ON THE MECHANISM OF THE REACTION OF DEATH OF FREE RADICALS IN POLYMETHYL METHACRYLATE

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Abstract

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ON THE MECHANISM OF THE REACTION OF DEATH OF FREE RADICALS IN POLYMETHYL METHACRYLATE

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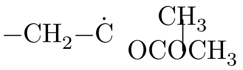
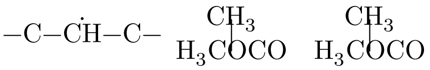
In polymethyl methacrylate (PMMA), under various actions—chemical, radiation, photochemical, mechanical—free radicals of the following structure have been found:



$-CH_2-\dot{C}\overset{CH_3}{\underset{OCOCH_3}{|}}$ $(\dot{R}_1)$,



$-C-\dot{C}H-C-\overset{CH_3}{\underset{H_3COCO}{|}}\ \overset{CH_3}{\underset{H_3COCO}{|}}$ $(\dot{R}_2)$,

$-C-OO^{\cdot}$ $(ROO^{\cdot})$

It may be assumed that radicals of the type

$$-C-CH_2(\dot{R}_3)$$

also arise upon chain scission, but they are unstable.

Table 1 collects values of the kinetic constants characterizing the reaction of death of radicals of different structure. The decrease in radical concentration is described by the equation for a second-order reaction. Radicals of type $\dot{R}_1$ are the most stable. Peroxide radicals $ROO^{\cdot}$ lose stability near room temperature. Radicals of type $\dot{R}_2$ can be observed only at temperatures below 0°.

Table 1

Values of the rate constant for death of free radicals in polymethyl methacrylate
(all measurements were performed by the EPR method; the accuracy of determining radical concentrations and the values of the rate constant does not exceed 30%)

Fig. 1

Figure 1: Fig. 1

Type of radicals	Method of initiation	Temp., °C	Rate constant, $cm^3 \cdot molecule^{-1} \cdot sec^{-1}$	Source
$-CH_2-\dot{C}$	Radiation	55	$k^{55^\circ} = 3 \cdot 10^{-22}$	(6)
$-CH_2-\dot{C}$	Same	25÷55	$k = 10^{-3} \exp\left(-\frac{28000}{RT}\right)$	(6)
$-CH_2-\dot{C}$	Mechanical actions	40÷100	$k = 10^{-7} \exp\left(-\frac{29000}{RT}\right)^{*}$	(7)
$-CH_2-\dot{C}$	Same	54	$k^{54^\circ} = 4 \cdot 10^{-21}$	Present work
$-C-OO^{\cdot}$	Radiation	20	$k^{20^\circ} = 6 \cdot 10^{-22}$	(6)
$-C-OO^{\cdot}$	Mechanical actions	5÷27	$k = 10^{-10} \exp\left(-\frac{16500}{RT}\right)^{**}$	(7)
$-C-OO^{\cdot}$	Same	0÷19	$k = 5 \cdot 10^{-9} \exp\left(-\frac{17000}{RT}\right)$	Present work
$-C-\dot{C}H-C-$	Mechanical actions	−36÷0	$k = 2 \exp\left(-\frac{26000}{RT}\right)$	Present work

* The value of the preexponential factor is apparently erroneous; the formula does not correspond to the experimental data of Fig. 2 (7).
** The formula was obtained by processing the experimental data of Fig. 3a (7).

Fig. 1 shows changes in the EPR spectra of radicals of type R_2 during prolonged storage of a PMMA sample in vacuum at −36°. The radicals were initiated by mechanical dispersion at −78° (for the procedure see (1)). The EPR spectra are superposed signals from 2 (radicals of type R_2, (2,3)) and 9 (5 + 4) components of the hyperfine structure (radicals of type R_1, (4,5)).

Fig. 1. EPR spectra of free radicals in polymethyl methacrylate after dispersion of the polymer in vacuum at −78° (a) and aging in sealed ampoules at −36° for 10 (b), 25 (c), and 72 (d) hours.

In the initial sample, radicals of type R_2 predominate (spectrum 1*a* is an almost

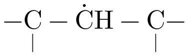
Fig. 2

Figure 2: Fig. 2

pure doublet), their concentration $[R_2^\bullet] = 7 \pm 2 \cdot 10^{18}$ g^{-1}. Over three days, the greater part of the $R_2^\bullet$ radicals perished, while the smaller part was converted into $R_1^\bullet$ radicals. The same measurements were performed at −18, −10, and 0°. From the changes in the EPR spectra, curves for the decrease in the concentration of $R_2^\bullet$ radicals were calculated. In Fig. 2a the experimental data are shown in the coordinates $[R_0]/[R]$, αt (termination—a second-order reaction). In the graph, the results of individual experiments are superposed on one another by changing the scale along the abscissa axis. The scale factor α shows how many times the rate of radical termination increased when the temperature was raised from −36° ($\alpha = 1$) to −18° ($\alpha = 40$), −10° ($\alpha = 110$), and 0° ($\alpha = 1100$). The dependence of the rate constant on temperature is shown in Fig. 2b. The effective value of the activation energy is 26 000 cal · mol^{-1} (see Table 1).

