at a known concentration[12]. Various substances can be made to react directly with the ozone in an inert solvent medium[13].

Solutions of ozone may be stored in stainless steel bottles[11] of 5, 10, and 15 l capacity (calculated as 100% ozone). Below -50° these solutions may be stored indefinitely. At room temperature the decomposition time of the ozone (time for 50% decomposition of the stored ozone) is of the order of weeks. As a rule, vessels containing dissolved ozone are stored at -30° and transported at -15°. At the latter temperature the solutions can be kept for one month. The rate of decomposition of the ozone depends on the nature of the Freon and on the shape of the vessel. Solutions of ozone in Freon-12 have been examined for sensitivity towards mechanical, electrical, and explosive shocks, and for temperature resistance[19]. The sensitivity of both the vapour phase and the liquid phase of a 10% solution of ozone in Freon-12 towards a high-voltage electrical discharge and towards detonation at high pressures was tested. No detonation took place when explosion was initiated in the gas or the liquid phase of a 12% solution of ozone in Freon-12 at -78° and 105 atm (of helium). The gas and the liquid phase were tested for shock resistance by dropping a 5.6 kg weight from 35 cm, but it was found that solutions containing 10 wt.% of ozone in Freon-12 are completely safe at -78°. Experiments on the effect of temperature showed that increase in temperature does not produce an explosion, or even appreciable decomposition of the ozone.

We have recently confirmed[20] that solutions of pure ozone in Freon-12 and -113 can be prepared, and handled with safety during liquid-phase reactions with alkalis and peroxidic compounds.

1. G.M.Platz and C.K.Hersh, Ind.Eng.Chem., 48, 742 (1956).
2. I.A.Semiokhin, G.M.Panchenkov, V.K.Korovkin, and A.V.Borisov, Zhur.Fiz.Khim., 33, 1933 (1959) [Russ.J. Phys.Chem., 226 (1959)].
3. Welsbach Co., U.S.P. 2 809 881 (1957); Chem.Abs., 52, 8646a (1958).
4. C.Brown, J.Chem.Phys., 23, 1342 (1955).
5. M.G.Terekhova, A.N.Mal'tsev, E.N.Eremin, and N.I.Kobozev, "Pervaya Vsesoyuznaya Mezhvuzovskaya Konferentsiya po Ozonu, Tezisy Dokladov" (Abstracts of Papers Presented to the First All-Union Intercollegiate Conference on Ozone), Izd.Moskov.Univ., Moscow, 1960, p.28.
6. G.A.Cook, "Ozone Chemistry and Technology", Advances in Chemistry Ser. 21, Amer.Chem.Soc., Washington, 1959, p.44.
7. E.Brinner and E.Perrottet, Helv.Chim.Acta, 22, 585 (1939).
8. T.S.Logan, U.S.P. 3 136 607 (1964); Chem.Abs., 61, 5229d (1964).
9. A.Chrétien, M.Servigne, and F.Mahieux, Bull.Soc.chim. France, 49 (1960).
10. F.Mahieux, Bull.Soc.chim.France, 746 (1960).
11. L'Air Liquide, No.40, 1–7 (1962).
12. F.Mahieux, Chim.et Industrie, 87, 756 (1962).
13. F.Mahieux, Bull.Soc.chim.France, 2 (1962).
14. M.Servigne and F.Mahieux, Bull.Soc.chim.France, 488 (1960).
15. F.Mahieux, Bull.Soc.chim.France, 2275 (1961).
16. F.Mahieux, French P. 1246273 (1960); Chem.Abs., 60, 11648a (1964).
17. L.Streng, J.Chem.Phys., 38, 1788 (1964).
18. A.G.Streng and A.V.Grosse, J.Amer.Chem.Soc., 81, 805 (1959).
19. C.S.Stones, W.J.Murphy, F.R.Flint, and A.E.Potter, Ind. Eng.Chem., 4, 176 (1965).
20. I.I.Vol'nov, S.A.Tokareva, V.I.Klimanov, and G.P.Pilipenko, Izv.Akad.Nauk SSSR, Ser.Khim., 1267 (1966).

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APPLICATION OF ELECTRON SPIN RESONANCE IN POLYMER CHEMISTRY

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Electron spin resonance (ESR) is the name given to the resonance absorption of the energy of an oscillating magnetic field by a paramagnetic substance in which the field induces transitions of unpaired electrons between split Zeeman levels. The ESR phenomenon was discovered by Zavoiskii[1] and interpreted theoretically for the first time by Frenkel'[2]. The ESR method is of particular value for the study of free radicals, because of its high sensitivity, the possibility of investigating free radicals directly in the course of reactions, and also the completeness and uniqueness of the information about their structure thus obtained. The number of ESR studies on free radicals is extremely large. In this review we shall confine ourselves to certain results relevant to the physics and chemistry of polymers.

I. THEORETICAL FOUNDATIONS OF THE ESR METHOD

1. The Basic Features of the Phenomenon

Consider a specimen containing unpaired electrons, for example a reaction mixture with free radicals. In the absence of an external magnetic field, all orientations of the spins and magnetic moments of the electrons have the same energies. An external magnetic field removes the degeneracy: only two orientations of the spins and magnetic moments of the electrons are now possible, along and against the field, since the electron spin is $S = 1/2$ and according to quantisation rules only $2S + 1 = 2$ states are possible. This means that the zero energy level splits into

two sublevels (Zeeman effect) and the electrons are distributed between these sublevels (Fig. 1) in accordance with the Boltzmann law:

$$\frac{n_1}{n_2} = e^{-\frac{\Delta E}{kT}}, \quad (1)$$

where n_1 and n_2 are the numbers of electrons in the upper and lower levels, ΔE is the energy difference between the levels, T is the absolute temperature, and k the Boltzmann constant. The magnitude of the Zeeman splitting is

$$\Delta E = g\beta H. \quad (2)$$

In this expression β is a Bohr magneton and g the spectroscopic splitting factor, which is 2.0023 for a "free" electron. For most of the radicals investigated, the g-factor differs only slightly from this value. If in addition to the permanent magnetic field H an oscillating magnetic field with frequency ν acts on the specimen such that

$$h\nu = g\beta H \quad (3)$$

and directed perpendicular to the permanent magnetic field, the electrons pass from the lower to the upper level with absorption of energy from the field. At the same time electron transitions from the upper to the lower level with emission of energy are induced. But, since according to Eqn. (1) the number of electrons n_2 in the lower level is higher than the number of electrons in the upper level, it follows that on average there will be more transitions per unit time from the lower to the upper level than in the reverse direction, i.e. the oscillating magnetic field will tend to equalise the populations of the levels and its energy will be absorbed.

At the same time there exist the so-called relaxation processes which tend to restore the initial "Boltzmann" distribution of electrons, whereby their excess energy is converted into thermal lattice vibrations (spin–lattice relaxation) or the energy is redistributed among the electrons themselves (spin–spin relaxation). The rates of these relaxation processes, which can be characterised by the corresponding relaxation times T_1 and T_2 (the times during which the excess energy decreases by a factor of e), determine the maximum intensity of the oscillating magnetic field for which the Boltzmann distribution is still maintained. If, as happens fairly frequently (for example in macroradicals in polymers), the relaxation times are relatively high, thermal equilibrium breaks down at relatively low intensities (of the order of 1 mV) and the energy absorbed by the specimen from the oscillating magnetic field ceases to be proportional to the incident energy (saturation effect). In the absence of saturation, the energy absorbed per unit mass of the paramagnetic substance is defined by the expression

$$P_\nu = \frac{\pi^2}{2} \frac{N_0 g^2 \beta^2}{3kT} S(S+1) H_\sim^2 \nu^2 I(\nu). \quad (4)$$

Here N_0 is the number of unpaired electrons per gramme of the substance, $H_\sim$ the amplitude of the oscillating magnetic field, and $I(\nu)$ a "function of the line form". This function takes into account the finite width of the paramagnetic absorption line and is normalised in such a way that $\int_{-\infty}^{+\infty} I(\nu)d\nu = 1$. Bearing in mind that for lines which are not too broad one can put with sufficient accuracy $\nu = \nu_{res}$, we obtain the following expression for the total integral energy absorbed by unit mass of the specimen with $S = 1/2$

$$P = \pi^2 \frac{N_0 g^2 \beta^2}{3kT} H_\sim^2 \nu_{res}^2 = \frac{\pi^2 g^4 \beta^2}{3kTh^2} H_{res}^2 H_\sim^2 N_0. \quad (5)$$

The condition of the absence of saturation can be written in the form

$$\frac{1}{4}\gamma^2 H_\sim^2 T_1 T_2 \ll 1 \quad (6)$$

where γ is the gyromagnetic ratio for the electron.

