and sensitive method of registration of the decomposition reaction.

In *Figure 12* kinetic curves of volatile product release in the decay of alkyl and peroxy radicals in both polystyrene and polyvinyl acetate in a vacuum are given. (In polyethylene and polypropylene the release of such volatile products is negligible.) In polyvinyl acetate the decay is accompanied by acetone release and in polystyrene, toluene, ethylbenzene and cumene are released in an amount comparable with the radical concentration.

Evidently, in the decomposition reaction either the monomer or the 'light' radical may split away from the macroradicals. In polystyrene either styrene or ethylbenzyl radicals are formed in this way. The diffusion of low molecular radicals appears to be a fairly efficient mechanism of free valence displacement.

The formation of low molecular products was observed in the process of peroxy radical decay when the reaction of hydrogen atom transfer ($\text{ROO}^\bullet \rightarrow \text{R}^\bullet$) is the primary step. To elucidate the results obtained the

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chemical mechanism of free valence migration may be supposed to be composed of a sequence of elementary steps. In the decay of peroxy radicals in polystyrene the following reactions may be expected:

- | | |
|---|--|
| (1) $r^{\cdot}, R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$ | free valence displacement at the bond distance with possible return along the axis |
| (2) $ROO^{\cdot} + \begin{array}{c} H \\ \\ -R- \end{array} \rightarrow ROOH + -R^{\cdot}-$ | valence transmission to the adjacent chain, i.e. displacement from one cage to another |
| (3) $-R^{\cdot}- \rightarrow R^{\cdot} + P-$ | shortening of the ends of a ruptured chain and high mobility of the end radicals |
| (4) $-R^{\cdot} \rightarrow -R^{\cdot} + m$ | displacement along the bond length and 'plasticization' of the cage by monomer |
| (5) $-R^{\cdot} \rightarrow -P + r^{\cdot}$ | } diffusion of low molecular radical |
| (6) $r^{\cdot} + -RH- \rightarrow rH + -R^{\cdot}-$ | |
| (7) Recombination of r^{\cdot}, R^{\cdot} and ROO^{\cdot} . | |

In the presence of oxygen or with sufficient activity of radicals r^{\cdot} and $-R^{\cdot}$ these cycles may repeat in a manifold way. Almost all of the processes presumed are accompanied by free valence displacement and the large kinetic cage radius alluded to above (*Figure 11*, $r_0 \sim 50 \text{ \AA}$) may be supposed to be bonded not only to inner segmental motion but also to the mobility depending on the reaction course 1 to 5.

At present, this scheme is a hypothetical one, the correlation of the constants of individual steps still not being established and the distances at which the free valence can be displaced not being known. On the other hand, the possibility of the participation of the reaction of hydrogen atom transfer as well as of radical decomposition in the processes of free valence migration may be considered established.

At the close of this short survey it must be pointed out that in polymer systems there are, actually, rare cases of free valence migration proceeding according to an arbitrary single definite mechanism. In the diffusion mechanism the inner motion in the cage may be more important than the cage-to-cage displacement. The segment mobility characteristic for the polymers is often associated with chemical mechanisms. 'Chemical' migration may be composed of a series of elementary steps, viz. following the reactions of free valence transfer the radical decomposes with release of low molecular compounds etc.

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