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Electron Spin Resonance Spectra, Conformation, and Chemical Properties of Free Radicals in Solid Polymers

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The structure and the chemical properties of polymeric radicals having their free valency on a carbon atom in the main chain are surveyed. Most of the information on radicals in solid polymers has been obtained by electron spin resonance. The first part of the review gives a detailed analysis of the hyperfine structure of the e.s.r. spectra, which is closely related to the structure and the conformation of the radicals. The second part deals with the chemical behaviour of polymeric radicals in solid matrices at low temperatures (80-300°K). All the data relate to radicals from polymers of the vinyl series, polyoxides, and polyamides. A list of 112 references is given.

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I. INTRODUCTION

In the vinyl series of polymers, radicals having their free valency on carbon atoms of the main chain can have the structures

$$\underset{\text{(I)}}{-CXY-\dot{C}H_2} \quad \underset{\text{(II)}}{-CH_2-\dot{C}XY} \quad \underset{\text{(III)}}{-CH_2-\dot{C}X-CH_2-} \quad \underset{\text{(IV)}}{-CXY-\dot{C}H-CXY-}$$

where X = H, CH_3, C_6H_5, OH, $COOCH_3$, $OCOCH_3$, CN, etc. and Y = H, CH_3, etc. The radicals (I)-(IV) are formed in polymers by the action of ionising radiation, ultraviolet irradiation, exposure to a laser beam, mechanically, thermally, chemically, and also during polymerisation of the monomers.

Action of Ionising Radiation

The action of X-rays, γ-rays, fast electrons, ultraviolet radiation, etc. on a polymer chain most often detaches a light atom (hydrogen) or a group of atoms, with the formation of radicals (III) or (IV). These have been detected and examined by e.s.r. in polyethylene[1,2], polyamides[3,4], polyisobutylene[5,6], poly(vinyl alcohol)[7], and other polymers. In individual cases, e.g. in the γ-irradiation[8,9] and the photolysis[10] of polyacrylate polymers, radicals of type (II) are observed.

Mechanical Treatments

Bonds in the main chain of various heterochain and carbon-chain polymers are ruptured by cutting[11-13], grinding[14-16], stretching fibres[17,18], and other types of destruction and deformation of specimens. Radicals (I) and (II) are the primary degradation products. In polyethylene[19,20], polypropylene[19], poly(vinyl alcohol)[21], polystyrene[22], and other polymers both terminal radicals have been recorded during the mechanical degradation of macromolecules distributed in a matrix of an inert substance (method of dispersion of frozen dilute solutions of polymers[21,23]). In polyethylene[19], poly(methyl methacrylate)[13], polyamides[20], polyformaldehyde[21], and several other polymers the active primary radicals are converted by secondary reactions into radicals having the free valency in the middle of the chain.

Polymerisation of Monomers

Terminal radicals of only one type, $-CH_2-\dot{C}XY$ (or $-CH_2-\dot{C}HX$), are observed in all cases in the polymerisation of monomers. In the liquid phase the steady-state concentration is usually low (10^{-9} M), and the radicals have been detected only by the initiation of polymerisation by means of redox systems directly in the resonator of a highly sensitive e.s.r. spectrometer[24-27]. Well resolved e.s.r. spectra of a large number of radicals have been obtained by this method. It is considerably easier to observe radicals at the gelatinisation stage[28], in the polymerisation of monomers which undergo cross-linking[29,30], during heterogeneous polymerisation, when the polymer is precipitated[31,32], and also in solid-phase polymerisation initiated by γ-rays or ultraviolet irradiation of the monomers[31,33-36].

Action of Atomic Hydrogen

The action of atomic hydrogen and other simple radicals on macromolecules provides a convenient chemical method for initiating polymer radicals. The hydrogen atoms are obtained by passing hydrogen over an incandescent tungsten filament[37], in a high-frequency discharge[38,39], by the photolysis of redox systems [e.g. frozen aqueous solutions of iron(II) sulphate plus sulphuric acid[40]], among other methods. The interaction of hydrogen atoms with molecules yields radicals either by addition (to the benzene ring in polystyrene[41], and to pyrimidine and purine bases in deoxyribonucleic acids[42]) or by detachment ($H + RH \rightarrow \rightarrow H_2 + R^{\cdot}$) at the site of a weak carbon–hydrogen bond.

Thus the structure of the primary radicals is determined by the type of action on the polymer: mechanical cleavage of macromolecules yields two terminal radicals; reactions with hydrogen atoms should produce radicals having the free valency in the middle of the chain or on lateral groups; polymerisation should involve the formation of $-CH_2-\dot{C}XY$ radicals; etc. Radiolysis, ultraviolet irradiation, and mechanical working are usually accompanied by secondary free-radical reactions, and the structure of the final radicals, which are stable under the given conditions, will depend in considerable measure on the nature, state, and properties of the polymer. Secondary

reactions can be inhibited by lowering the temperature, using inert matrices, or other methods.

In many cases the generation of radicals is accompanied by changes in the structure and the properties of the polymer chain: new functional groups appear, the molecular weight diminishes, cross-links are formed between molecules, the secondary structure of the polymer changes, etc. These changes must be taken into account in analysing the properties of the radicals and the kinetics of the secondary free-radical reactions.

II. ELECTRON SPIN RESONANCE SPECTRA AND CONFORMATION OF POLYMERIC RADICALS

The chief characteristic of the e.s.r. spectra of polymer radicals is their hyperfine structure. The number and position of the lines constituting this structure depend on the location of the free valency in the macromolecule and the conformation of the radical, the angle of rotation about the $C(\alpha)-C(\beta)$ bond. The hyperfine structure of the spectra of alkylated radicals results from interaction of the unpaired electron with the magnetic nuclei of the α- and β-hydrogen atoms:

$$\rangle C_{(\beta)}H-\dot{C}_{(\alpha)}H-\dot{C}_{(\beta)}H\ .$$

The hyperfine interaction with α-protons comprises two parts—isotropic and anisotropic—the latter depending on the orientation of the $C(\alpha)-H$ bond in the magnetic field[43]. The position of a line in the e.s.r. spectra of polycrystalline and amorphous specimens is determined solely by the isotropic portion of the hyperfine interaction, while the anisotropic part merely broadens the line[44]. With oriented specimens the anisotropy of the hyperfine interaction leads to a considerable shift in individual components of the spectrum[2,45]. Hyperfine interaction with β-protons is mainly isotropic.

It is as yet impossible to calculate theoretically the hyperfine interaction in complicated radicals, and analysis of the spectra is based on semi-empirical relations established[24,26,46-50] from the study of dozens of spectra. Quantitative estimates of the isotropic hyperfine interaction constants are founded on measurements of the e.s.r. spectra of radicals of low molecular weight in the liquid phase, where the hyperfine structure is well resolved and the positions of the lines are fixed with great accuracy.

1. Semi-empirical Rules for the Analysis of Electron Spin Resonance Spectra

The width of an e.s.r. spectrum—the distance between the extreme lines of the hyperfine structure—is given by the sum of the values for the splitting on all the α- and β-protons:

$$\Sigma a_H = \Sigma a_H(\alpha) + \sum_i a_H(\beta_i)\ . \qquad (1)$$

According to McConnell[47] the spectroscopic splitting constant $a_H(\alpha)$ for each α-proton is given by

$$a_H(\alpha) = Q_\alpha \cdot \rho \qquad (2)$$

where ρ is the spin density of the unpaired electron on the α-carbon atom, and Q_α a coefficient of proportionality, whose value depends on the nature of the bonds and the type of substituents.

In substituted alkyl radicals the density of the unpaired electron on the α-carbon atom is determined by the nature of the substituents[46,49]. In radicals of the type

$$X-\dot{C}(Z)-Y$$

the value of ρ can be calculated by means of the formula

$$\rho = (1-\Delta X)(1-\Delta Y)(1-\Delta Z)\ . \qquad (3)$$

The quantity ΔX indicates the fraction of the spin density which the substituent X attracts to itself, it being assumed that each substituent behaves independently of the others. Table 1 gives the values of ΔX for various functional groups, all calculated from experimental data[46,49]. For the methyl groups theoretical calculations have also been made[51]. For the hydrogen atom $\Delta H = 0$, and the decrease in spin density for alkyl substituents and groups of the types CH_2R and COOR does not exceed 10%. The "strongest" substituents are the carbonyl, ether, and hydroxyl groups, where the diminution in density reaches 15–18%.

Table 1. Values of the parameter $\Delta(X)$ for various substituents in alkyl radicals[46,49].

X	Δ(X)	X	Δ(X)
—H	0.000	—COOR	0.072
$-CH_3$	0.081	—OCHO	0.136
$-C_2H_5$	0.082	$-OCH_2CH_3$	0.180
$-CH_2CH_2OH$	0.092	—OH	0.160
$-CH_2OH$	0.079	—CN	0.148
$-CH_2COOR$	0.080	$-C_6H_5$	0.290*
$-CH_2NH_2$	0.034	$-[CH_2-C(CH_3)(COOH)]_n$	0.101
—CH(OH)COOH	0.041	$-[CH_2-CH(COOH)]_n$	0.050
$-C(C_2H_5)_3$	0.044		

*For the radicals $C_6H_5\dot{C}(CH_3)_2$ of isopropylbenzene $a_H(CH_3) = 17.5$ oersteds. Hence according to Eqns. (3) and (11) $\rho = 17.5/29.3 \simeq 0.6$ and $\Delta(C_6H_5) \simeq 0.290$.

Table 2 gives values of the parameter Q_α for α-protons in alkyl and alkylated radicals. When the substituent X is bound to the α-carbon atom by a C–C bond (CH_2R, COOH, etc.), the values usually fluctuate within the limits $Q_\alpha = 24.1 \pm 0.7$ oersteds. The alkyl radicals $R_1\dot{C}HR_2$ (where $R = CH_3$, C_2H_5, etc.) form an exception, Q_α being rather larger. For radicals in which the substituent is bound to the α-carbon atom by a C–O bond, the parameter Q_α is almost 5 oersteds smaller: $Q_\alpha = 19.4 \pm 1.0$ oersteds.

The hyperfine structure constant for β-protons depends on the conformation of the radical[48]—the angle of rotation about the $C(\alpha)-C(\beta)$ bond:

$$a_H(\beta) = Q_\beta \cdot \rho \cdot \cos^2\theta, \qquad (4)$$

where Q_β is a constant whose value for alkylated radicals is 58.6 oersteds[24,26], and θ is the angle between the axis of the $2P_Z$-orbital of the unpaired electron and the projection of the $C(\beta)-H$ bond on a plane perpendicular to the $C(\alpha)-C(\beta)$ bond (Fig. 1).