2. Parameters of the Spectral Line

Fig. 2 shows the variation of the energy of the oscillating magnetic field P absorbed by the paramagnetic specimen with the strength of the steady magnetic field H for a constant frequency of the variable magnetic field. This is the relation one has in mind when one speaks of the ESR "spectrum". Fig. 2 shows the singlet spectrum corresponding to the structure of the energy levels in Fig. 1. The ESR spectrum can be characterised by the following fundamental parameters: intensity, g-factor (or the resonance strength of the magnetic field H_{res}), and the width and form of the lines.

Intensity of the spectrum. The intensity of the ESR spectrum is understood as the area S under the curve describing the variation of the energy of the oscillating magnetic field absorbed by the specimen with the strength H of the steady magnetic field (Fig. 2). It follows from Eqn. (4) that, other conditions being equal, the intensity of the spectrum is proportional to the number of unpaired electrons per gramme of the test substance:

$$N_0 = \alpha S, \quad (7)$$

where α is a proportionality coefficient which depends on the units in which S is measured and on the parameters of

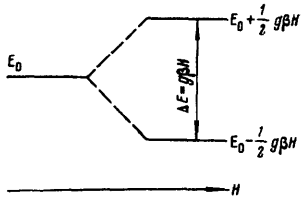


Fig. 1. Schematic representation of the Zeeman splitting of electronic levels.

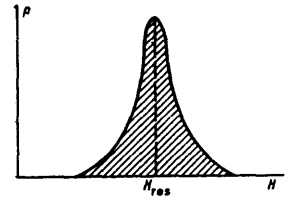


Fig. 2. A singlet ESR spectrum.

the measuring system. Thus if the coefficient α is known, the determination of the concentration of unpaired electrons in the specimen requires the experimental measurement of S. On the other hand, if α is unknown it is necessary to determine under identical conditions the values of S and S_{st} for the test specimen and a standard specimen with a known concentration N_{st} of unpaired electrons. Then the concentration of unpaired electrons in the test specimen is given by the expression

$$N_0 = N_{st}\frac{S}{S_{st}}. \quad (8)$$

The second method is in fact normally used in practice.

The g-factor. The g-factor is a measure of the contribution of the orbital magnetism to the total magnetic moment of the unpaired electron. The weaker is the interaction between the spin and the orbital momenta, the smaller is the difference between the g-factors of the paramagnetic substance under test and that of the free electron. As already stated, this is in fact what happens in free radicals. Since in most cases free radicals are complex asymmetric species, their orbital degeneracy is removed by the internal electric field, which arises from the surrounding atoms, and the orbital magnetism is greatly suppressed. For this reason, the spin–orbital coupling of the unpaired electron in free radicals is usually very weak. Only in rare cases does the g-factor of free radicals differ from that of the free electron by more than several thousandths (for example, $g > 2.01$ for radicals with an unpaired electron at a sulphur atom). On the other hand, in paramagnetic ions whose unpaired electrons belong to a deeply embedded d-shell, appreciable spin–orbital coupling is often observed. Since the g-factor can be determined with very high accuracy, its measurement can provide definite information about the magnitude of the spin–orbital coupling and can be used for the identification of free radicals.

It should be noted that, generally speaking, the g-factor is a tensor quantity. Therefore in single-crystal (or strongly oriented) specimens anisotropy of the g-factor can be sometimes observed. In other cases the anisotropy of the g-factor can cause some broadening of the resonance lines.

The form and width of the lines. The lifetime of unpaired electrons in the excited state, i.e. in the upper Zeeman level, determines the width of the ESR spectral line, in accordance with the uncertainty principle. The following fundamental processes determine the lifetime of excited unpaired electrons: (a) spin–lattice interaction; (b) spin–spin dipole interaction; (c) exchange interaction.

The transfer of energy from unpaired electrons to the molecules of the substance or to the lattice constitutes the basis of the mechanism of the *spin–lattice* relaxation. The coupling between the spin system and the lattice is magnetic (spin–orbital interaction). However, as already stated, the spin–orbital coupling in free radicals is weak. Therefore the spin–lattice relaxation time T_1 is relatively large (it can reach several seconds) and cannot make an appreciable contribution to the broadening of the resonance line. At the same time the large value of T_1 can in fact be responsible for the saturation effect.

Spin–spin interaction. Each unpaired electron in the constant external magnetic field H is acted upon, apart from the external field, by the local fields H_{loc} due to the magnetic moments of other electrons. The result is that the resonance condition (3) can be satisfied for individual unpaired electrons at various values of H, i.e. the resonance line is broadened. The strength of the local fields is inversely proportional to the cube of the distance between the unpaired electrons. Therefore spin–spin interaction increases with the concentration of unpaired electrons in the specimen and their interaction often in fact determines the width and form of the spectral lines. Two limiting cases of spin–spin interaction are possible.

a. The paramagnetic species are at large distances from one another and interact only during collisions, the duration of which is short compared with the periods between the collisions (this case obtains in gaseous and liquid phases at low concentrations of the paramagnetic species). The line form is then described by a Lorentzian curve:

$$I_L(H) = \frac{I_L(H_0)}{1+\left(\frac{H-H_0}{\Delta H_L}\right)^2}. \quad (9)$$

b. The paramagnetic species are in different quasi-steady-state local magnetic fields (solid phase, high concentration of paramagnetic species). In the absence of exchange interaction, the line form is in this case gaussian

$$I_G(H) = I_G(H_0)e^{-\frac{(H-H_0)^2}{\Delta H_G}}. \quad (10)$$

The characteristic line parameters ΔH_L and ΔH_G are related in the following way to the experimental line width $\Delta H_{1/2}$ at half the peak height:

$$\Delta H_L = 0.5\ \Delta H_{1/2};\quad \Delta H_G = \frac{1}{2\ln 2}\Delta H_{1/2}. \quad (11)$$

Exchange narrowing. If the local magnetic fields in which the paramagnetic species are situated change fairly rapidly, they become averaged out and line narrowing results. Such averaging out can be due to an exchange effect. The exchange effect arises when, as a result of their high concentration the electron clouds of the paramagnetic species begin to overlap. Extensive delocalisation of the unpaired electrons and rapid motion of the paramagnetic species can also lead to the averaging out of the local magnetic field. In all these cases the paramagnetic resonance lines become narrower in the central region, approaching Lorentzian line shape.

3. Hyperfine Structure (HFS) of the ESR Spectra

The hyperfine structure of the ESR spectra is due to the interaction of the unpaired electrons with the paramagnetic nuclei. According to the quantisation rules, the magnetic moment of a nucleus with a spin I has $2I + 1$ possible orientations relative to the external magnetic field. An additional magnetic field, set up by the nucleus at the location of the electron, has values corresponding to each of these orientations. Therefore each level is split into $2I + 1$ sublevels. The oscillating magnetic field does not give rise to reorientation of the nucleus, since its frequency does not correspond to resonance with respect to the nuclear transitions. Consequently the following selection rules operate for the electronic transitions: $\Delta M_I = 0$ and $\Delta S_Z = \pm 1$ (M_I is the nuclear magnetic quantum number and S_Z the projection of the electron spin in the direction of the field). As a result $2I + 1$ lines at equal distances appear in the spectrum. Fig. 3 shows as an example (in a schematic form) the splitting of the electronic levels in the interaction of an unpaired electron with a single proton ($I = 1/2$). It is seen

that a doublet is obtained instead of a singlet spectrum. In most modern ESR spectrometers the derivative of the absorption line with respect to the magnetic field (dI/dH) is recorded, rather than the line itself. For this reason, the spectral lines are of the form shown in the lower part of Fig. 3.

If the unpaired electron interacts with several magnetic nuclei, $\prod_r (2I_r + 1)$ lines of equal intensity appear in the spectrum (I_r is the spin of nucleus r). If the splitting due to different nuclei is such that the corresponding numbers of lines are integral multiples of one another, some lines overlap. The intensities of the components of such a spectrum bear simple multiple relations to one another. In practice, one frequently encounters the case where the interaction of an unpaired electron with several protons is the same. The number of lines in this spectrum is then $n + 1$ (where n is the number of protons) and the relative intensity of the kth line from the beginning of the spectrum is given by the coefficients of Newton's binomial:

$$C_n^{k-1} = \frac{n!}{(k-1)!\,(n-k+1)!}. \qquad (12)$$

Thus interaction with two protons gives rise to three lines with intensity ratios of 1 : 2 : 1 and interaction with three protons gives rise to four lines with intensity ratios of 1 : 3 : 3 : 1.

The interaction of electron spin with the magnetic moment of the nucleus consists of two parts [3]. The first part is analogous to the usual dipole–dipole interaction between two magnetic moments. This interaction depends on the direction of the external magnetic field relative to the radius vector joining the electron to the nucleus, and is therefore referred to as anisotropic. The second part is due to the isotropic contact interaction, which is independent of the direction and is proportional to the square of the modulus of the electronic wave function at the point where the nucleus is located.