In parallel experiments with similarly prepared polymer samples, the yield of low-molecular products formed in polymethyl methacrylate containing free radicals was measured. The low-molecular products were collected in a vacuum apparatus by freezing them into a trap cooled to −196°. Mass-spectrometric analysis showed that the low-molecular fraction consists mainly of the monomer —methyl methacrylate.

Fig. 2. Kinetics of termination of radicals of the type



$$-\underset{|}{C}-\dot{C}H-\underset{|}{C}-$$

in PMMA. a—decrease in radical concentration at −36° (1), −18° (2), −10° (3), and 0° (4) in vacuum; b—dependence of the rate constant on temperature (according to the Arrhenius equation).

Figure 3 shows curves for the yield of the low-molecular fraction for PMMA samples containing radicals $R_1^\bullet$, $R_2^\bullet$, and $ROO^\bullet$. At 20°, the rate of monomer evolution on the linear portion is $0.6 \cdot 10^{15}$ molecules · cm^{-3} · s^{-1}, which is tens of times greater than the rate of termination of $R_1^\bullet$ radicals under these conditions. At −36°, the monomer yield is approximately 10 ± 3 molecules for each pair of terminated radicals of type $R_2^\bullet$. Termination of peroxide radicals $ROO^\bullet$ at −22° is accompanied by evolution of low-molecular products with a yield exceeding the concentration of radicals severalfold.

The formation of low-molecular products in a polymer containing free radicals indicates the possibility of radical decomposition at low temperatures.

The most probable path for the decomposition of terminal radicals of the type $R_1^{\cdot}$ is the elimination of a monomer unit; in this case a single bond is broken and a double bond is formed. The activation energy of decomposition is equal to the

Fig. 3

Figure 3: Fig. 3

sum of the activation energies for the reaction of addition of a monomer molecule to a radical and the heat of polymerization. For PMMA $E_d = 18\,500 \pm 1000$ cal $\cdot$ mole^{-1}. The depolymerization rate constant was determined at 167°: $k_d^{167^\circ} = 5.8 \cdot 10^2$ sec^{-1} (8). Hence, using the Arrhenius equation, one can estimate the value of k_d at 20°: $k_d^{20^\circ} \approx 10^{-3}$ sec^{-1}; at a radical concentration $[R_1^{\cdot}] \approx 10^{18}$ g^{-1}, one may expect that at +20° the depolymerization rate will be about 10^{15} molecules $\cdot$ cm^{-3} $\cdot$ sec^{-1}. The experimental value of this quantity (Fig. 3a) is close to the calculated one.

Fig. 3. Formation of low-molecular-weight products in PMMA containing free radicals of various structures: **a** –radicals of type $R_1^{\cdot}$, $[R_1^{\cdot}] = 10^{18}$, g^{-1}, $t = 20°$; **b** –radicals of type $R_2^{\cdot}$, $[R^{\cdot}] = 7 \pm 2 \cdot 10^{18}$ g^{-1}, $t = -36°$; **c** –radicals of type $R_1^{\cdot}$ (curve 1) and $ROO^{\cdot}$ (curve 2), $[R^{\cdot}] = 10^{18}$, $t = -22°$.

It may be assumed that decomposition of radicals of type $R_2^{\cdot}$, with the free valence in the middle of the chain, proceeds as follows:

$$-\mathrm{C} - \dot{\mathrm{C}}\mathrm{H} - \mathrm{C}- \rightarrow -\mathrm{C} - \mathrm{CH_2} + \mathrm{C} = \mathrm{CH} - \mathrm{C}-;$$

here, too, a double bond and a terminal radical are formed. The radical $R_3^{\cdot}$ is unstable and either abstracts a hydrogen atom from a neighboring molecule (most likely from the methylene group), or eliminates a monomer molecule; depolymerization may continue until it encounters a neighboring radical or until a monomer molecule is added, when the radical $R_3^{\cdot}$ is converted into the more stable radical $R_1^{\cdot}$. With depolymerization proceeding to the end of the macromolecule, low-molecular-weight radicals capable of diffusing through the polymer may be formed.