The relation (4) is valid provided the amplitude of oscillations of the $C(\alpha)-C(\beta)$ bond about the equilibrium position θ_0 is small. With large amplitudes (tens of degrees) we must replace $\cos^2\theta$ in Eqn. (4) by the value

$\langle\cos^2\theta\rangle$,[57] averaged over the internal motions in the radical (vibrations or rotation). The averaged value is connected with the equilibrium value by the formula

$$\langle\cos^2\theta\rangle = A + B\cos^2\theta_0 \qquad (5)$$

where A and B depend on the temperature and the form of the potential curve for the internal motions in the radical. As $T \to 0$, we have $A \to 0$ and $B \to 1$.

Table 2. Value of the parameter $Q(\alpha)$ for X–$\dot{C}$H–Y radicals (calculated from data of Refs. 24, 26, 46, 52–55).

X	Y: –H	Y: –CH_3, –CH_2CH_3	Y: –CH_2NH_2, –CH_2OH
–H	23.0	24.2±0.2	—
–CH_3	—	26.1±0.1	—
–CHR_1R_2 (R=H, CH_3OH, COOH, NH_2)	—	24.9±0.1	—
–COOR (R=H, CH_3, C_2H_5)	23.5	23.7±0.2	23.9±0.3
–COR (R=CH_3, C_2H_5)	24.2	23.6(?)	24.6
–CN	25.4(?)	25.4	25.3±0.3
–OH	20.9±0.4	20.4±0.4	22.3
–OR (R=C_2H_5, CHO)	—	18.1±0.6	—
–C_6H_5	23.2*	—	—

*Value obtained from $a_H(\alpha)$ = 16.4 oersteds for the benzyl radical[56].

In polymer radicals in the solid phase at low temperatures, movements in the radicals are usually strongly retarded, and Eqn. (4) can perfectly well be used for analysing the hyperfine structure of the e.s.r. spectra. Equation (5) must be employed to investigate the temperature dependence of the splitting on the β-protons.

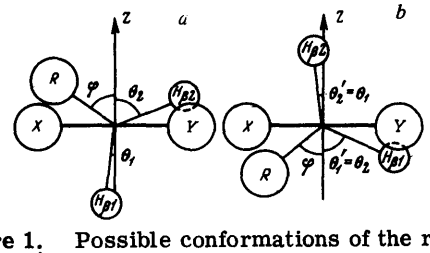


Figure 1. Possible conformations of the radical R–CH_2–$\dot{C}$XY.

The influence of the conformation of the radicals on the form of the e.s.r. spectra is best seen from the example of radicals have a β-methylene group

$$\mathrm{R{-}CH_2{-}\dot{C}{-}X}$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad\quad \mathrm{Y}$$

In Fig. 1 the carbon atom C is located in the plane of the paper, the thick lines indicate the projections of the $C_{(\alpha)}$–X and $C_{(\alpha)}$–Y bonds, while the ordinary lines represent $C_{(\beta)}$–H and $C_{(\beta)}$–R bonds. The Z-axis is the axis of the orbital of the unpaired electron. The angle φ, where (see Fig. 1)

$$\theta_1 = \frac{\pi}{3} + \varphi, \quad \theta_2 = \frac{\pi}{3} - \varphi, \qquad (6)$$

characterises the conformation of the radical.

The two equilibrium positions (a) and (b) are energetically equivalent. The lifetime of the radical in each of these positions is

$$\tau = \tau_0 \exp\left(\frac{E}{RT}\right) \qquad (7)$$

where τ_0 is the period of the oscillations and E the height of the potential barrier which must be overcome for transition from one conformation to the other. The number of components of the hyperfine structure in the e.s.r. spectrum depends on the relation between the frequency of the conformational transitions and the quantity $\nu_a - \nu_b$,[58] in which ν_a and ν_b are the frequencies of hyperfine interaction for β-protons in conformations (a) and (b). This difference $\nu_a - \nu_b$ is usually close to 10^7–10^8 s^{-1}. Three cases are possible.

With a high barrier at low temperatures, $\tau \gg (\nu_a - \nu_b)^{-1}$, and the e.s.r. spectrum consists of the sum of the signals corresponding to conformations (a) and (b) (the β-protons are non-equivalent). Then

$$a_H(\beta\text{-}1) = Q_\beta \cdot \rho\cos^2\left(\frac{\pi}{3} + \varphi\right) \text{ and } a_H(\beta\text{-}2) = Q_\beta \cdot \rho\cos^2\left(\frac{\pi}{3} - \varphi\right). \qquad (8)$$

The constants $a_H(\beta\text{-}1)$ and $a_H(\beta\text{-}2)$ are interrelated. In Fig. 2 the ordinates represent $f_1 = \cos^2(\frac{1}{3}\pi + \varphi)$ and $f_2 = \cos^2(\frac{1}{3}\pi - \varphi)$, while the abscissae are the conformational angles φ. When $\varphi = 0$ and 90° the splitting is the same on the two β-protons. Over the range $20° < \varphi < 40°$ the splitting on one of the β-protons is small, and is hardly observable in poorly resolved e.s.r. spectra of polymer radicals.

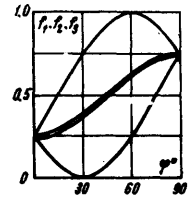


Figure 2. Graphs of the functions

$$f_1 = \cos^2\left(\frac{\pi}{3} + \varphi\right),$$
$$f_2 = \cos^2\left(\frac{\pi}{3} - \varphi\right)$$

and

$$f_3 = \tfrac{1}{2}\left[\cos^2\left(\frac{\pi}{3} + \varphi\right) + \cos^2\left(\frac{\pi}{3} - \varphi\right)\right]$$

(double line).

Rapid alternation of conformations results in an averaging of the hyperfine interaction constants, and when $\nu \ll (\nu_a - \nu_b)^{-1}$ the β-protons are equivalent:

$$a_H(\beta\text{-}1) = a_H(\beta\text{-}2) = \tfrac{1}{2}Q_\beta \cdot \rho\left[\cos^2\left(\frac{\pi}{3} + \varphi\right) + \cos^2\left(\frac{\pi}{3} - \varphi\right)\right]. \qquad (9)$$

The dependence of $f_3 = \frac{1}{2}[\cos^2(\frac{1}{3}\pi + \varphi) + \cos^2(\frac{1}{3}\pi - \varphi)]$ on φ for this case is shown by the double line in Fig. 2. The splitting is a maximum at $\varphi = 90°$.

In the intermediate case, when the frequency of interchange is comparable with the frequency of conformational transitions, i.e. $\tau \simeq (\nu_a - \nu_b)^{-1}$, exchange broadening of the central lines of the spectrum will be observed. This comparatively rare case has been examined in detail[24,46].

From Eqns. (8) and (9) it is seen that the total splitting on the β-protons is independent of the frequency of the transitions, being determined solely by the conformation of the radical. We always have

$$a_H(\beta\text{-}1) + a_H(\beta\text{-}2) = Q_\beta \cdot \rho \left[\cos^2\left(\frac{\pi}{3} + \varphi\right) + \cos^2\left(\frac{\pi}{3} - \varphi\right)\right] . \quad (10)$$

Calculation of the hyperfine interaction constants is considerably simplified for the radicals

$$CH_3-\dot{C}(Y)-X$$

containing a β-methyl group, since even at low temperatures the methyl groups rotate about the $C_{(\alpha)}-C_{(\beta)}$ bond at a frequency exceeding that of the hyperfine interaction (free rotation[46,59]), and all three β-protons are equivalent. With free rotation

$$\cos^2\theta = {}^1/_2\pi \int_0^{2\pi} \cos^2\theta d\theta = {}^1/_2 \text{ and } a_H(CH_3) = {}^1/_2 Q_\beta \rho = 29.3\rho . \quad (11)$$

Thus, in the analysis of the e.s.r. spectra of alkylated radicals, the hyperfine structure constants for α-protons and the protons of β-methyl groups can be estimated to ~ 5% from Eqns. (2), (3), and (11) and Tables 1 and 2. With $a_H(\alpha)$ and $a_H(CH_3)$ known, the total width of the spectrum depends solely on the splitting on the β-protons, of CH_2R or CHR_1R_2 groups, i.e. on the angle of rotation about the $C(\alpha)-C(\beta)$ bond. Consequently the conformation of the radical can be determined when the total width of the spectrum is known; and conversely, if the conformation is known, the position of all the lines in the spectrum can be predicted.

Actual examples of the analysis of e.s.r. spectra of polymer radicals belonging to various types will be examined in the following section.

2. Electron Spin Resonance Spectra of the Main Types of Polymer Radicals

Data on the e.s.r. spectra at 77°K of polymer radicals having the free valency at the ends and in the middle of the chain are assembled in Figs. 3–5. In most cases we have determined the values of ρ, Q, a_H, and φ from an analysis of the e.s.r. spectra published by various authors; the hyperfine structures were analysed according to the rules formulated in the preceding Section. Individual spectra and the corresponding schemes of energy levels are shown in Figs. 3 and 4. In most cases there is no doubt about the reliability of the interpretation of the spectra, which either is proved by direct methods (investigation of oriented specimens[2,4,60], deuteriated radicals[3,61], etc.) or is supported by many indirect data, from the method of preparing the radicals to analysis of the expected conformation.

In compiling the tables the hyperfine structure constants for α-protons $a_H(\alpha)$ and the protons of methyl groups $a_H(CH_3)$ were calculated by means of Eqns. (2) and (11). Values of ρ were estimated by means of Eqn. (3) with the data in Table 1 taken into account; the electron density drawn off by the polymer chain was taken to be 0.08. The constant Q_α was determined from Table 2. The splitting on β-protons of CHX and CH_2 groups was found as the difference between the total width of the spectrum† and the value of the expression $\Sigma a_H(\alpha) + \Sigma a_H(CH_3)$. The ratios between $a_H(\beta\text{-}1)$ and $a_H(\beta\text{-}2)$ and the conformational angle φ were determined from the graph in Fig. 2.

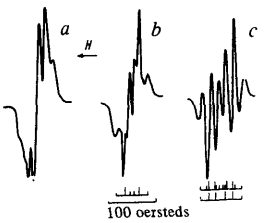


Figure 3. Electron spin resonance spectra of terminal radicals (at 80°K) in: *a*, *b*) poly(vinyl alcohol); *c*) polyethylene.

(a) R–$\dot{C}H_2$ radicals

Terminal CXY–$\dot{C}H_2$ radicals are distinguished by high chemical activity in reactions involving transfer of the free valency (see Section III, 1), so that it is very difficult to isolate and investigate them. Radicals of type (I) have been fixed by the low-temperature mechanical degradation of polymers (linear polyethylene[19,20], polycaprolactam[20]), by the dispersion of frozen dilute solutions of poly(vinyl alcohol)[21], polystyrene[22], and certain other polymers, and by the radiolysis of polyformaldehyde[60].