Since the majority of free radicals have been investigated in the non-crystalline (or polycrystalline) state, the anisotropic interaction in them as a rule does not give rise to hyperfine structure, resulting only in the broadening of the spectral line. For this reason, the hyperfine structure of the spectrum of free radicals is usually caused by the isotropic interaction. This interaction is non-zero only when the density of the unpaired electron cloud is non-zero at the point where the nucleus is located. Only atomic s-orbitals or molecular σ-orbitals have a finite electron density at the nucleus and consequently can participate in the isotropic hyperfine interaction.

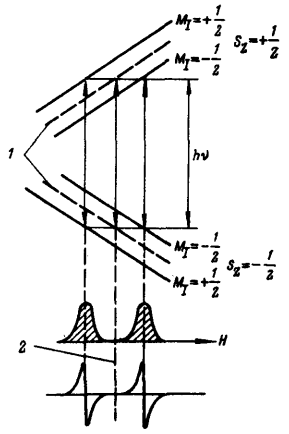


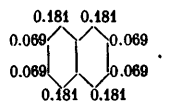
Fig. 3. Formation of the hyperfine structure of the ESR spectrum:
1) initial electronic levels; 2) position of the line in the absence of hyperfine splitting.

From this point of view, there should be no contact hyperfine interaction in aromatic free radicals, since the unpaired electrons in these radicals are located in π-orbitals with zero electron density in the plane of the ring where the hydrogen atoms are located. Nevertheless, the spectra of the majority of aromatic free radicals have a complex and highly resolved hyperfine structure. This can be understood within the framework of configurational interaction [4]. The result of such interaction is that a certain proportion of the excited σ-orbital state becomes combined with the purely π-orbital state of the electron. This leads to non-zero electron density in the plane of the ring and the appearance of hyperfine structure.

The hyperfine splitting ΔH can be calculated from the formula

$$\Delta H = Q\rho \qquad (13)$$

where Q is a constant (28 Oe for the aromatic CH bond) and ρ the unpaired electron density at the carbon atom to which the given hydrogen atom is joined. The distribution of electrons in conjugated systems between various carbon atoms is calculated by the usual methods of quantum chemistry — the valence bond or molecular orbital methods. We shall quote the distribution of electron density in the naphthalene radical-ion $C_{10}H_8^-$, which is a well-known initiator of anionic polymerisation. Calculation by the molecular orbital method yields the following distribution:



Consequently, theory predicts that, as regards their interaction with an unpaired electron, protons can be divided into two groups. Each group includes four protons and therefore a spectrum consisting of (4 + 1)(4 + 1) = = 25 lines may be expected, and is in fact observed experimentally.

In non-conjugated systems the principal mechanism of the interaction of the unpaired electron with hydrogen atoms is the so-called hyperconjugation. The phenomenon consists essentially in the overlapping of the orbitals of the radical π-electron with the electron clouds of other atoms. As a result, non-zero unpaired electron density can appear at the location of the nuclei of these atoms. For example, in ethyl radicals $CH_3-\dot{C}H_2$ the unpaired electron interacts not only with the two protons of the methylene group but also with the three protons of the methyl group. The spectrum of ethyl radicals produced on irradiation of ethane [5] shows that the unpaired electron interacts somewhat more strongly with the protons of the methyl group. This gives rise to a hyperfine structure of twelve lines (Fig. 4). The theory of hyperconjugation was developed by Mulliken and coworkers [6-9] and applied for the first time by McLachlan [10] to the calculation of ESR spectra. Vol'kenshtein and Milevskaya [11,12] used this theory to calculate the spectra of polymeric radicals. They obtained expressions

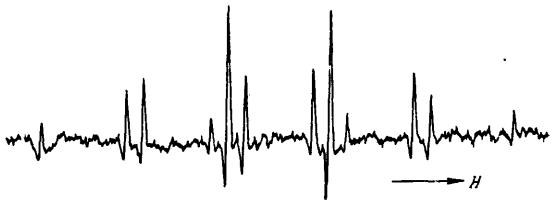


Fig. 4. ESR spectrum of the ethyl radical.

for the hyperfine splitting by the protons of the methyl and methylene groups joined to the carbon atom with the unpaired electron. When the possible conformations of the macroradicals and the statistical weights of these conformations are known, these expressions make it possible to estimate the hyperfine structure of the spectrum. Conversely, when a highly resolved structure of the ESR spectrum is available, it can be used to estimate the conformations of the radicals.

II. ELECTRON SPIN RESONANCE TECHNIQUE

The vast majority of the ESR spectrometers used nowadays operate in the ultrahigh frequency range, namely in the vicinity of 10^{10} c/s (wavelength 3 cm). The strength of the constant magnetic fields is then about 3000 Oe. Fig. 5 shows the block-circuit of an ESR spectrometer. The principal elements of this circuit are present in the majority of spectrometers, despite the wide variety of designs employed. A reflex klystron is normally used as a source of electromagnetic waves. The electromagnetic waves are conducted via a wave guide to a cavity resonator in which the test specimen is located. The frequency of the klystron oscillations is maintained to a high accuracy, with the aid of a special electronic circuit, at the value equal to the resonant frequency of the cavity. The resonator is positioned between the poles of a magnet (usually an electromagnet) in such a way that the ultrahigh frequency magnetic field in the specimen is perpendicular to the steady magnetic field.

The resonator is connected by a second wave guide to a crystal ultrahigh frequency detector. If the strength of the magnetic field is now altered, then under resonance conditions the ultrahigh frequency power dissipated in the resonator increases and a smaller power is applied to the detector. Various ways of recording the paramagnetic resonance signal are possible. In one of them the strength of the steady magnetic field is adjusted close to the resonance value and then an additional low-frequency magnetic field, whose amplitude greatly exceeds the width of the absorption line, is established in the gap of the magnet with the aid of special coils. This gives rise to a signal at the output from the detector corresponding to the form of the absorption line, at a frequency equal to twice the modulation frequency. After amplification with a broad-band amplifier, the signal can be detected on the oscilloscope screen. However, the need to use a broad-band amplifier in this method of signal detection greatly reduces the sensitivity of the spectrometer, because, in addition to the useful signal, the interfering noise signals which may originate from the klystron oscillator and the detector, are also amplified. Therefore this method can be used only when the test specimen contains a large number of free radicals.

If high sensitivity is required, another method of detecting the ESR signal is used. In this method the field of the electromagnet is varied linearly with time (Fig. 6) and passes through the resonance value. At the same time a radio-frequency magnetic field is set up with the aid of modulation coils. However, now its amplitude must be smaller than the width of the resonance line. It is readily seen that in this case we shall have at the output from the detector a variable potential with a frequency equal to the modulation frequency. This potential is amplified by a narrow-band resonance amplifier and is rectified with a phase-sensitive detector fitted with a very narrow-band filter. The form of the rectified signal corresponds to the first derivative of the absorption line. The signal is recorded with a pen recorder. The possibility of using very narrow-band filters (about 0.1 c/s) in this method of recording greatly increases the useful signal : noise ratio, since the noise is proportional to the square root of the transmission band width. The reduction of noise is also facilitated by the fact that a fairly high (up to 1 Mc/s) modulation frequency of the magnetic field is usually chosen.

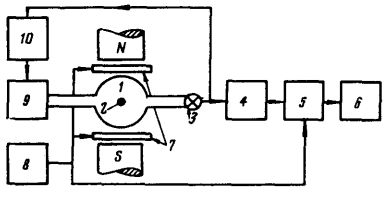


Fig. 5. Block-circuit of an ESR spectrometer:
1) cavity resonator; 2) specimen; 3) crystal detector; 4) amplifier; 5) phase-sensitive detector; 6) pen recorder; 7) modulating coils; 8) modulation generator; 9) Klystron; 10) AFC (automatic frequency control).

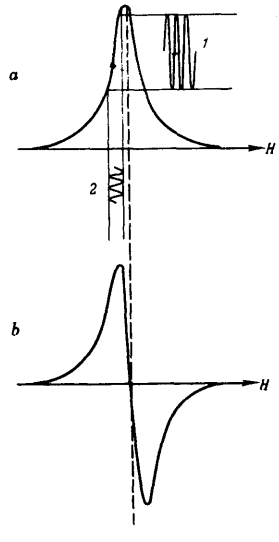


Fig. 6. Method using low amplitude modulation of the magnetic field:
1) resultant modulation of the ultrahigh frequency signal; 2) modulation of the magnetic field.

This makes it possible to avoid to a large extent the low-frequency noise from the crystal detector which occurs at the spectral density maximum. This spectrometer is one of the most widely used.