During depolymerization the free valence moves at a rate of k_d units per second. The probability that a mobile radical will encounter an immobile one when displaced by 1 unit is equal to $[R_2^{\cdot}]M/6 \cdot 10^{23}$ (M is the molecular weight of the unit). For all mobile radicals the rate of combination is:

$$-\frac{d[R^{\cdot}]}{d\tau} = \frac{k_d M}{6 \cdot 10^{23}}[R_3^{\cdot}][R_2^{\cdot}], \quad \text{i.e.} \quad k_c = \frac{k_d M}{6 \cdot 10^{23}} \frac{\mathrm{cm}^2}{\text{molecule} \cdot \text{sec}}.$$

The elementary reactions caused by decomposition of radicals of type $R_2^{\cdot}$ can be represented by the following scheme:

1. Decomposition of radical $R_2^{\cdot}$

2. Stabilization of radical $R_3^{\cdot}$ by abstraction of an H atom from a neighboring molecule
3. Depolymerization
4. Addition of monomer or depolymerization to the end of the macromolecule
5. Combination of radicals

$$\left. R_2^{\cdot} \underset{k_2}{\overset{k_1}{\rightleftarrows}} R_3^{\cdot} + P^{\cdot} \quad \right\}$$

$$R_3^{\cdot} \xleftarrow{k_d} R_3^{\cdot} + M$$

$$R_3^{\cdot} \xrightarrow[(+M)]{k_4} R_1^{\cdot}$$

$$R_2^{\cdot} + R_3^{\cdot} \rightarrow P$$

Hence, at $[R_3^{\cdot}] = \text{const}$, $k_2 > k_4$ and $(k_2 + k_4) > k_c(R_2^{\cdot})$, we obtain:

$$-\frac{d[R_2^{\cdot}]}{dt} = \frac{2k_1 k_c}{k_2}[R_2^{\cdot}]^2 \quad \text{and} \quad K_{\text{eff}} = \frac{M k_1 k_d}{3 \cdot 10^{23} k_2} \frac{\text{cm}^3}{\text{molecule} \cdot \text{sec}}.$$

From experiment, $k_{\text{eff}}^{-36^\circ} = 6 \cdot 10^{-24}$ cm$^3 \cdot$ molecule$^{-1} \cdot$ sec^{-1}; if one assumes that $k_1 : k_2 = 1 : 10$, then for radicals $R_3^{\cdot}$, $k_d \approx 10^{-1}$ sec^{-1}. The activation energy of termination is $E_{\text{eff}} = E_1 + E_d - E_2 = 26$ kcal $\cdot$ mol^{-1}. By analogy with liquid-phase reactions, one may suppose that $E_2 = 5 \div 10$ kcal, and $E_d = 18$ kcal$\cdot$mol^{-1}. Then the activation energy for decomposition of radicals $R_2^{\cdot}$ is $13 \div 18$ kcal$\cdot$mol^{-1}. This value is close to the activation energy of the depolymerization reaction.

The reaction scheme (1-5) explains the qualitative regularities of the termination reaction of radicals $R_2^{\cdot}$. Radical decomposition and migration of the free valence by the depolymerization—polymerization mechanism apparently do indeed occur; as yet there is only no proof that this mechanism is the only one.

The depolymerization reaction of radicals is probably associated with the formation of monomer during the mechanical degradation of polymethyl methacrylate and of some other polymers, which was discovered several years ago in works ([9,10]).

The formation of low-molecular products during termination of peroxide radicals can likewise be explained by decomposition and depolymerization of alkyl radicals. The primary act of the termination process is the reaction

$$\mathrm{ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}}$$

or the decomposition of a peroxide radical. The resulting radical $R_2^{\cdot}$ then initiates a chain of reactions of type 1-5. In an inert atmosphere the process ends with the formation of the long-lived radical $R_3^{\cdot}$ (reaction 4), while in the presence of oxygen it continues according to the scheme:

$$\begin{array}{llll} \text{A.} & \mathrm{ROO^{\cdot} \rightarrow R^{\cdot}.} & \text{B.} & \mathrm{R^{\cdot} \rightarrow R^{\cdot} + M.} \\ . & \mathrm{R^{\cdot} + O_2 \rightarrow ROO^{\cdot}.} & . & \mathrm{R^{\cdot} + ROO^{\cdot} \rightarrow P.} \end{array}$$

At a high oxygen concentration and $[R^{\cdot}] = \text{const}$,

$$-\frac{d[\mathrm{ROO^{\cdot}}]}{dt} = \frac{2Mk_A k_C}{6 \cdot 10^{23} k\,[O_2]}[\mathrm{ROO^{\cdot}}]^2,$$

whereas in an inert atmosphere (deficiency of O_2),

$$-\frac{d[\mathrm{ROO^{\cdot}}]}{dt} = 2k_A[\mathrm{ROO^{\cdot}}].$$

The main feature of the process is that the migration of the free valence, leading to termination of active centers, takes place without the participation of oxygen, by a mechanism specific to the termination of alkyl radicals; therefore the oxygen consumption and the yield of oxidation products per pair of terminated radicals are 10–100 times smaller than in a purely oxidative migration mechanism (alternation of reactions A– (7)).

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