Radicals CXY–$\dot{C}H_2$ are formed together with radicals of other types (II) and (III), and the e.s.r. spectra are usually the result of the superposition of two or three signals. As a rule, however, lines belonging to radicals of type (I) are less easily saturated than are the remaining signals. This facilitates the isolation and interpretation of the spectra of CXY–$\dot{C}H_2$ radicals (Table 3). However, the accuracy with which the hyperfine interaction constants are determined remains low (1–3 oersteds).

Fig. 3 shows as example the spectra (*a*) and (*b*) of free radicals formed at the site of cleavage of the polymer chain of poly(vinyl alcohol) (1% frozen solution in D_2O after dispersion in a vacuum at 90°K). The spectrum 3*a* corresponds to a low microwave power and 3*b* to a high microwave power (~ 0.5 and ~ 50 mV respectively). With a low power the lines of the $CH(OH)\dot{C}H_2$ and $CH_2\dot{C}H(OH)$ signals make roughly the same contribution to the overall spectrum, whereas at high microwave powers the signal due to the latter radicals is saturated, and the symmetrical spectrum of CH(OH)–$\dot{C}H_2$ radicals predominates (Fig. 3*b*). The width of the latter is 80 oersteds, and the splitting on each α-proton is $a_H(\alpha) = Q_\alpha\rho = 24.4 \times 1 \times 1 \times (1 - 0.08) = 22$ oersteds. Hence $a_H(\beta) = 80 - 2 \times 22 = 36$ oersteds. The set of levels of the hyperfine structure is shown below the spectrum.

† The total width of the spectrum was determined with the finite width of individual components allowed for[62].

The e.s.r. spectrum of the terminal radicals $CH_2-\dot{C}H_2$ is obtained by the mechanical disintegration of linear polyethylene in an inert atmosphere at 80°K.[19,20] The total width of the spectrum[20] is 115 oersteds, while $a_H(\alpha) = 22$ oersteds, and the splitting on the β-protons is $a_H(\beta\text{-}1) + a_H(\beta\text{-}2) = \Sigma a_H - 2a_H(\alpha) = 115 - 2 \times 22 = 71$ oersteds. Hence with $Q_\beta = 58.6$ and $\rho = 0.92$, we have

$$\frac{^1/_2\,[a_H(\beta\text{-}1) + a_H(\beta\text{-}2)]}{58.6 \cdot 0.92} = 0.66.$$

In Fig. 2 the ordinate 0.66 intersects the double line of the graph at the conformational angle $\varphi = 68°$. With non-equivalent β-protons and $\varphi = 68°$, we have $a_H(\beta\text{-}1) = 53$ oersteds and $a_H(\beta\text{-}2) = 18$ oersteds. The upper set of hyperfine structural levels below the spectrum 3*c* corresponds to these values. The actual splittings on the β-protons, 50 and 21 oersteds respectively, differ by ±3 oersteds from the calculated values (see lower scheme in Fig. 3*c*). The difference may be due to strong internal motion about the $C(\alpha)-C(\beta)$ bond. The barrier to rotation in the $CH_2-\dot{C}H_2$ radical is probably low, and the exact equation (5) should be used instead of the approximate formula (4) for a rigorous calculation of $a_H(\beta)$.

In $CHX-\dot{C}H_2$ and CH_2-CH_2 radicals, in contrast to $\rangle C-CH_3$ radicals, there is no free rotation about the $C(\alpha)-C(\beta)$ bond, and the conformational angle φ depends on the nature of the substituent X (see Table 3). With radicals containing a single β-proton, the same value of $a_H(\beta)$ may correspond to two different conformations (the angles φ_1 and φ_2, where $\varphi_1 + \varphi_2 = 2\pi/3$). Table 3 gives only the angle φ_1.

Table 3. Parameters of e.s.r. spectra of $R-\dot{C}H_2$ radicals (at 80°K).

Polymer radical	Σa_H, oersteds	ρ	Q_α	$a_H(\alpha)$, oersteds	$a_H(\beta\text{-}1)$, oersteds	$a_H(\beta\text{-}2)$, oersteds	$\varphi°$	Preparation of radical*	Ref.
$-CH_2-\dot{C}H_2$ Polyethylene, polycaprolactam	115	0.92	24.4	22	53	18	68	M*	19, 20
$-CH(OH)-\dot{C}H_2$ Poly(vinyl alcohol)	80	0.92	24.4	22	36	—	25	M	21
$-CH(C_6H_5)-\dot{C}H_2$ Polystyrene	77	0.92	24.4	22	33	—	21	M	22
$-O-\dot{C}H_2$ Polyformaldehyde	36	0.84	18.4	18	—	—	—	R	5,60
$-CH(OCOCH_3)-\dot{C}H_2$ Poly(vinyl acetate)	81	0.92	24.4	22	37	—	26	M	22
$-CH(COOCH_3)-\dot{C}H_2$ Poly(methyl acrylate)	84	0.92	24.4	22	40	—	30	M	22
$-NH-\dot{C}H_2$ Polycaprolactam	38	—	—	19	—	—	—	M	20

*In Tables 3–5 M = mechanical degradation, R = radiolysis, P = polymerisation, and UV = ultraviolet irradiation.

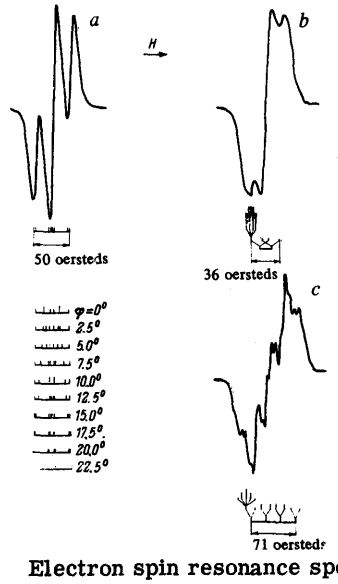


Figure 4. Electron spin resonance spectra and scheme of hyperfine levels for the radicals:
a) $-CH_2-\dot{C}H(COOCH_3)$, poly(methyl acrylate);
b) $-CH_2-\dot{C}H(C_6H_5)$, polystyrene;
c) $-CH_2-\dot{C}(CH_3)(C_6H_5)$, poly-$\alpha$-methylstyrene.

Table 4. Parameters of e.s.r. spectra of $CH_2-\dot{C}XY$ radicals (at 80°K).

Structure of radical	Form of spectrum: No. of hyperfine components	Form of spectrum: Σa_H, oersteds	ρ	Q_α, oersteds	$a_H(\alpha)$, oersteds	$a_H(CH_3)$, oersteds	$a_H(\beta\text{-}1)$, oersteds	$a_H(\beta\text{-}2)$, oersteds	φ	Production of radical	Ref.
$-CH_2-\dot{C}H(CH_3)$ Polypropylene	8	162	0.82	26.2	22	25	48	17	67	M	19
$-CH_2-\dot{C}H(COOCH_3)$ Poly(methyl acrylate)	3	46	0.85	23.5	20	—	25	3	15	M,R,P	11, 22, 33, 34
$-CH_2-\dot{C}H(COOH)$ 1)	3	46	0.85	23.5	20	—	25	3	16	M,P	11, 35
Polyacrylic acid 2)	5	46	0.85	23.5	20	—	14	11	3	R,P	9, 63
$-CH_2-\dot{C}H(C_6H_5)$ Polystyrene	3	36	0.65	23.2	15	—	21	2	17.	M,P	15, 63
$-CH_2-\dot{C}H(CN)$ Polyacrilonitrile	3	44	0.78	25.4	20	—	24	3	17	P	33
$-CH_2-\dot{C}(CH_3)_2$ Polyisobutene	15	162	0.78	—	—	23	11	13	2	M,P	6, 12
$-CH_2-\dot{C}(CH_3)(COOH)$ Polymethacrylic acid	9	92	0.78	—	—	22.5	14	11	3	M,R,P	9, 11, 50
$-CH_2-\dot{C}(CH_3)(COOCH_3)$ Poly(methyl methacrylate)	9	92	0.78	—	—	22.5	14	11	3	M,R,P	8–12, 28, 31, 33, 63 etc.
$-CH_2-\dot{C}(CH_3)(C_6H_5)$ Poly-α-methylstyrene	16	84	0.60	—	—	1) 17.5 2) 17.5	11 17	5 2	5 15	M,R	63
$-CH_2-\dot{C}(CH_3)(CN)$ Polymethacrylonitrile	9	86	0.72	—	—	21	11.5	11.5	0	R	31

(*b*) $CH_2-\dot{C}HX$ and $CH_2-\dot{C}(CH_3)X$ radicals

In most cases polymer radicals of type (II) can be obtained by the polymerisation of monomers in viscous and solid media. Hence there is no doubt that the e.s.r. spectra in Table 4 do actually belong to $CH_2-\dot{C}XY$ radicals.

Fig. 4*a* shows the spectrum of $CH_2-\dot{C}H(COOCH_3)$ radicals, which is a triplet of width 46 ± 1 oersteds. In this case $a_H(\alpha) = 23.5 \times 1 \times (1 - 0.08)(1 - 0.07) = 20$ oersteds. For the determination of $a_H(\beta\text{-}1)$ and $a_H(\beta\text{-}2)$ Fig. 4*a* shows a scheme of hyperfine levels corresponding to values of the angle φ from 0 to 22.5°. A triplet 46 oersteds wide can be obtained with $a_H(\beta\text{-}1) = 25$ oersteds and $a_H(\beta\text{-}2) = 3$ oersteds ($\varphi = 15°$).

The spectrum in poly-α-methylstyrene comprises 16 hyperfine components each separated by 5.5 oersteds (Fig. 4*c*), this splitting being due to interaction of the unpaired electron with the *ortho*- and *para*-protons of the benzene ring. A similar "aromatic" hyperfine structure has been observed in the spectra of the relatively simple radicals $C_6H_5\dot{C}H_2$, $C_6H_5\dot{C}H(CH_3)$, etc.[56,64] A 16-component spectrum of $CH_2-\dot{C}(CH_3)(C_6H_5)$ radicals can be obtained with two values of φ: when $\varphi = 6°$, we have $a_H(\beta\text{-}1) = 11$ and $a_H(\beta\text{-}2) = 5$ oersteds; the corresponding values with $\varphi = 15°$ are 17 and 2 oersteds. Choice of the correct alternative requires a knowledge of the relative intensities of the spectral lines: i.e. the spectrum in the liquid phase must be obtained.

No splitting on the protons of the benzene ring is detected in the spectrum of $CH_2-\dot{C}H(C_6H_5)$ radicals (Fig. 4*b*). In this case, perhaps, the "aromatic" hyperfine structure is obscured by the splitting of 3 oersteds on one of the β-protons of the methylene group.