The type of resonator used in the spectrometer is determined by the specific features of the investigation. It is possible to use not only the transmission cavity shown in Fig. 5 but also a reflection cavity with an ultrahigh frequency compensating network. The superheterodyne method of signal detection is also employed, abeit much more rarely.

However, we shall not consider these problems in detail, the readers being referred to the appropriate literature [13,14]. In conclusion of this section we shall only mention that the maximum sensitivity of the existing spectrometers corresponds to 10^{-12}–10^{-13} mole of crystalline diphenylpicrylhydrazyl (DPPH) free radicals. But, since in most cases one deals not with crystalline materials but with solutions (or, for example, with polymerisation mixtures), greater interest attaches to concentration sensitivity, i.e. the minimum concentration of radicals which can be measured. Under most favourable conditions (specimen with small dielectric losses, correctly chosen relative dimensions of the resonator and specimen), the sensitivity corresponds approximately to 10^{-7} M for a spectral width of about 3 Oe.

III. INVESTIGATION OF FREE RADICALS BY THE ELECTRON SPIN RESONANCE METHOD

All studies on the electron spin resonance of free radicals can be divided into two large groups – the study of stable free radicals and the study of active intermediate radicals and reactions in which they participate.

1. Stable Free Radicals. Inhibition of Polymerisation

Apart from the naphthalene radical-ion discussed above, numerous stable and semistable radicals with a more or less complex system of conjugated bonds have been investigated: triphenylmethyl, semiquinones, $\alpha\alpha$-diphenyl-β-picrylhydrazyl, and many others. In recent years much attention has been given to the synthesis of polymers with a system of conjugated π-bonds. These polymers are organic semiconductors and frequently give a narrow singlet ESR signal.

Semistable and stable radicals are formed from radical reaction (oxidation and polymerisation) inhibitors. These are radicals derived from quinones and semiquinones, aromatic amines, aromatic nitro-compounds, and polycyclic hydrocarbons. The ESR method permits a quantitative approach to inhibition processes.

The study of the inhibition of polymerisation by this method [15] led to the discovery of a new important fact, namely that up to four inhibitor molecules are consumed and an equal number of stable radicals are formed for each active radical destroyed. This very large "stoichiometric coefficient", given by the expression

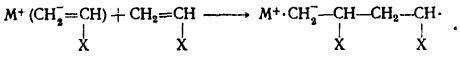
$$\frac{\text{number of inhibitor molecules consumed,}}{\text{number of deactivated radicals}}$$

implies that in the reaction of an active radical with an inhibitor molecule there forms initially a "hot" radical with an excess of vibrational energy, which is capable of further reactions with the monomer or other inhibitor molecules. Only after several such steps is the energy of the radicals reduced so much that they no longer initiate polymerisation. When an inert solvent is introduced into the system, the hot radicals are "cooled" as a result of collisions with solvent molecules and the stoichiometric coefficient tends to unity. The presence of hot radicals in polymerisation is evidence that energy chains can occur even in liquid-phase reactions.

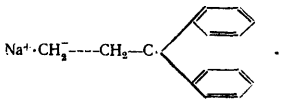
2. Active Free Radicals. Polymerisation

As already stated, the sensitivity of modern ESR spectrometers is in most cases insufficient to investigate free-radical reactions in the liquid phase. However, it proved possible with their aid to solve certain important problems of polymerisation theory. An example of this kind is the mechanism of the initiation of polymerisation by alkali metals.

The hypothetical polymerisation mechanism was as follows. A complex consisting of the monomer molecule and a metal atom (charge-transfer complex) attacks a new monomer molecule and gives rise to a radical-ion which subsequently either recombines at the radical centre or grows in two directions at once:



To confirm this mechanism, it was necessary to detect the free radicals in the polymerising system. This was done in the polymerisation of diphenylethylene under the action of metallic sodium [16]:



In this case the radical proved to be so stable that it did not recombine and chain growth took place at the anionic centre.

The classical examples of radical polymerisation could be investigated only under special conditions. In 1953 Bamford and Jenkins showed [17] that in the polymerisation of certain monomers, in which the polymers formed are insoluble, part of the macroradicals are captured by the precipitated gel and stabilised. The ESR spectra of such radicals in polyacrylonitrile were investigated by Bamford and coworkers [18].

In 1958 Ingram and coworkers [19] succeeded in investigating the spectra of many free macroradicals by adding a precipitant to the polymerisation system. Another method of producing a large number of macroradicals was used by Fraenkel et al. [20] and Atherton et al. [21] It consists in the addition to the system of a certain amount of a cross-linking agent. During polymerisation part of the radicals remain trapped in the three-dimensional network formed. Finally, the spectra of radicals trapped in poly(methyl methacrylate) and poly(vinyl acetate) after the onset of the so-called gel-effect in photopolymerisation have been investigated [20,22]. However, it has been shown [22] that the trapped radicals are a side-product of the reaction and their concentration is not directly related to the process kinetics.

O'Donnell et al. [23] investigated the solid-phase polymerisation of barium methacrylate dihydrate. Irradiation at -196° of a single crystal of barium methacrylate dihydrate

gives rise to a fully isotropic spectrum which is attributed to $(CH_3)_2\dot{C}COO^-$ radicals formed when hydrogen adds to the double bond of the methacrylate ion. When the specimen is heated to 20°, a new, anisotropic spectrum appears, with nine lines if the magnetic field is parallel to the *a* or *b* axes of the pseudo-orthorhombic crystal and with 13 lines if the field is parallel to the *c* axis. This spectrum is attributed to the radical of the growing chain:

$$RCH_2\dot{C}(CH_3)COO^-.$$

The anisotropic properties of the spectrum showed that the growing radicals have a definite crystallographic orientation, or, in other words, the distribution of the monomer molecules in the crystal lattice determines the position of the growing macroradical.

3. Macroradicals in Solid Polymers. Structure and Spectra

In 1951 Schneider and coworkers[24] observed the ESR spectrum of X-irradiated poly(methyl methacrylate). Their results and also subsequent studies showed that polymers are excellent media for the trapping of free radicals. The great advantage of polymeric matrices is the possibility of investigation of the radicals formed therein at relatively high temperatures (up to the softening temperature of the polymers), because of the powerful inhibition of the motion of the polymeric chains. This greatly extends the range of free-radical processes which can be studied by the ESR method, the polymer constituting an irreplaceable model system for the investigation of fundamental free radical reactions. A wide variety of methods for the preparation of radicals are used: radiolysis under the action of radiation of all types, trapping of free radicals in polymerisation processes, mechanical destruction of polymers.

The greatest number of studies on the electron spin resonance of irradiated polymers were undertaken to interpret the ESR spectra and to determine the structure of macroradicals. It can now be regarded as established[25-27] that, on irradiation of polyethylene at a low temperature, alkyl radicals are formed as a result of the scission of hydrogen atoms:

$$\sim CH_2-CH_2-\dot{C}H-CH_2-CH_2\sim.$$

Their spectrum consists of six lines corresponding to the interaction of the unpaired electron with one α-proton and with four β-protons. On raising the temperature (and also when the irradiation is carried out at room temperature), the spectrum disappears and the spectrum of another radical with an odd number of lines is observed. The latter is most likely due to radicals of an allyl type:

$$\sim CH_2-\dot{C}H-CH=CH_2\sim.$$

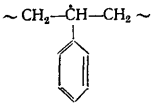
Such radicals are also produced as a result of the migration of the unpaired electron along the polymeric chain (via a consecutive relay-type transfer of hydrogen atoms) and its trapping by the double bond formed in consequence of radiolysis.

The ESR spectrum of the macroradicals in irradiated Teflon has also been investigated[28-30]. The spectrum is due to fluoroalkyl radicals:

$$\sim CF_2-CF_2-\dot{C}F-CF_2-CF_2\sim.$$

At room temperature the spectrum consists of ten lines due to the interaction of the unpaired electron with the fluorine atoms in the α- and β-positions. At a high temperature (250°) it is possible to observe an additional splitting caused by the interaction of the unpaired electron with the fluorine atoms in the γ-position.