Table 4 shows that $a_H(\beta\text{-}1) \neq a_H(\beta\text{-}2)$ for all radicals of type (II) at 77°K: i.e. the frequency of conformational transitions is low. In $CH_2-\dot{C}HX$ radicals other than $CH_2-\dot{C}H(CH_3)$ the angle of rotation about the $C(\alpha)-C(\beta)$ bond lies within the range $\varphi = 15-17°$: i.e. the nature of the substituent X (COOH, $COOCH_3$, C_6H_5, CN) has no great effect on the conformation of the radical. The conformation is also practically independent of X for all $CH_2-\dot{C}X(CH_3)$ radicals, the angle φ being in this case 0–5°. The appearance of a second substituent on the α-carbon atom leads to a diminution in the angle φ.

Electron spin resonance spectra of radicals have recently been obtained by the irradiation of frozen monomers such as isobutene[65], methyl methacrylate[36], and methacrylonitrile[33]. These spectra are attributed to $CH_2-\dot{C}(CH_3)X$ radicals, but the hyperfine structure constants for the β-protons differ from the values in Table 4. The discrepancy can be explained on the assumption that the angle φ in the radicals of the irradiated monomers is ~ 15° instead of 0–5°. The reasons for the appearance of such a conformation in the solid-phase polymerisation of monomers are still not clear.

With rise in temperature from 80° to 320°K the β-protons remain non-equivalent in the e.s.r. spectrum of $CH_2-\dot{C}(CH_3)X$ radicals[50]. The energy barrier to conformational transitions is lower in $CH_2-\dot{C}HX$ than in $CH_2-\dot{C}(CH_3)X$ radicals, and in the liquid phase at room temperature the β-protons become equivalent[24,27].

(*c*) $CXY-\dot{C}H-CXY$ and $CH_2-\dot{C}X-CH_2$ radicals

Table 5 gives the parameters of the e.s.r. spectra for "central" radicals of types (III) and (IV). In polymers containing quaternary carbon atoms in the main chain—poly(methyl methacrylate), polyisobutene, poly-α-methylstyrene—the spectrum of the $CXY-\dot{C}H-CXY$ radicals is a doublet with a separation of 21 oersteds. In polyformaldehyde ($O-\dot{C}H-O$ radicals) the splitting on the α-proton is considerably smaller: $a_H(\alpha) = 15$ oersteds. In polymers containing tertiary carbon atoms the hyperfine structure of the e.s.r. spectra of the $CH_2-\dot{C}X-CH_2$ radicals depends on the conformation of the radical.

The spectrum of the $CH_2-\dot{C}H-CH_2$ radicals in polyethylene comprises six hyperfine components, its overall width being 160–165 oersteds. With $a_H(\alpha) = 24.4 \times 0.84$ [? × 0.92 (Ed. of Translation)] = 22 oersteds the total splitting on the β-protons of each methylene group is $\frac{1}{2}(162 - 22) = 70$ oersteds. In order to obtain a six-component spectrum it must be supposed that the β-protons are already equivalent at 77°K: $a_H(\beta\text{-}1) = a_H(\beta\text{-}2) = 35$ oersteds. Barriers to internal movements are probably low in the polyethylene radical $-CH_2-\dot{C}H-CH_2-$.

The conformation of the chains in polymers of regular structure in the crystalline state has been established by means of X-ray and electron diffraction[74]. The conformation of a macromolecule, like that of a radical, can conveniently be characterised by the angles ψ of internal rotation about a C–C bond of the carbon skeleton. For the fragment $R_1-C_\beta H_2-C_\alpha HX-R_2$, for example, this is the angle between the projections of the $C-R_1$ and $C-R_2$ bonds on a plane perpendicular to the $C_\alpha-C_\beta$ bond.

For crystalline polymers having planar *trans*-bonds—polyethylene, poly(ethylene oxide), poly(vinyl alcohol)—the angle $\psi = 180°$. In polymers which crystallise in the form of 3_1-spirals (isotactic polypropylene and polybut-1-ene) the methylene groups on the left and on the right of the α-carbon atom ($CH_2-C_\alpha HX-CH_2$) are characterised by the angles $\psi_1 = 180°$ and $\psi_2 = 60°$.

The angle ψ may change on formation of a radical having its free valency in the middle of the polymer chain $CH_2-\dot{C}X-CH_2$. In all the polymer radicals investigated (Table 5) the two methylene groups are characterised by the same conformational angle (radicals have been observed in amorphous specimens of isotactic polypropylene and polybut-1-ene).

Table 6 gives the angles of internal rotation in polymeric molecules ψ and radicals ψ', together with the difference between them. The rotation of the portions of macromolecules about a C–C bond on abstraction of a hydrogen atom and formation of a radical is extremely large, amounting to several tens of degrees.

3. Conformations of Polymer Radicals

For all polymer radicals the hyperfine interaction constants of the α-protons vary within the range 15–22 oersteds depending on the nature and the number of substituents. The radical cannot contain more than two α-protons, and there is usually no difficulty about assigning their lines in the e.s.r. spectrum. The character of the spectrum—its width, number of components, intensity ratio—is determined in considerable measure by interaction of the unpaired electron with the β-protons, the number of which may reach 6–9. The splitting on each β-proton may vary from 0 to 50 oersteds, and is directly connected with the conformation of the radical, the angle of rotation about the $C(\alpha)-C(\beta)$ bond. When the conformational angles for the groups $C(\beta)H_2$ and $C(\beta)HX$ are known, the whole spectrum can be constructed for a given radical.

Theoretical calculation of the conformations of free radicals, like that of molecules, requires the many-elec-

Table 5. Parameters of e.s.r. spectra of "central" radicals at 80°K.

Structure of radical	Form of spectrum: No. of hyperfine components	Form of spectrum: Σa_H, oersteds	ρ	Q_α, oersteds	$a_H(\alpha)$, oersteds	$a_H(CH_3)$, oersteds	$a_H(\beta\text{-}1)$, oersteds	$a_H(\beta\text{-}2)$, oersteds	φ^*	Production of radical	Ref.
$-CH_2-\dot{C}H-CH_2-$* Polyethylene	6	162	0.85	25	21	—	35	35	70	M,R,UV	1, 2, 11, 66
$-CH_2-\dot{C}(CH_3)-CH_2-$ Polypropylene**	6	130	0.78	—	—	23	30	3	25	M	19
$-CH_2-\dot{C}(C_2H_5)-CH_2-$ Polybut-1-ene	4	88	0.78	—	—	—	29	2	20	M,R	67, 68
$-CH_2-\dot{C}(OH)-CH_2-$ Poly(vinyl alcohol)	3	70	0.71	—	—	—	35	1	37	R	7
$-O-\dot{C}H-CH_2-O-$ Poly(ethylene oxide)	3	36	0.77	18	15	—	21	3	13	M	21
$-CO-NH-\dot{C}H-CH_2-$ Polycaprolactam	5	75	0.70		18	—	37	19	68	M,R	4, 17, 69
$-O-\dot{C}H-O-$ Polyformaldehyde	2	15	0.70		15	—	—	—	—	M,R	5, 21
$-C(CH_2)(COOCH_3)-\dot{C}H-$ $-C(CH_3)(COOCH_3)-$ Poly(methyl methacrylate)	2	21	0.85	25	21	—	—	—	—	M	13, 70
$-C(CH_3)_2-\dot{C}H-C(CH_3)_2-$ Polyisobutene	2	21	0.85	25	21	—	—	—	—	M,R	5, 6, 70
$-C(CH_3)(C_6H_5)-\dot{C}H-$ $-C(CH_3)(C_6H_5)-$ Poly-α-methylstyrene	2	21	0.85	25	21	—	—	—	—	M	70

*For radicals containing two or three β-methylene groups they all have the same conformation. For the radical $CH\beta_1H\beta_2-\dot{C}X-CH\beta_3H\beta_4$, for example, $a_H(\beta_1) = a_H(\beta_3)$ and $a_H(\beta_2) = a_H(\beta_4)$.
**The structure of the radicals formed by the irradiation of polypropylene has not yet been established unambigously, in spite of the large amount of work done[71-73].

tron problem to be solved, and has not yet been accomplished. However, analysis of the experimental data enables several qualitative relations to be established for the effect of various substituents on the conformation of alkyl radicals and on the height of the potential barrier determining the frequency of conformational transitions.

The angle of rotation about the $C_{(\alpha)}-C_{(\beta)}$ bond is determined by interaction of the substituents on the α-, β-, and γ-carbon atoms both among themselves and with neighbouring molecules. At low temperatures the e.s.r. spectra of a given radical in different matrices are usually the same: i.e. the medium in which the radicals are distributed probably has no effect on their conformation, and intermolecular interactions can be disregarded to a first approximation‡.

In all alkyl radicals having a β-methyl group $H_3C-\dot{C}XY$ the barrier to rotation about the $H_3C-C_{(\alpha)}$ bond is low, not exceeding 100 cal mole^{-1}; the methyl groups rotate freely down to 10°K.[59,75] On passing to radicals containing a β-methylene group $R-CH_2-\dot{C}XY$ (and also $>CH-\dot{C}XY$) the height of the barrier to internal rotation about the $C_\alpha-C_\beta$ bond rises sharply (by factors of 10–100); the equilibrium conformation of the radical is governed by the energetically most favourable relative arrangement of the substituents attached to the α- and β-carbon atoms. The sharp rise in the barrier is connected with the change in symmetry of the substituent (from C_{3V} for the CH_3 group to C_{1V} for RCH_2) when one of the methyl hydrogen atoms is replaced by an alkyl group R. The rise in the barrier can be regarded as resulting from interaction of the group R with the α-substituents X, Y and the unpaired electron.

‡ The height of the potential barrier to internal movements in the radicals, i.e. the temperature dependence of the hyperfine structural constants, is probably connected with the nature of the matrix.

Table 6. Change in conformation of polymer chain on formation of "central" radicals.

Polymer	Radical	ψ^* (mol.)	ψ' (radical)	$(\psi - \psi)^\circ$
Polyethylene	$R-CH_2-\dot{C}H-CH_2-R$	180	160	20
Poly(vinyl alcohol)	$R-CH_2-\dot{C}(OH)-CH_2-R$	180	127**	53
			53	127
Poly(ethylene oxide)	$R-O-\dot{C}H-CH_2-O-R$	180	103	77
			77	103
Polypropylene	$R-CH_2-\dot{C}(CH_3)-CH_2-R$	180	115	65
		60	115	55
			65	5
Polybut-1-ene	$R-CH_2-\dot{C}(C_2H_5)-CH_2-R$	180	110	70
		60	110	50
			70	10

*From Ref. 74.
**The ambiguity in the value of the angle ψ' for the radical is due to the two possible orientations of the group R relative to the orbital axis of the unpaired electron.

In the simplest terminal radical $CH_2-CH_2-\dot{C}H_2$ (polyethylene, Table 3) let us denote by R the polymer chain beginning with the γ-carbon atom. The conformation of the radical is shown in Fig. 5*a*. The angle of rotation about the $C_{(\alpha)}-C_{(\beta)}$ bond is determined to a first approximation by the interaction of the group R with the α-substituents—the two hydrogen atoms and the unpaired electron—and has the value 68°. The group R is remote from the orbital of the unpaired electron (the *Z*-axis): i.e. it is more strongly repelled from it than from the hydrogen atoms.