The spectrum of free polystyrene radicals has been investigated in the course of the mechanical destruction of polystyrene in a vacuum[31,32] (Fig. 7). It consists of a poorly resolved triplet with a separation of 19 Oe between the components. Most probably this spectrum is due to radicals of the type



which can form as a result of the removal of hydrogen atoms from the polymeric chain by the more active primary radicals generated in the mechanical destruction of polystyrene. The hyperfine structure is formed as a result of the interaction of the unpaired electron with the protons of the neighbouring methylene groups. The non-equivalence of the protons (equivalent interaction of the unpaired electron with four protons would have given rise to a five-line spectrum) can be explained by the impossibility of free rotation of these groups about the C–C bonds. The relatively low extent of hyperfine splitting of the spectrum is due to the considerable delocalisation of the unpaired electron in the phenyl ring and the decrease of its density at the carbon atoms of the chain. Such delocalisation is possible if the plane of the ring coincides with the plane of the corresponding section of the chain. At the same time the electron density at the individual atoms within the ring is insufficient to give rise to additional lines and is responsible only for a certain broadening of the main lines. It is interesting that the hyperfine splitting in the spectrum of radicals generated in the mechanical destruction of isotactic polystyrene[31] is 34 Oe. This difference can be explained by the fact that the phenyl rings in isotactic polystyrene lie in planes almost perpendicular to the main chain and therefore they cannot withdraw the unpaired electron by conjugation. The ratio of the extents of splitting in the spectra of atactic and isotactic polystyrene is in good agreement with the ratio of the unpaired electron densities at the α-atom of the polystyrene radical calculated by the molecular orbital method for parallel and perpendicular orientations of the phenyl ring[12].

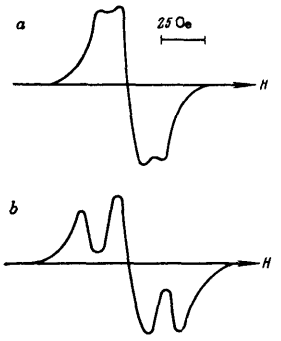


Fig. 7. ESR spectra of polystyrene macroradicals:
a) atactic polystyrene; *b*) isotactic polystyrene.

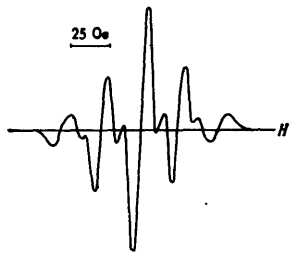
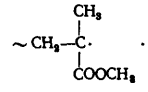


Fig. 8. ESR spectrum of poly(methyl methacrylate) macroradicals.

Fig. 8 shows the spectrum of the macroradicals in poly(methyl methacrylate). It is of the same form regardless of the methods of obtaining the radicals and is a result of the superposition of two series of hyperfine structure lines, a quintuplet and a quadruplet, with binomial intensity distributions in each series. The distances between the neighbouring lines in both series are the same and equal to 26 Oe. The centres of these spectra coincide, so that the quadruplet lines are located in the gaps between the quintuplet lines.

In 1958 Ingram et al.[19] and Abraham et al.[33] put forward the hypothesis that the ESR spectrum of poly(methyl methacrylate) is due to growing polymeric chain radicals:



The presence of two series of lines in the spectrum is then explained by the existence of definite conformations of these radicals, arising because of the impossibility of free rotation of the methylene group. In one of the conformations both protons of the methylene group are close to the nodal plane of the π-electron cloud of the unpaired electrons, interacting only weakly with the latter. This conformation corresponds to the quadruplet spectrum, which reflects the equivalent interaction of the unpaired electron with the three protons of the methyl group. In the other conformation one of the protons of the methylene group is located close to the meridian plane of the unpaired electron cloud and interacts with the latter in the same way as the protons of the methyl group. The four protons give rise to the quintuplet. On the other hand, the second proton of the methylene group interacts only very weakly with the unpaired electron. This hypothesis was subsequently confirmed in experiments on deuteriated derivatives of poly(methyl methacrylate)[34,35]. When both hydrogen atoms of the methylene group are replaced by deuterium atoms, only the quadruplet series remains in the ESR spectrum. This is explained by the fact that the hyperfine structure associated with deuterium atoms is usually unresolved. For this reason, the replacement of a hydrogen atom by deuterium is equivalent to the elimination of this atom from participation in the generation of the hyperfine structure. The quadruplet spectrum remaining after the substitution of the hydrogen atoms of the methylene group by deuterium corresponds to the interaction of the unpaired electron with the protons of the methyl group. When the protons of the methyl group are replaced by deuterium, there remains only a doublet spectrum corresponding to the interaction of the unpaired electron with one of the protons of the methylene group. Recently Fischer[36] investigated the polymerisation of methyl methacrylate in aqueous emulsion and established that the spectra produced in this process consist of the familiar groups of four and five lines, but each of these lines is in turn split into several further lines. This is probably due to the fact that, when the spectra of radicals in the liquid phase are observed, it is possible to achieve the resolution of the additional splitting by the protons of the methylene group, which in the solid phase is masked as a result of the line broadening caused by the anisotropic interaction.

IV. REACTIONS OF MACRORADICALS IN POLYMERS

1. Destruction of Macroradicals

The processes involved in the destruction of macroradicals in polyethylene after radiolysis were studied by several groups of investigators. In all these experiments it was established that the alkyl radicals are rapidly destroyed on raising the temperature of the specimen, while the destruction of the allyl radicals is very much slower. The kinetics of the destruction of radicals proved to be different in the experiments of various workers. Thus Lawton et al.[27] found that the kinetics of the destruction of alkyl radicals is consistent with a first-order equation. Charlesby et al.[37] observed the destruction of alkyl radicals according to a bimolecular law. Cracco et al.[38] established that alkyl radicals recombine according to a first-order law but with two different rate constants. On the other hand, allyl radicals are destroyed by a process which is neither of first nor of second order according to Charlesby et al.[37] and which is of first order according to Lawton et al.[27] Lawton[27] explains the kinetics of radical destruction (which he observed) as a result of the non-uniform distribution of the radicals in space. Charlesby et al.[37] suggest a uniform distribution of radicals and believe that a mechanism involving the migration of the radical state along the chain is responsible for their destruction.

The reason for the differences between the rates of destruction of radicals in the studies quoted above should probably be sought in the differences between the polyethylene specimens investigated (for example, it has been established[37] that the rate of destruction of alkyl radicals in specimens of low-pressure polyethylene is much higher than in high-pressure polyethylene). Possibly this is the explanation of the different kinetics of the destruction processes.

The recombination of radicals in Teflon has been investigated in detail by Tsvetkov et al.[39], who studied the recombination of both the initial fluoroalkyl radicals and the peroxy-radicals produced in the interaction between the initial radicals and oxygen. They established that the recombination in Teflon can be described by the usual bimolecular law, assuming that the recombination rate constant in the amorphous phase is higher than in the crystalline phase (specimens of different degrees of crystallinity were investigated). The recombination rate constants were determined from the rates of recombination of the peroxy- and fluoroalkyl radicals.

Ohnishi and Nitta[40] studied the destruction of radicals in irradiated poly(methyl methacrylate). They established that several hours after the beginning of the reaction the bimolecular law comes to hold exactly for the destruction of

radicals. On the other hand, in the first few hours deviations from the second-order law are observed. Shida et al.[41] investigated the destruction of radicals in irradiated poly(methyl methacrylate) during the initial period (up to 20 min) and found that the destruction of radicals is governed by a monomolecular law. Ohnishi and Nitta[40] determined the activation energy for radical recombination, which proved to be 28 kcal mole^{-1}. They believe that the radicals recombine as a result of the rotation of molecular segments, the activation energy for which has the same value[42]. Ohnishi and Nitta[40] found that the destruction of radicals is accelerated by oxygen, but failed to explain this phenomenon.

The recombination of macroradicals in γ-irradiated poly(vinyl chloride) has been investigated by Kuri et al.[43] and also by Egorova et al.[44] In both studies it was established that the destruction of radicals proceeds according to a second-order law with an activation energy of 38 kcal × × mole^{-1} [43] or 44 kcal mole^{-1}.[44] Like Ohnishi and Nitta[40], Kuri et al.[43] noted that oxygen accelerates the destruction of radicals.

It is noteworthy that in all the studies examined (with the exception perhaps of the work of Charlesby et al.[37]) it was assumed that the destruction of radicals in polymers occurs in the course of the collision during the rotation or displacement of smaller or larger sections of the polymeric chains. However, analysis of the available data[45,46] on the diffusional mobility of polymeric molecules shows that the idea of the interaction of macroradicals via collisions is inapplicable to the solid phase. Furthermore, the mechanism of the destruction of free radicals in polymers involving simply their collision as a result of mechanical displacement cannot account for the accelerating effect of oxygen on the destruction of macroradicals and the different rates of destruction of peroxy- and hydrocarbon radicals. Therefore it must be assumed that a different mechanism of the interaction between radicals obtains in polymers. Such mechanism is migration of radical states, whose existence has been established by Bresler et al.[32] This mechanism consists in the removal by the macroradicals of hydrogen atoms from the neighbouring chains, which results in the migration of the radical centre within the polymer. Such migration continues until two radical centres collide and annihilate one another by recombination or disproportionation. These workers investigated the destruction of macroradicals produced in the mechanical breakdown of polystyrene, poly(methyl methacrylate), and poly(vinyl acetate). The experiments showed that the destruction of radicals in the initial stages of the process is fully consistent with bimolecular kinetics and the reaction rate constants determined from the kinetic curves are consistent with the Arrhenius equation. The rate constants for the destruction of macroradicals are listed in Table 1.

It is noteworthy that the constants listed in Table 1 were determined with an accuracy limited by a factor having the dimensions of volume. The explanation is that, as shown by experiments on the reactions of macroradicals produced in the mechanical degradation of polymers by various gaseous agents, these radicals are not distributed uniformly throughout the bulk of the polymer, but are concentrated in a thin surface layer whose thickness is unknown. When oxygen is admitted into the tube containing the particles of the polymer with the macroradicals, the radicals are oxidised at a very high rate and are converted into peroxy-radicals with a characteristic asymmetric spectrum (Fig. 9). At temperatures below -50° the number of peroxy-radicals does

TABLE 1.

Polymer	$K = k/V$, mole^{-1} s^{-1}
Poly(methyl methacrylate)	$10^{18} \exp [(-29000 \pm 2000)/RT]$
Poly(vinyl acetate)	$10^{20} \exp [(-23000 \pm 1000)/RT]$
Polystyrene	$10^{20} \exp [(-24000 \pm 2000)/RT]$

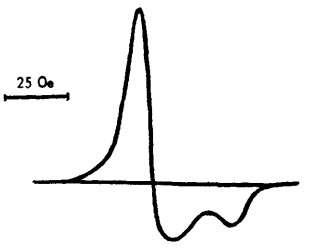


Fig. 9. ESR spectrum of peroxy-macroradicals.

not change at an appreciable rate. On raising the temperature, they begin to interact and disappear many times faster than the radicals with an unpaired electron at a carbon atom. In this case the equation for bimolecular kinetics is fully satisfied. The rate constants for the destruction of the peroxy-radicals are listed in Table 2.

It is seen that in polystyrene, for example at 20°, the peroxy-macroradicals disappear one thousand times faster than the intrinsic macroradicals of polystyrene. This is irreconcilable with the explanation of the radical destruction by collisions, because it is clear that the mechanical mobility of the initial and peroxy-radicals is identical. From the standpoint of the hydrogen removal process, the entire picture is clear: the primary radicals are relatively inactive and remove hydrogen from the neighbouring chains with difficulty. On the other hand, the peroxy-radicals are very reactive in the hydrogen removal step. There is yet another observation confirming the mechanism involving the migration of radical states. If after complete oxidation of the initial radicals the pressure of oxygen is reduced, the rate of destruction of radicals falls. At first sight this finding appears to be extremely surprising, because it would appear that molecular oxygen can have no influence on the behaviour of peroxy-radicals. However, from the standpoint of the radical state migration mechanism this phenomenon is quite natural. If there were no excess of dissolved oxygen in the polymer, the migration process would come to a stop when the peroxy-radicals became converted into secondary hydrocarbon radicals. No further reaction would then occur. On the other hand, when the system contains oxygen, the latter again adds to the new radical, removes hydrogen once more, etc. until two radicals annihilate one another as a result of a random

TABLE 2.

Polymer	$K = k/V$, mole^{-1} s^{-1}	Oxygen pressure, mmHg
Poly(methyl methacrylate)	$10^{21} \exp [(-23000 \pm 500)/RT]$	760
Poly(vinyl acetate)	$10^{14} \exp [(-14500 \pm 500)/RT]$	760
Polystyrene	$10^{15} \exp [(-12000 \pm 500)/RT]$	760
Polystyrene	$10^{14} \exp [(-12000 \pm 500)/RT]$	0.1

encounter. Thus the relay-type hydrogen transfer process is accompanied by chain oxidation of the polymer:

$$R\cdot + O_2 \rightarrow RO_2^{\cdot};\ RO_2^{\cdot} + R'H \rightarrow ROOH + R'\cdot;\ R'\cdot + O_2 \rightarrow R'O_2\cdot$$

and so on. The accumulation of peroxides in the polymer was confirmed by a special experiment.

2. Oxidation

The possibility of studying the reactions of macroradicals in polymers with various gaseous agents was demonstrated in several investigations. Thus Kuri and Ueda [47] studied the effect of sulphur dioxide on the radicals of various irradiated polymers. Kuri et al. [43] established that gases such as H_2S, NO, NO_2, and I_2 very rapidly destroy the radicals in irradiated poly(vinyl chloride), while hydrogen and sulphur dioxide do not react with the radicals. In another study Kuri et al. [48] observed the reactions of various gases with radicals in irradiated acrylamide and methacrylamide. The reactions of polymeric radicals with various gaseous agents were studied by Tsvetkov et al. [49]; they investigated the oxidation of fluoroalkyl radicals and their interaction with hydrogen and nitric oxide.

Several typical reactions, such as oxidation, removal of hydrogen, and the addition of monomers, were studied by Bresler et al. [50] In this investigation macroradicals were produced by mechanical destruction of polystyrene, poly(methyl methacrylate), and poly(vinyl acetate). The oxidation of radicals was studied at an oxygen pressure of 760 mmHg and at low temperatures. The kinetics of the process were followed by observing the increase of the intensity of the spectrum due to peroxy-radicals. In order to separate the overlapping spectra of the peroxy-radicals and the initial hydrocarbon radicals, the experiments were performed at a relatively high level of microwave power in the cavity (about 25 mV). Under these conditions strong saturation of the spectra of the primary radicals takes place, so that they are virtually undetectable and the spectra of the peroxy-radicals, which are saturated to a much smaller extent, are observed against what is virtually a zero background. The kinetics of the oxidation reaction are satisfactorily consistent with a monomolecular law, showing that the radicals are located in the immediate vicinity of the surface formed on breakdown of the polymers. Table 3 presents the oxidation rate constants calculated from the experimental data. It should be borne in mind that such determination does not yield the true oxidation rate constant but the product of the constant and the concentration of oxygen. Since on changing the temperature the concentrations of adsorbed and desorbed oxygen also change, the dissolution and adsorption of oxygen in polymers were studied and the temperature variation of the concentration of sorbed oxygen was determined [51] in order to find the true oxidation rate constant. The true constants k for the oxidation of polymeric radicals were determined by dividing the experimental constants K by the concentration of oxygen $[O_2]$.

TABLE 3.

Polymer	$K = k[O_2]$, s^{-1}	k, $cm^3\ s^{-1}$
Poly(methyl methacrylate)	$20 \exp[(-4000 \pm 200)/RT]$	$6.0 \cdot 10^{-15} \exp[(-7900 \pm 500)/RT]$
Poly(vinyl acetate)	$3 \exp[(-2000 \pm 200)/RT]$	$1.6 \cdot 10^{-15} \exp[(-5900 \pm 500)/RT]$
Polystyrene	$0.2 \exp[(-1200 \pm 200)/RT]$	$4.0 \cdot 10^{-17} \exp[(-5300 \pm 500)/RT]$

3. Removal of Hydrogen

The next type of reaction which has been investigated is the abstraction of hydrogen by macroradicals. Cumene was used as the hydrogen donor. When cumene vapour is admitted into the tube with the specimen containing free radicals, the intensity of the spectrum due to the initial radicals decreases. A new spectrum does not appear because the low-molecular cumenyl radicals formed in this reaction rapidly recombine. Since the diffusion coefficients of cumene in polymers are very low, it was to be expected that the reaction of radicals with cumene would occur only on the surface of the polymer. Indeed experiment shows that the destruction of radicals is entirely consistent with monomolecular kinetics. The rate constants K calculated from the experimental data are presented in Table 4.

If the cumene adsorption constants are taken into account, the true constants k for the removal of hydrogen are obtained (last column of Table 4). In the temperature range investigated polystyrene radicals do not react with cumene at an appreciable rate. This finding may appear surprising, since, judging from the activation energies for the recombination and oxidation of radicals, polystyrene radicals should be no less active than the other radicals investigated. Thus we see that there is no direct correlation between the activity of the radical in a given reaction and the corresponding activation energy. This is because the preexponential factor, which can vary markedly from radical to radical, is no less rate-determining than the activation energy. Indeed, if, for example, we calculate the exponential terms in the rate constant expressions for the reactions of poly(methyl methacrylate) and poly(vinyl acetate) radicals with cumene at 250°K, we find that they differ only by a factor of 50. At the same time, the preexponential factors for these constants differ by a factor of 10^5.