In the radical $CH_2-\dot{C}(CH_3)_2$ (polyisobutene, Fig. 5*b*, φ = 2°) the substituent R is "overshadowed" by the orbital of the unpaired electron. Consequently the most important factor here is repulsion of the group R from the α-methyl groups, while interaction with the unpaired electron is less effective.

It is seen from these two examples that, in alkyl radicals, repulsion of the β-group R (CH_3, C_2H_5, etc.) from the α-substituents becomes stronger in the sequence

$$\text{Hydrogen atom} < \text{Unpaired electron} < \text{Alkyl substituent} . \qquad (12)$$

This sequence is consistent also with an analysis of a large number of e.s.r. spectra for the lower alkyl radicals, and can be used to predict the conformations of alkyl radicals having various structures.

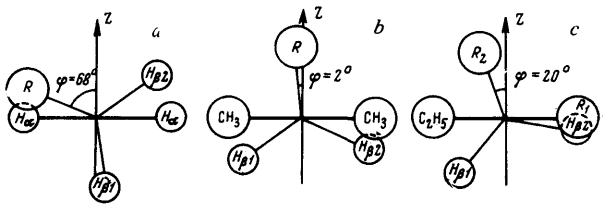


Figure 5. Conformation of polymer radicals:
a) terminal radical in polyethylene $R-CH_2-\dot{C}H_2$;
b) terminal radical in polyisobutene $R-CH_2-\dot{C}(CH_3)_2$;
c) central radical in polybut-1-ene $R_1-\dot{C}(C_2H_5)CH_2-R_2$.

The conformations of the radicals in polyalkenes (Tables 3–5) show good consistency with the requirements of the sequence (12). As example let us examine the conformation and the e.s.r. spectrum of radicals having the free valency in the centre of the chain in polybutene

$$R_1\underset{(3)}{-CH_2-}\underset{(1)}{\dot{C}}(C_2H_5)\underset{(2)}{-CH_2-}R_2$$

(Fig. 5*c*). There is no generally accepted interpretation of the e.s.r. spectrum of this radical[67,68]. We shall regard the 1-ethyl group and the right-hand part of the chain as substituents on the α-carbon atom. The group R_1 (the left-hand portion of the polymer chain) is repelled from the alkyl substituents CH_2-R_2 and C_2H_5 more strongly than from the unpaired electron; consequently the angle should be small, and from the graph in Fig. 2 the splitting on one β-proton will be negligible, while that on the other will be close to half the maximum value ($Q_{\beta\rho}$). The conclusion remains unchanged if the groups C_2H_5, R_1, and R_2 change places: i.e. only one β-proton will be involved in the splitting in each of the three methylene groups, and the e.s.r. spectrum should be a quadruplet 70–80 oersteds wide. The spectrum observed on the radiolysis and the mechanical degradation of amorphous polybutene actually comprises four hyperfine lines with $a_H(\beta) = 29$ oersteds.

Prediction of the conformations (and the e.s.r. spectra) of radicals containing the substituents CN, NH_2, COOH, $OCOCH_3$, C_6H_5, etc. is difficult because of differences in the nature of the forces of interaction between polar groups, groups capable of forming hydrogen bonds, etc. For radicals $CH_2-\dot{C}XY$, where X and Y are bulky substituents, the conformation can be established by constructing models.

Fig. 6 shows as example photographs of models of the terminal radicals in (*a*) polyethylene and (*b*) polyisobutene. The photographs illustrate the role of steric hindrance in determining the conformation of the radicals. In polyethylene the hydrogen atoms are freely arranged, and rotation to any angle is in principle possible about the $C(\alpha)-C(\beta)$ bond. In polyisobutene the chain is considerably more compact, and the angle of rotation about the $C(\alpha)-C(\beta)$ bond in the terminal radical is restricted to values at which the van der Waals radii of the substituents do not overlap. In poly(methyl methacrylate) and poly-α-methylstyrene the possible conformation of terminal radicals found from electron models agrees with results obtained by the e.s.r. method (Table 5).

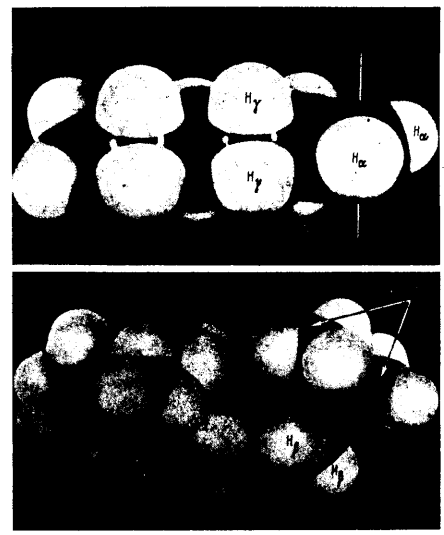


Figure 6. Models of the radicals $\sim CH_2-CH_2-\dot{C}H_2$ (polyethylene) and $\sim CH_2-C(CH_3)_2-CH_2-\dot{C}(CH_3)_2$ (polyisobutene). The axis of the orbital of the unpaired electron is shown by the white line.

Thus the conformations of alkyl radicals and certain complicated substituted radicals can be predicted from a consideration of the forces of interaction between the substituents and an examination of electron models. The accuracy with which the conformational angles can be predicted is not good (10–15°), but even such estimates are of great value in analysing poorly resolved e.s.r. spectra of polymer radicals in the solid phase.

III. CHEMICAL PROPERTIES AND STABILITY OF POLYMERIC RADICALS

The chemical behaviour of polymer radicals at low temperatures is governed primarily by the reactivity of the radicals and the molecules with which they interact, and secondarily by the possibility of encounters and contacts between the reactant species. These two factors are undoubtedly closely interlinked.

The lifetime of radicals in solid polymers may be unlimited, the reason being solely the impossibility of their moving and meeting one another. Under the most favourable conditions (rubbers of low molecular weight in a highly elastic state) the coefficient of self-diffusion at 370°K does not exceed 10^{-13}–10^{-14} $cm^2\ s^{-1}$:[76,77] i.e. several hours are required to overcome a distance of 10^2–10^3 Å [$x = (2Dt)^{\frac{1}{2}}$], where D is the coefficient of self-diffusion, x the diffusion

distance, and t the time]. In the vitreous state the movement of macromolecules is retarded, and radicals in such systems are said to be frozen.

The rate of diffusion of substances of low molecular weight in solid polymers is also low, usually less than the rate of many chemical reactions. Thus the rate of interaction with monomers of chain carriers is governed by the diffusion of these compounds to the polymer radicals [78]. The addition of oxygen molecules to polymeric alkyl radicals in films and massive specimens is also limited by the diffusion of oxygen [78,79].

In analysing the kinetics of reactions in highly viscous media use is made of the concept of a cage, cell, or element of volume, inside which the particles react with one another. In order to react, the particles must be present in the same cage. An important factor in decomposition reactions is the escape of the newly formed particles from the cage. This approach was first formulated by Frank and Rabinowitch [80], and is now generally accepted. The e.s.r. method has recently been used to detect polymer radicals [81] and those of low molecular weight [82] at distances of several Ångström units from one another.

The formal kinetic equation for the rate of a bimolecular reaction in the solid phase, which takes into account the stages of migration of active centres when their distribution is homogeneous§ and interaction of the reactant particles in a single element of volume, is [84]

$$\frac{dC_A}{dt} = k_m C_A \ln\left(1 - \frac{k_i V^* C_B}{k_i + k_m}\right) \qquad (13)$$

where C_A and C_B are the concentrations of the mobile reactant A particles and the stationary reactant B particles, k_m is the frequency (in s^{-1}) with which A particles jump from one cage to another, k_i (s^{-1}) the reaction rate constant inside the cage, and V^* the volume of the cage.

When $k_i V^* C_B \ll k_i + k_m$ the kinetic law is described by the usual second-order equation

$$-\frac{d\bar{C}_A}{dt} = k_{eff} C_A C_B \qquad (14)$$

where

$$k_{eff} = \frac{k_i \cdot k_m}{k_i + k_m} \cdot V^*. \qquad (15)$$

When radicals combine with one another in solid polymers, the rate of migration is always less than the reaction velocity in the cage ($k_m \ll k_i$), so that

$$\frac{dc}{dt} = 2k_m C \ln(1 - V^* C) \ . \qquad (16)$$

In most cases the rate constant and the activation energies for the reactions of radicals in solid polymers are characteristic of the process of migration of the free valency (k_m)¶, not the actual chemical activity of the reactant species (k_i). This category of experimental data includes the results of numerous kinetic investigations of the destruction of radicals in polymers [85-90], as well as individual measurements of the rate constants for reactions of radicals with monomers and chain-transfer agents [78].

Information on the reactivity of radicals has been obtained in systems in which polymer radicals are surrounded by reactant molecules. This case is realised firstly in the interaction of radicals with neighbouring molecules of their own polymer, and secondly in the reactions of polymer radicals distributed in a matrix of a chemically reactive substance of low molecular weight. The method of studying the reactivity of polymer radicals in frozen dilute solutions is based on this principle [23,91,92]. The polymer radicals are generated by mechanical treatment of the solution.

Mechanical grinding of frozen dilute solutions results in cleavage of the macromolecules at bonds in the main chain, with the formation of terminal polymer radicals $\cdot R_0$, which then react with the surrounding solvent molecules. In the course of grinding, fine particles are deformed, and individual layers of material are displaced relative to one another; under such conditions the reaction velocity is proportional to the reactant concentrations:

$$\frac{d[R_0^{\cdot}]}{d\tau} = W - k_i [R_0^{\cdot}] [M] \qquad (17)$$

and

$$\alpha = \frac{1}{k_i [M] \tau} (1 - e^{-k_i [M] \tau});$$

when

$$\tau \gg k_i [M] \quad \alpha \simeq \frac{1}{k_i [M] \tau} \qquad (18)$$

where W is the rate of formation of initial $\cdot R_0$ polymer radicals, while τ is the duration of dispersion, k_i is the rate constant for reaction of these radicals with surrounding molecules of the reactant M, and $\alpha = [\cdot R_0]/([\cdot R_0] + [R\cdot])$, with $[R\cdot]$ the concentration of radical reaction products and $1 - \alpha$ the degree of conversion.

The accuracy with which α can be determined from e.s.r. spectra is usually low, and only the order of magnitude of the rate constant can be estimated by this method.