4. Monomer Addition Reaction

The addition of the methyl methacrylate monomer to the macroradicals in polystyrene and poly(vinyl acetate) has been investigated. When the monomer vapour at a pressure of 10 mmHg is admitted into the tube containing a specimen of the ruptured polymer, the spectrum of the initial methyl methacrylate radicals changes at a very high rate (close to room temperature). The kinetics of the process were followed in this case by observing the increase in the intensity of the new spectrum, since it is much broader than the spectrum of the initial radicals and the extreme lines of its hyperfine structure do not overlap with the initial spectral lines, which makes it possible to separate the spectra of methyl methacrylate and other radicals. Here too the shape of the kinetic curves is entirely consistent with monomolecular kinetics and the temperature variation of the reaction rate constants agrees with the Arrhenius law. The rate constants K are listed in Table 5, which also includes the constants determined taking into account the monomer adsorption constants.

TABLE 4.

Polymer	$K = k$[cumene], s^{-1}	k, $cm^3\ s^{-1}$
Poly(methyl methacrylate)	$2 \cdot 10^8 \exp[(-13000 \pm 1000)/RT]$	$2 \cdot 10^4 \exp[(-38000 \pm 1500)/RT]$
Poly(vinyl acetate)	$3 \cdot 10^{10} \exp[(-16000 \pm 1000)/RT]$	$2 \cdot 10^9 \exp[(-36000 \pm 1500)/RT]$

TABLE 5.

Polymer	$K = k[\text{monomer}]_0$, s^{-1}	k, $cm^2\ s^{-1}$
Poly(vinyl acetate)	$3 \cdot 10^{13} \exp[(-22000 \pm 1000)/RT]$	$10^{13} \exp[(-35000 \pm 1500)/RT]$
Polystyrene	$2 \cdot 10^{13} \exp[(-7500 \pm 500)/RT]$	$2 \exp[(-19800 \pm 1000)/RT]$

5. Some Problems of the Reactivity of Macroradicals

In the examination of the experimental data obtained[32,50] attention is drawn to the high activation energies for the reactions investigated compared with those for reactions in gas or liquid phases. Indeed the recombination of radicals in gas and liquid phases involves very low (virtually zero) activation energies. On the other hand, the activation energies found for macroradical destruction processes in solid polymers exceeds 20 kcal $mole^{-1}$. The reaction involving the removal of hydrogen by macroradicals may be compared with the chain transfer reaction in polymerisation. However, the activation energy for chain transfer in liquid-phase radical polymerisation of vinyl monomers is on average 10–15 kcal $mole^{-1}$, i.e. lower by a factor of more than two than the experimental activation energies for the reactions of macroradicals with cumene. The same may be said of the monomer addition reaction: the analogous chain growth reaction in polymerisation involves much smaller activation energies.

We shall now examine the problem of the absolute rate of destruction of macroradicals which should obtain on the basis of the radical state migration mechanism. For a free radical to be capable of removing a hydrogen atom from a neighbouring unit of the polymeric chain, it must first of all migrate over a distance δ separating it from this unit, i.e. on average over a distance of 3–5 Å (cross-sectional diameter of the polymeric chain). The time required for this is given by the formula

$$\tau = \tau_0 \exp(E_m/RT) \tag{14}$$

where E_m is the activation energy for the migration of the radical centre and the preexponential factor $\tau_0 = h/kT$ (h is the Planck constant, k the Boltzmann constant, and T the absolute temperature). Consequently, the frequency of the collisions of the given radical with hydrogen atoms is

$$\nu = \frac{1}{\tau} = = \frac{kT}{h} \exp(-E_m/RT). \tag{15}$$

However, each collision does not of course lead to the removal of hydrogen. The frequency of effective collisions, i.e. those which can lead to the removal of hydrogen atoms by the radical, is evidently

$$\nu_{eff} = \nu e^{\frac{-E_1 + S_1 T}{RT}} \tag{16}$$

where E_1 is the activation energy and S_1 the entropy of activation in the hydrogen removal reaction.

The average rate of movement of the radical centre is in this case

$$V = \delta \nu_{eff} = \delta \frac{kT}{h} e^{S_1/R} e^{-\frac{E_m + E_1}{RT}}. \tag{17}$$

Hence we find that the number of collisions of radical centres with each other per unit time is

$$N = V \sigma n^2 = \frac{\delta kT}{h} e^{S/R} e^{-\frac{E_m + E_1}{RT}} \sigma n^2 \tag{18}$$

where σ is the effective cross-section for the collision of two radical centres, and n the number of radical centres per unit volume. Knowing the number of collisions, we can express the rate of the bimolecular recombination or disproportionation reaction in the form

$$-\frac{dn}{dt} = N e^{S_2/R} e^{-E_2/RT} \tag{19}$$

where S_2 is the entropy of activation in the reaction of radicals with one another and E_2 the activation energy for this reaction. On combining Eqns. (18) and (19), we obtain finally

$$-\frac{dn}{dt} = A e^{\frac{S_1 + S_2}{R}} e^{-\frac{E_m + E_1 + E_2}{RT}} n^2. \tag{20}$$

Thus we see that the measured activation energy is the sum of the activation energies for three processes. In order to determine the activation energy for the intrinsic macroradical recombination process, it is necessary to subtract from the experimental value the activation energies for the migration of the radical centre and for the removal of hydrogen. The first of these energies probably does not differ markedly from the activation energy for the diffusion of low-molecular substances in polymers, say the monomer, i.e. is 13–15 kcal $mole^{-1}$. The activation energies for the removal of hydrogen should probably be the same as those for chain transfer in polymerisation, i.e. about 10–15 kcal $mole^{-1}$. Thus the sum of these two activation energies is 23–30 kcal $mole^{-1}$. We see that these values are very close to the experimental activation energies for the destruction of the initial hydrocarbon radicals. Hence follows the conclusion that the activation energy for the intrinsic macroradical recombination process is virtually zero, in complete agreement with all data on the recombination of radicals in gas and liquid phases.

It is readily seen that, for reactions of macroradicals with various reagents, the diffusion coefficients of the low-molecular reagents in the solid polymers should be included as multipliers in the rate constants for the reactions†. This is clear from the following considerations. Diffusion in solids is known[52] to be effected by successive jumps of the molecules (or atoms) between certain equilibrium positions. Suppose that the residence time of the molecules of the low-molecular reagent in an equilibrium position is τ and the distance between two neighbouring equilibrium positions is δ. Then the average rate of migration of these molecules is

$$\bar{u} = \delta/\tau \tag{21}$$

and the number of binary collisions of the reagent molecules with free radicals per second is

$$N = \bar{u} \sigma [R][C] \tag{22}$$

where σ is the effective collision cross-section and [R] and [C] are the concentrations of the radicals and the reagent molecules. According to Frenkel'[52], the diffusion coefficient can be expressed as follows in terms of δ and τ:

$$D = \frac{\delta^2}{\tau}. \tag{23}$$

† It must be emphasised that what is meant here is not the diffusion of these molecules from outside into the polymer but their thermal motion within the surface layer, which is so thin that the time required for the attainment in it of a steady-state concentration of the reacting molecules is much smaller than the reaction time.

From the last three equations, we obtain for the number of binary collisions the expression

$$N = A_1 D [R][C]. \quad (24)$$

Hence the reaction rate constant can be written thus:

$$k = A_1 D e^{-\frac{\epsilon}{RT}} \quad (25)$$

where ϵ is the activation energy for the reaction. However, the diffusion coefficient D also depends on temperature:

$$D = D_0 e^{-\frac{E}{RT}}. \quad (26)$$

Here E is the activation energy for the diffusion process. On substituting Eqn. (26) in Eqn. (25), we obtain the final expression for the reaction rate constant:

$$k = A_2 e^{-\frac{E+\epsilon}{RT}}. \quad (27)$$

Thus the experimental activation energy is essentially the sum of the activation energies for the intrinsic reaction of the radical with the reagent molecule and for the diffusion of the latter. Table 6 presents the values for monomer addition reactions obtained by subtracting from the experimental activation energies (Table 5) the activation energies for the diffusion of the monomer in polymers.

It is seen that the activation energies thus obtained are very close to the values known for liquid-phase reactions. This is evidence in favour of the validity of the hypothesis concerning the effect of diffusion on the rate of reaction.

On the basis of the data presented, one may arrive at certain conclusions concerning the relative reactivity of macroradicals in oxidation, hydrogen removal, and double bond opening reactions. Data on the interaction of macroradicals with cumene and methyl methacrylate show that the activation energy is not a fully comprehensive characteristic of the reactivity of free radicals. The preexponential factor is often decisive.

From the standpoint of the theory of absolute reaction rates, the difference in the reactivities of radicals is explained by the difference in the free energies of the active complexes. The free energy, which comprises the energies of the atoms combined in the molecule minus the molecular entropy multiplied by the absolute temperature, can in fact serve as a true measure of the activity of a particular radical. It is by no means surprising that, on transition to the active-complex state, the number of degrees of freedom of a system consisting of a radical and molecule which it is attacking can change significantly, if only because such attack presupposes a highly specific mutual disposition of the two species. This means that there is also a marked change in the entropy of the system, i.e. ultimately considerable deviations of the preexponential factor from the value predicted by the collision theory are obtained. It is remarkable that a phenomenon similar to that described above is also observed in the usual radical polymerisation. Table 7 presents data on chain propagation rates in the polymerisation of certain vinyl monomers. The data were taken from Bengough and Melville[53].