The literature contains hardly any rigorous or systematic data on the temperature dependence of the rates of the elementary reactions undergone by polymer radicals in the solid phase, so that approximate procedures must be used to estimate activation energies. When the polymer radical and the reactant molecule are located in the same cage, in a state of continuous contact as it were, the reaction velocity will be a maximum, and the pre-exponential factor in the Arrhenius equation cannot exceed 10^{13} s^{-1}. Under ordinary conditions transformations of radicals can be detected if their concentration changes appreciably during the course of hours or tens of hours, i.e. if $k \simeq 10^{-4}$–10^{-5} s^{-1}. Hence

$$E \leqslant 2.3RT \lg \frac{k_0}{k} \quad \text{or} \quad E \leqslant 80T. \qquad (19)$$

Thus if the temperature at which a particular elementary reaction takes place is known, an upper limit to possible values of the activation energy can be estimated. For example, it follows from the relation (19) that reactions having an activation energy exceeding 6 kcal $mole^{-1}$ will not be observed at the boiling point of nitrogen (80°K).

Reactions involving addition, substitution, decomposition, and combination are characteristic of free radicals. All these classes of elementary reactions play an important part in the chemistry and the physical chemistry of polymers; they take place under the influence of ionising radiations, ultraviolet irradiation, mechanical constraints, aging and fatigue, chemical modification, thermal and thermo-oxidative degradation of polymeric materials, etc. Published data on elementary reactions in the solid phase are fragmentary, authors most often confining themselves

§ The kinetic laws of reactions in non-homogeneous non-uniform systems are considerably more complicated. An example of such a reaction is the "stepwise" recombination of radicals in irradiated solids, which has been analysed in Ref. 83.

¶ The form of the constant k_m is discussed in Ref. 78.

to reporting the fact of interaction and analysing the reaction products; more rarely rate constants are measured, and only in isolated cases are the activation energy and the pre-exponential factor determined. The results of investigations of the reactivity at low temperatures of polymer radicals in the principal classes of reactions are examined below. The elementary reactions of addition, substitution, and decomposition are analysed separately from those involving the destruction of radicals, the rates of which in solid polymers are always determined by processes of migration of the free valency.

1. Elementary Addition, Substitution, and Decomposition Reactions

Addition reactions

Addition reactions include the interaction of polymer radicals with substances containing double or triple bonds (including aromatic compounds), oxygen, nitric oxide, and other unsaturated molecules. The reactions between radicals and vinyl monomers have been studied in the greatest detail [22,78]†.

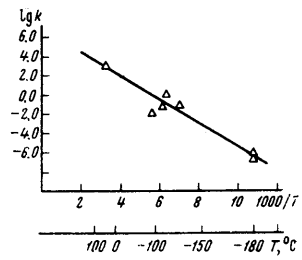


Figure 7. Temperature dependence of rate constant for the addition of certain monomers (styrene, α-methylstyrene, methyl acrylate, and acrylic acid) to $\sim CH_2-\dot{C}(CH_3)(COOCH_3)$ radicals.

Rate constants for addition of the monomers have been measured at low temperatures (80–100°K) in frozen solutions [22]. The dependence of the addition rate constant for radicals of poly(methyl methacrylate) on temperature over the range 100–400°K is shown in Fig. 7 plotted as $\lg k$ against $1000/T$. The upper left-hand point corresponds to the rate constant of chain growth in the liquid-phase polymerisation of methyl methacrylate; over the range 330–380°K we have $k = 6 \times 10^5 \exp(-4700/RT)$ $M^{-1}\,s^{-1}$, [93] and the slope of the straight line has been determined from these data. The points in the lower right-hand part of the graph correspond to measurements of the rate constant for the addition of various monomers (styrene, α-methylstyrene, methyl acrylate‡) to radicals of poly(methyl methacrylate) $CH_2-\dot{C}(CH_3)(COOCH_3)$ in frozen solutions [22]. The values of $k_{100°K}$ for various monomers lie in the range 10^{-5}–10^{-4} $M^{-1}\,s^{-1}$. The graph shows that to a first approximation the activation energy and the pre-exponential factor remain the same in the solid phase at low temperatures as in the liquid phase at 350–400°K.

Fused-ring aromatic compounds (anthracene, acridine) and quinones (benzoquinone, tetrachlorobenzoquinone) readily add to the terminal radicals of poly(methyl methacrylate), polystyrene, and other vinyl polymers at 100°K. [92] The addition rate constants for these compounds at 100°K vary over the range 10^{-6}–10^{-4} $M^{-1}\,s^{-1}$.

The polymer radicals $-CHX-\dot{C}H_2$, $-CH_2-\dot{C}H(OCOCH_3)$, and $-CH_2-\dot{C}H(COOCH_3)$ are the most active in addition reactions at low temperatures. They are approached by $-CH_2-\dot{C}H(C_6H_5)$ radicals. The last position in the sequence is occupied by $-CH_2-\dot{C}(CH_3)(COOCH_3)$ and $-CH_2-\dot{C}(CH_3)(C_6H_5)$ radicals. The addition of monomers to central radicals of the type $-CXY-\dot{C}H-CXY$ has not been observed in frozen solutions. The same sequence of activities is maintained in reactions with quinones, anthracene, and acridine [92].

In the solid phase at low temperatures $-CH_2-\dot{C}H(C_6H_5)$ radicals are more active than $-CH_2-\dot{C}(CH_3)(COOCH_3)$ radicals; this is inconsistent with the theory of ideal reactivity and results for the liquid-phase copolymerisation of monomers [93]. It may be assumed that the steric factor plays a more important part in the solid than in the liquid phase. Therefore radicals having the structure $-CH_2-\dot{C}HX$ are generally more active than $-CH_2-\dot{C}(CH_3)X$ radicals, while radicals having the free valency in the middle of the chains, of the type $-C(CH_3)X-\dot{C}H-C(CH_3)X-$, such as poly(methyl methacrylate), etc., do not undergo addition reactions at all in frozen solutions.

Oxygen reacts with all alkylated polymeric radicals at temperatures of 150–200°K and below [11,78,79,90,94,95], with the formation of peroxy-radicals ROO•, distinguished by a characteristic anisotropic e.s.r. signal [5]. Peroxy-radicals have been observed in polyethylene [8], polypropylene [5,96], poly(vinyl chloride) [89,94], polystyrene [78], poly(methyl methacrylate) [78,85,95], and other carbon-chain and heterochain polymers, including those which occur naturally. The addition of oxygen has been studied in massive specimens [79], films [96], turnings [78], and finely divided powders [95]. When the material is sufficiently thick, oxidation is limited by the diffusion of oxygen inside the polymer [78,79].

The activation energy of the reaction $R\cdot + O_2 \rightarrow ROO\cdot$ has the values 6, 5.3, 5.9, and 7.9 kcal $mole^{-1}$ for polytetrafluoroethylene [79], polystyrene [78], poly(vinyl acetate) [78], and poly(methyl methacrylate) [78].

A summary of kinetic results for the reactions of polymer radicals with various molecules (O_2, NO, etc.) from the gas phase will be found in Ref. 90.

Substitution reactions

The chief reactions studied have been those involving abstraction of a hydrogen atom by a polymer radical from neighbouring macromolecules [19,20,97] or compounds of low molecular weight having weak C–H, N–H, O–H, or S–H bonds [92]. Intermolecular transfer of a hydrogen atom probably plays an important part in the stabilisation of radical states in solid polymers.

Polymer radicals of the type $R-CXY-\dot{C}H_2$ exhibit the highest activity [92] in $R\cdot + HR_1 \rightarrow RH + R_1\cdot$ reactions. In frozen dilute solutions, with HR_1 representing an aromatic hydrocarbon (toluene, ethylbenzene, isopropylbenzene, etc.), reaction at 80–100°K yields the simple radicals

† Solid-phase polymerisation is not discussed in the Review.

‡ It is impossible by the e.s.r. method to observe the interaction of poly(methyl methacrylate) radicals with methyl methacrylate.

$C_6H_5\dot{C}H_2$, $C_6H_5\dot{C}HCH_3$, $C_6H_5\dot{C}(CH_3)_2$, etc., which have all been recorded by the e.s.r. method[64]. On passing from toluene to ethylbenzene the reaction rate constant increases several times to reach 10^{-5} M^{-1} s^{-1}, in conformity with the decrease in strength of the C–H bond. It follows from the relation (19) that the activation energy for abstraction of a hydrogen atom from toluene cannot exceed 7–8 kcal mole^{-1}. For the reaction of methyl radicals with toluene vapour at 400–600°K we have $k = 10^8 \exp(-8300/RT)$ M^{-1} s^{-1}:[98] i.e. the activation energy for transfer of a hydrogen atom to R–CXY–$\dot{C}H_2$ radicals in the solid phase is lower than—or in the extreme case equal to—the activation energy of the analogous reaction for simple methyl radicals in the gas phase.

The reaction of terminal radicals of polyethylene with a neighbouring chain

$$-CH_2-\dot{C}H_2 + -CH_2-CH_2-CH_2- \longrightarrow -CH_2-CH_3 + -CH_2-\dot{C}H-CH_2-,$$

which occurs at a measurable rate at 140°K, has an activation energy of only 4 ± 1 kcal mole^{-1}.[19] Yet for the reaction of methyl radicals with butane in the gas phase E = 8.3 kcal mole^{-1}.[98] Thus the transfer of a hydrogen atom to R–$\dot{C}H_2$ radicals, whether in polyethylene or in frozen solutions of aromatic hydrocarbons (toluene, ethylbenzene, etc.), is possible at low temperatures (110–140°K), and has an unexpectedly low activation energy§.

The radicals R–CH_2–$\dot{C}HX$ and R–CH_2–$\dot{C}XY$ are less active than are R–$\dot{C}H_2$ radicals, and do not interact with hydrocarbons at low temperatures[92]. There is almost no information on the reactions of these radicals with "their own" macromolecules. Only in polypropylene at 140°K are terminal radicals CH_2–$\dot{C}H(CH_3)$ converted into central radicals[19]. In poly(methyl methacrylate), polystyrene, and several other polymers the terminal radicals are stable up to 330–350°K and above (see Tables 9 and 10), which is evidence of their low activity in reactions involving the transfer of a hydrogen atom.

Peroxy-radicals ROO• react with various types of polymer molecules—polycaprolactam, polystyrene, poly(methyl methacrylate), etc.—and in a vacuum at 200–270°K we can observe the conversion of ROO• into R• radicals, accompanied by a usually appreciable fall in the total concentration of radicals[97]. The primary act is transfer of a hydrogen atom to the peroxy-radical with formation of a polymer radical having the free valency in the middle of the chain. The rate constant of this reaction has been measured by two different methods (chemiluminescence and e.s.r.) in poly(methyl methacrylate)[97]. Over the temperature range 250–360°K,

$$k = 10^{6\pm1} \exp\left(-\frac{12000 \pm 2000}{RT}\right) M^{-1} s^{-1}$$

the product of the reaction being –$C(CH_3)(COOCH_3)$–$\dot{C}H$–$C(CH_3)(COOCH_3)$– radicals. In polypropylene[100] $k = 10^{5.3} \times \exp(-9000/RT)$ (at 380–410°K). There are no published data on the rate of this reaction for other polymers, but since the conversion ROO• → R• is observed over roughly the same temperature range, the activation energy will not greatly change on passing to other polymers.

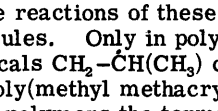
Table 7 gives rate constants for reactions of the radicals R–$\dot{C}H_2$, R–CH_2–$\dot{C}HX$, R–CH_2–$\dot{C}XY$, and ROO• with a series of compounds containing a reactive hydrogen atom (aromatic amines, phenols, thiols, etc.)[92]. The rate constants were measured in frozen dilute solutions, where the polymer radicals were surrounded by molecules of the reactant (see relation 18).

Polymer radicals of varying structure differ from one another in reactivity considerably more strongly in substitution than in addition reactions. Radicals for which data are available on their chemical activity in hydrogen-transfer reactions from phenols, amines, and thiols can be arranged in the sequence[92]

$$\left\{\begin{array}{l} R-\dot{C}H_2 \\ -CH_2-\dot{C}H(OCOCH_3) \\ ROO^{\cdot} \end{array}\right\} > -CH_2-\dot{C}H(C_6H_5) > -CH_2-\dot{C}(CH_3)X$$

where X = CH_3, C_6H_5, $COOCH_3$. For R–$\dot{C}H_2$, –CH_2–$\dot{C}H(OCOCH_3)$, and ROO• radicals the transfer rate constants at 100°K always exceed 10^{-4} M^{-1} s^{-1}. The activity of the peroxy-radicals is almost independent of the structure of the carbon skeleton. The rate constant for the interaction of –CH_2–$\dot{C}(CH_3)(COOCH_3)$ radicals with phenols and amines at 100°K is less than 10^{-7} M^{-1} s^{-1}.

Table 7. Rate constants of elementary substitution reactions for alkyl (R•) and peroxide (ROO•) polymer radicals with certain compounds at 80–100°K.

Reactant	Initial radical	k, M^{-1} s^{-1}
$C_6H_5CH_3$, $C_6H_5CH_2CH_3$	R'*	10^{-6}–10^{-5}
	R•	~10^{-5}
	ROO•	≥10^{-4}
C_6H_5–NH–C_6H_5	R•	10^{-6}–10^{-4}
	ROO•	≥10^{-4}
C_6H_5–SH	R•	—
	ROO•	≥10^{-4}
$(C_6H_5)_3C$–Cl	R•	10^{-6}–10^{-5}

*R• = –CHX–$\dot{C}H_2$, –CH_2–$\dot{C}HX$, –CH_2–$\dot{C}XY$.

Decomposition reactions

The decomposition of polymer radicals plays an important part at high temperatures in processes of thermal and thermo-oxidative degradation[101,102]. Recently the decomposition of polymer radicals has been detected even at room temperature[97].

The simplest decomposition reaction is depolymerisation—detachment of a monomer from a terminal polymer radical:

$$-CH_2-CXY-CH_2-\dot{C}XY \rightarrow -CH_2-\dot{C}XY + CH_2=CXY$$

Elimination of a monomer is the opposite reaction to polymerisation, and its activation energy is $E_d = E_{gr} + Q$, where E_{gr} is the activation energy of chain growth during polymerisation and Q is the heat of polymerisation. Values of E_d, E_{gr}, and Q for various polymers are listed in Table 8. The activation energy of depolymerisation is largest in polyethylene, where it reaches 28 kcal mole^{-1}. Methyl methacrylate is characterised by low values of Q and E_{gr}, and depolymerisation is the principal way in which poly(methyl methacrylate) decomposes[101]. The rate of depolymerisation of poly(methyl methacrylate) to be expected at room temperature is

$$W = k_0 \exp\left(-\frac{18000}{1.98 \cdot 290}\right)[R^{\cdot}] = 10^{-3}[R^{\cdot}]$$

§ Methyl radicals also have enhanced activity in the solid phase: at 77°K they abstract a hydrogen atom from a polyphenylmethylsiloxane molecule[99].

The rate of separation of monomer is a specimen of the polymer containing 10^{17}-CH_2-$\dot{C}(CH_3)(COOCH_3)$ radicals was close to the calculated value[86].

Modes of decomposition of polymer radicals other than depolymerisation are also possible. Mainly alkylated derivatives of benzene—toluene, ethylbenzene, isopropylbenzene—separate in polystyrene[97]. These compounds are probably formed by the breakdown of central radicals with further separation of radicals of low molecular weight by reactions of the type

$$\sim R^{\cdot}\sim \rightarrow \sim \Pi + R^{\cdot}\sim$$
$$\sim R^{\cdot} \rightarrow \sim \Pi + r^{\cdot}$$

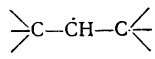
where Π represents the polymer and r• the simple radical.

Table 8. Some parameters of processes of polymerisation[93] and depolymerisation.

Monomer	Q, kcal mole^{-1}	E_{gr}, kcal mole^{-1}	E_d, kcal mole^{-1}
Ethylene	22.3	5.5[103]	27.8
Vinyl acetate	21.3	4.2	25.5
Styrene	16,1—16,7	7.2	23—24
Methyl acrylate	18.7	4.7	23.4
Methyl methacrylate	13.0	4.7	17.7

"Volatile" radicals r• have been detected by the e.s.r. method among the products of the radical degradation of polyethylene and polypropylene at high temperatures[102]. Whether breakdown of the central radical ~R•~ and ejection of the simple radical r• take place in a single act or in two stages in unknown.

No study has been made of the kinetics of the breakdown of radicals having the free valency in the middle of the chain. In poly(methyl methacrylate) the



radicals decompose at lower temperatures than do $-CH_2-\dot{C}(CH_3)(COOCH_3)$ radicals[86]. Radicals having their free valency in the middle of the chain probably break down more easily than do terminal radicals in other polymers, too. However there is as yet no direct evidence to support this suggestion.

2. Nature of Processes of Migration of the Free Valency and the Destruction of Radicals

The loss of radicals in solid polymers is the most convenient reaction for investigating the nature of the processes involving migration of the free valency. Decay of polymer radicals may be due either to diffusion or to chemical mechanisms of transfer of the free valency. Analysis of the conditions for destruction will give the first information on the nature of processes involving migration of the free valency in polymers of various structures. Data on the stability of alkylated and peroxide radicals of various types in vinyl polymers and in polyoxides are assembled in Table 9¶. The measure of stability adopted in compiling Table 9 was the temperature range within which the concentration of radicals of the given type drops sharply when the specimens are heated. In some polymers, radicals of one type disappear by being converted into other, more stable radicals; in this case the total radical concentration either diminishes or remains constant.

Table 9. Temperature range of destruction of polymer radicals.

Polymer	T_{ds}, °K Refs.104, and 105	Temperature of stability, °K			
		R—$\dot{C}H_2$	R—$\dot{C}XY$	"central radicals"	ROO•
Polyethylene	188	120—140[19, 20]	—	260—280[106, 107]	260—280[106, 108]
Polypropylene	256	<90	120—140[19]	250—290[19]	300[108]
					300—340[96]
Polyisobutene	200	<90	200—220	200—220	200—220
Polystyrene	370	120—140*	330—350[111]	—	260—280[111]
Poly(methyl methacrylate)	380—390	<90*	330—350[85, 86, 111]	250—270[86]	260—280[86, 97]
Poly(vinyl alcohol)	358	120—140[21]*	—	330—360[109]	200—220
Polyformaldehyde	250	250—270[80]		350—370[80, 87]	200—220
Polycaprolactam	320	120[20]	—	280—290[17]	

*Data for frozen solutions of polymers in inert solvents.

In a rigorous approach the stability must be characterised by the rate constant of destruction or by the constants k_0 and E in the Arrhenius expressions. Such measurements are collected together in Table 10. They relate to cases in which the loss of radicals obeys a second-order equation. With the values of k_0 and E known, we can estimate the temperature limits of stability, i.e. the range within which the lifetime of the radicals decreases to minutes ($10^4 > \tau > 10^2$ s), while the destruction rate constants lie in the range $10 > k_{ds} > 10^{-1}$ M^{-1} s^{-1} {with destruction having second-order kinetics $k_{ds} \simeq 1/\tau[R^{\cdot}]$; usually $[R^{\cdot}] = 0.001$ M}. In several polymers radicals of different types (terminal, central, and peroxide) are destroyed under roughly the same conditions, at temperatures above the glass point of the polymer, in air and in a vacuum; in such a case diffusion may be expected to make a great contribution to migration of the free valency. The primary example of such polymers is polyisobutene (Table 9). In polystyrene, poly(methyl methacrylate), and other polymers radicals of different types differ markedly in their stability. It may be assumed that in these polymers the mechanism of migration of the free valency is determined not so much by the flexibility of the macromolecules as by the structure and the chemical activity of the radical.

Radicals of type R-$\dot{C}H_2$

The radicals are usually stable at temperatures below 150°K. Under these conditions at a diffusion mechanism of migration is excluded, and their disappearance is most likely due to their great activity in reactions involving the intramolecular and intermolecular transfer of a hydrogen atom. The example of polyethylene (subsection 1) shows that the term "destruction" is inexact in relation to R-$\dot{C}H_2$ radicals: they interact with a neighbouring polymer chain, and are converted into more stable radicals with the free

¶ The stability of radicals depends on the state of the polymer, but this aspect has not yet been investigated systematically. Radicals are more stable in crystalline than in amorphous specimens (polypropylene[110], polybutadiene[67]).

valency in the middle of the chain[19]. At low temperatures this process is limited. At higher temperatures (260–280°K) the loss reactions develop further, and the total concentration of radicals falls.

The activity of R–CHX–$\dot{C}H_2$ radicals depends little on the nature of the substituent X, and under otherwise similar conditions the reaction velocity is determined by the stability of the C–H bonds in the polymer molecule. The stability of these bonds is greatest in polyethylene, and therefore R–$\dot{C}H_2$ radicals are most easily detected in this polymer. The radicals R–O–$\dot{C}H_2$ are less active than R–CHX–$\dot{C}H_2$, and in polyformaldehyde transfer of a hydrogen atom begins to play a part at temperatures above 250°K.

Table 10. Rate constants of the destruction of alkyl and peroxide polymer radicals.

Polymer	Radicals	E, kcal mole^{-1}	$\lg k_0$ (M^{-1} s^{-1})	Refs.
Poly(vinyl acetate)		23	15	111*
Polystyrene	$-CH_2-\dot{C}H(C_6H_5)$	24	14	111*
Poly(methyl methacrylate)	$-CH_2-\dot{C}(CH_3)(COOCH_3)$	28	17	85
	$-CH_2-\dot{C}(CH_3)(COOCH_3)$	29	17	111*
	$-\overset{\displaystyle|}{C}-\dot{C}H-\overset{\displaystyle|}{C}-$	26	21	86
Poly(methyl acrylate)	$-CH_2-\dot{C}H(COOCH_3)$	44	31	31
Polyformaldehyde	$-O-\dot{C}H-O-$	19	14	87
Poly(vinyl chloride)		44	24	88
		38	20	89
Polypropylene		23	14	90
Poly(methyl methacrylate)	peroxide	17	12	86
	ditto	18	12	111**
Poly(vinyl acetate)	»	18	13	111**
Polystyrene	»	18	14	111**

*Values of k_0 given in Ref. 111 are probably wrong. The values of k_0 in Table 10 have been calculated by us from the data in Fig. 1 of Ref. 111.
**Values of E and k_0 calculated by us from data of Fig. 3 in Ref. 111.

Radicals of type R–CH_2–$\dot{C}XY$

The loss rate constants and activation energies for radicals of this type have been measured in poly(methyl methacrylate), polystyrene, poly(vinyl acetate), and certain other polymers (Table 10). These radicals differ markedly among themselves in stability. In polypropylene (see Table 9) transformations begin at 120–140°, but in poly(methyl methacrylate) and polystyrene the radicals are stable in a vacuum up to 350°K. Let us examine these extreme cases.

The CH_2–$\dot{C}H(CH_3)$ radicals in polypropylene probably disappear by the same mechanism as radicals of type R–$\dot{C}H_2$: The primary act is detachment of a hydrogen atom from a neighbouring chain. The former radicals should be more active than –CH_2–$\dot{C}H_2$ radicals in this reaction, but the C–H bonds are a few kilocalories less stable in polypropylene than in polyethylene. Therefore intermolecular transfer of the free valency is possible for both radicals at low temperatures.

In the activity sequence for substitution reactions CH_2–$\dot{C}(CH_3)(COOCH_3)$ radicals are nearly last (see subsection 1), and furthermore in the poly(methyl methacrylate) chain the methylene group containing the active hydrogen atom is located between quaternary carbon atoms carrying bulky substituents, so that migration of the free valency is sterically hindered. Nevertheless, breakdown (depolymerisation) of these radicals is quite rapid even at room temperature[86]. During depolymerisation the free valency moves along the chain at a speed of k_d chain units per second, and the possibility arises of encounters between radicals. If it is supposed that no energy barrier opposes the combination of radicals with each other, the loss rate constant with this mechanism of migration of the free valency is $k_m = k_d M/1000$ M^{-1} s^{-1}, where M is the molecular weight of the chain unit. At 330°K

$$k_d = 10^{12} \cdot \exp\left(-\frac{18000}{1.98 \cdot 330}\right) 10\ s^{-1}$$

whence $k_m \simeq 1$ M^{-1} s^{-1}, which coincides in order of magnitude† with the actual rate of loss at 330°K (Table 10), the conbination of each pair of radicals being accompanied by the separation of several monomer molecules[86]. At higher temperatures the rate of loss comes to exceed the calculated value ($E_{ds} = 28$ kcal, while $E_d = 18$ kcal). It is probable that, as the glass point is approached, migration of the free valency by a diffusion mechanism is not excluded.

Radicals with free valency in middle of chain

In poly(methyl methacrylate) these radicals become unstable at 250–270°K, and it may be supposed that the mobility of the free valency is largely due not to diffusion but to chemical reactions. At 250–300°K both hydrogen transfer and breakdown of the radicals may play a part. The relative rates of these reactions depend on the nature of the polymer:

$$\frac{W_{tr}}{W_d} = \frac{k_{0,tr}[M]}{k_{0,d}} \cdot \exp\left(\frac{E_d - E_{tr}}{RT_{st}}\right) \qquad (20)$$

where [M] is the concentration (molarity) of the polymer (in most cases $10 < [M] < 30$), $k_{0,tr}$ and E_{tr} are the preexponential factor and the activation energy for transfer of a hydrogen atom (it may be supposed that in solid polymers $k_{0,tr} \simeq 10^{6 \pm 1}$ M^{-1} s^{-1}—see subsection 1), and $k_{0,d}$ and E_d are the corresponding parameters for decomposition of the radicals (in order of magnitude $k_{0,d} \simeq 10^{12}$–10^{13} s^{-1}). Thus $W_{tr}/W_d = 10^{-5 \pm 1} \exp[(E_d - E_{tr})/RT_{st}]$. At $T_{st} = 250$–300°K with $E_d - E_{tr} > 8$ kcal mole^{-1}, we always have $W_{tr} > W_d$; conversely, when $E_d - E_{tr} < 6$ kcal mole^{-1}, the rate of decomposition will be higher than that of migration of the free valency.

In polyethylene and polypropylene $E_d > 25$ kcal mole^{-1}, while $E_{tr} < 15$ kcal mole^{-1}, i.e. $E_d - E_{tr} > 10$ kcal mole^{-1}, and near the stability temperature the rate of migration of the free valency should be much greater than the rate of decomposition of the radicals.

In polymers containing quaternary carbon atoms in the main chain E_d does not exceed 15–20 kcal mole^{-1} (Table 8) and $E_d - E_{tr}$ is small. In poly(methyl methacrylate)

† Under real conditions the probability of the reverse reaction increases as the monomer accumulates, and migration of the free valency takes place as a result of depolymerisation–polymerisation processes.

$E_d - E_{tr} \leq 5-6$ kcal mole^{-1}: i.e. the loss of radicals having the free valency in the middle of the chain would be due to decomposition reactions. This conclusion is supported by experiment: in poly(methyl methacrylate)[86], polystyrene[97], and other polymers of analogous structure loss is always accompanied by the ejection of products of low molecular weight, the quantity of which equals or exceeds the concentration of radicals [in polyalkenes the quantity of volatile products evolved at $T \leq T_{St}$ is smaller by factors of 10–1000 than in poly(methyl methacrylate)[112]].

Breakdown is followed by a series of further changes, leading to migration of the free valency and combination of the radicals. In poly(methyl methacrylate) the following reactions are possible[86]:

1. Breakdown of radicals:

$$-CXY-\dot{C}H-CXY- \longrightarrow -CXY-\dot{C}H_2 + CXY=CH-CXY-.$$

2. Depolymerisation with the separation of several monomer units.

3. Stabilisation

$$-CXY-\dot{C}H_2 + -CXY-CH_2-CXY- \rightarrow CXY-CH_3 + -CXY-\dot{C}H-CXY-$$

$$-CXY-\dot{C}H_2 + CH_2=CXY \rightarrow -CXY-CH_2-CH_2-\dot{C}XY;$$

4. Combination of mobile active radical $-CXY-\dot{C}H_2$ with fixed radicals $-CXY-\dot{C}H-CXY-$ or $-CH_2-\dot{C}XY$.

In polystyrene[97] decomposition is accompanied by the separation of the simple radicals $C_6H_5\dot{C}H_2$, $C_6H_5CH_2\dot{C}H_2$, etc., which diffuse into the interior of the polymer, and either combine with fixed radicals or abstract a hydrogen atom and are converted into saturated compounds—toluene, ethylbenzene, etc.

Breakdown always leads to migration of the free valency, which may occur as a consequence of construction of the ends of the disintegrated chain, depolymerisation, the formation and diffusion of simple radicals, etc. As a consequence of migration, radicals having the free valency in the middle of the chain are partly destroyed and partly stabilised, i.e. converted into a more stable form [in poly(methyl methacrylate) and polystyrene, for example, into radicals of the types $-CH_2-\dot{C}XY$ and $-CH_2-\dot{C}HX$]. The proportion of radicals lost

$$\omega = \frac{[R_0^{\cdot}] - [R_{st}^{\cdot}]}{[R_0^{\cdot}]} \qquad (21)$$

depends on the relative rates of combination and stabilisation. In poly(methyl methacrylate) $\omega \simeq 0.4$.[86,97]

Peroxy-radicals

In most vinyl polymers peroxy-radicals are lost in almost the same temperature range as are radicals having the free valency in the middle of the chain. The conversion of alkylated radicals of types (II) and (III) into the peroxide form

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot} \qquad (22)$$

is almost always equivalent to an increase in activity in hydrogen-transfer reactions

$$ROO^{\cdot} + HR_1 \rightarrow ROOH + R_1^{\cdot}. \qquad (23)$$

It would seem that repeated alternations of reactions (22) and (23) in the presence of oxygen should lead to migration of the free valency and loss of radicals[111]. Such a mechanism of migration represents an unbranched chain oxidation of the polymer. In most cases, however, the chain is relatively short, the number of oxygen molecules absorbed in the loss of one radical being respectively 5, 3–6, 3–7, and 1.5 in polyethylene[106], polypropylene[96], poly(vinyl chloride)[94,96], and poly(methyl methacrylate)[97]. Thus this mechanism, though at first glance extremely simple, cannot be regarded as the principal or only mechanism of migration of the free valency in the presence of oxygen.

A peculiar feature of reaction (23) is that abstraction of a hydrogen atom results in the formation of radicals having the free valency in the middle of the chain, whose stability is roughly the same as that of the ROO• radicals. Consequantly reaction (23) causes further migration of the free valency by a mechanism which is specific for a given polymer. In polyalkenes this may be stepwise transer of the free valency[94,107]. In poly(methyl methacrylate) and polystyrene, radicals having the free valency in the middle of the chain break down with the separation of products of low molecular weight[97]. The migration is accomplished quite rapidly—more rapidly than oxidation of the alkylated radicals formed—and the next oxygen molecule adds to the already stabilised decomposition products. Therefore many similar rules apply to the loss of peroxy-radicals and of radicals having the free valency in the middle of the chain[97] (volatile products having the same composition, same stability, etc.).

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Of the two parts of the review the first—the e.s.r. spectroscopic section—will probably leave a more complete impression than the second, more chemical part. The non-equivalence of these sections reflects the present-day state of research into the structure and the properties of polymer radicals.

One of the chief tasks of the e.s.r. spectroscopy of polymer radicals is to study the relation between the structure of radicals and their e.s.r. spectra. Work in this field is still far from complete, but considerable progess has been made during the past few years. Two or three years ago tens of investigations were devoted to deciphering a single spectrum, but now the possibility is already being discussed of predicting the hyperfine structure of the spectra due to very simple radicals.

Research on elementary radical reactions in solid polymers is at an earlier stage of development: theoretical concepts have not yet been established, and there is no generally accepted view on the formal kinetic laws, while many conclusions must for the present be compared with results for analogous reactions in liquid and gaseous phases. However, estimates have already appeared for the kinetic constants of radical reactions in the solid phase, and the elementary mechanism of complicated processes, such as the migration and destruction of radical states, oxidation, etc., is being discussed. It may be hoped that in the near future more serious generalisations will appear, with conclusions on the nature of the reactions undergon by radicals in solid polymers.

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