TABLE 6.

Polymer	E, cal mole^{-1}
Poly(vinyl acetate)	11000±2000
Polystyrene	6800±1000

TABLE 7.

Monomer (T = 30°)	Rate constant, litre × mole^{-1} s^{-1}	E, kcal mole^{-1}	Preexponential factor $10^7 A$, litre × ×mole^{-1} s^{-1}
Vinyl acetate	1240	7.3	24.0
Styrene	55	7.8	2.2
Methyl methacrylate	143	6.1	0.5
Methyl acrylate	720	7.1	10.0

It is seen that, within the vinyl series alone, the absolute rates of chain propagation can vary by a factor as large as 25 (vinyl acetate–styrene). At the same time, the activation energies are almost identical. This implies that all the differences are due to the steric factor, i.e. the steric conditions which obtain when the macroradical approaches the monomeric molecule.

The macroradicals which have been investigated by the present authors can be arranged in the same activity series as regards the monomer addition and oxidation reactions: vinyl acetate, styrene, methyl methacrylate. In the reaction involving the removal of hydrogen from cumene the activity series changes, since styrene proves to be virtually inert at the temperatures investigated.

V. MACRORADICALS IN THE MECHANICAL DEGRADATION OF POLYMERS

In 1959 Bresler et al.[31] observed for the first time by the ESR method the free radicals which are generated in polymers on their mechanical breakdown. Subsequently this method of producing radicals in polymers was used by other workers[54,55]. The ESR study of the free radicals produced in the mechanical breakdown of polymers will undoubtedly play a major role in the elucidation of the physics of mechanical action on polymers themselves. Thus Zhurkov et al.[56] investigated the radicals produced on unidirectional compression of ebonite and their accumulation as deformation increases. When the deformation is relaxed, the number of radicals falls. The study of radicals produced on stretching Kapron‡ fibres[57] revealed a considerable similarity between the radical accumulation curves and the creep curves for the material, which indicates a relation between the creep and the number of ruptured chemical bonds.

1. E.K. Zavoiskii, Doctoral Thesis, FIAN (Institute of Physics, USSR Academy of Sciences), Moscow, 1944.
2. Ya.I. Frenkel', Zhur. Eksper. Teor Fiz., 15, 409 (1954).
3. A. Abraham and M.H.L. Pryce, Proc. Roy. Soc., A 205, 135 (1951).
4. H.M. McConnel and D.B. Chestnut, J. Chem. Phys., 27, 984 (1957).
5. R.W. Fessenden and R.H. Schuler, J. Chem. Phys., 33, 935 (1960).
6. R.S. Mulliken and C.C.J. Roothaan, Chem. Rev., 41, 219 (1947).
7. R.S. Mulliken and C.A. Rieke, J. Amer. Chem. Soc., 63, 41, 1770 (1941).
8. R.S. Mulliken, J. Chem. Phys., 7, 339 (1932).
9. N. Miller, L.W. Picket, and R.S. Mulliken, J. Amer. Chem. Soc., 76, 4770 (1954).

‡ Material similar to Nylon produced in the USSR (Ed. of Translation).

10. A.D.McLachlan, Mol.Phys., 1, 233 (1958).
11. I.S.Milevskaya and M.V.Vol'kenshtein, Optika i Spektrosk., 11, 349 (1961).
12. I.S.Milevskaya and M.V.Vol'kenshtein, Optika i Spektrosk., 12, 381 (1962).
13. G.Feher, Bell System Tech.J., 36, 4444 (1957).
14. D.J.E.Ingram, "Free Radicals as Studied by Electron Spin Resonance", London, 1958.
15. F.Tüdös, "Some Problems of the Kinetics of Radical Polymerisation" (Translated into Russian), Budapest, 1965.
16. K.Hirota and K.Kuwata, J.Polymer Sci., 60, S52 (1962).
17. C.H.Bamford and A.D.Jenkins, Proc.Roy.Soc., A249, 445 (1959).
18. C.H.Bamford, A.D.Jenkins, D.J.E.Ingram, and M.C.R.Symons, Nature, 175, 894 (1955).
19. D.J.E.Ingram, M.C.R.Symons, and M.G.Townsend, Trans. Faraday Soc., 54, 409 (1958).
20. G.K.Fraenkel, J.M.Hirshon, and C.Walling, J.Amer.Chem. Soc., 76, 3606 (1954).
21. M.M.Atherton, H.W.Melville, and D.H.Whiffen, Trans. Faraday Soc., 54, 1300 (1958).
22. S.E.Bresler, E.N.Kazbekov, and E.M.Saminskii, Vysokomol.Soed., 1, 1519 (1959).
23. J.H.O'Donnell, B.McGarvey, and H.Morawetz, J.Amer. Chem.Soc., 86, 2322 (1964).
24. E.E.Schneider, M.J.Day, and G.Stein, Nature, 168, 644 (1951).
25. A.T.Koritskii, Yu.N.Molin, V.N.Shamshev, N.N.Buben, and V.V.Voevodskii, Vysokomol.Soed., 1, 1182 (1959).
26. B.Smaller and M.S.Matheson, J.Chem.Phys., 28, 1169 (1958).
27. E.J.Lawton, J.S.Balwit, and R.S.Powell, J.Chem.Phys., 33, 295 (1960).
28. E.E.Schneider, J.Chem.Phys., 23, 978 (1955).
29. H.N.Rexroad and W.Gordy, J.Chem.Phys., 30, 399 (1959).
30. Ya.S.Lebedev, Yu.N.Tsvetkov, and V.V.Voevodskii, Optika i Spektrosk., 8, 811 (1960).
31. S.E.Bresler, S.N.Zhurkov, E.N.Kazbekov, E.M.Saminskii, and E.E.Tomashevskii, Zhur.Tekh.Fiz., 29, 359 (1959).
32. S.E.Bresler, E.N.Kazbekov, V.N.Fomichev, F.Sech, and P.Smeitek, Fiz.Tverd.Tela, 5, 675 (1963).
33. R.J.Abraham, H.W.Melville, D.W.Ovenall, and D.H.Whiffen, Trans.Faraday Soc., 54, 1133 (1958).
34. P.Kourim and K.Vacek, Tetrahedron Letters, 23, 1051 (1962).
35. M.Lazar and F.Szocs, Polymers Letters, in the press.
36. H.Fischer, J.Polymer Sci., 2, 529 (1964).
37. A.Charlesby, D.Libby, and M.G.Ormerod, Proc.Roy.Soc., A262, 207 (1961).
38. F.Cracco, A.J.Arvia, and M.Dole, J.Chem.Phys., 37, 2449 (1962).
39. Yu.D.Tsvetkov, Ya.S.Lebedev, and V.V.Voevodskii, Vysokomol.Soed., 3, 882 (1961).
40. S.I.Ohnishi and J.Nitta, J.Polymer Sci., 38, 451 (1959).
41. S.Shida, J.Higuchi, R.Kusaku, and T.Miyamae, Symposium on Radiation Chemistry, Japan, 1958 (quoted after Bresler et al.[31]).
42. J.G.Powels, J.Polymer Sci., 22, 79 (1956).
43. Z.Kuri, H.Ueda, and S.Shida, J.Chem.Phys., 32, 371 (1960).
44. Z.S.Egorova, Yu.M.Malinskii, V.L.Karpov, A.E.Kalmanson, and L.A.Blyumenfel'd, Vysokomol.Soed., 4, 64 (1962).
45. F.Bueche, W.M.Cashin, and P.Debue, J.Chem.Phys., 20, 1956 (1952).
46. T.G.Fox and P.J.Flory, J.Appl.Phys., 21, 581 (1950).
47. Z.Kuri and H.Ueda, J.Polymer Sci., 50, 349 (1961).
48. Z.Kuri, H.Ueda, and S.Shida, J.Chem.Phys., 32, 371 (1960).
49. Yu.D.Tsvetkov, Ya.S.Lebedev, and V.V.Voevodskii, Vysokomol.Soed., 1, 1934 (1959).
50. S.E.Bresler, E.N.Kazbekov, and V.N.Fomichev, Kinetika i Kataliz, 6, 820 ((1965).
51. E.N.Kazbekov, Candidate's Thesis, Institute of Macromolecular Compounds, USSR Academy of Sciences, Leningrad, 1963.
52. Ya.I.Frenkel', "Kineticheskaya Teoriya Zhidkosti" (Kinetic Theory of Liquids), Izd.Akad.Nauk SSSR, Moscow, 1945.
53. W.J.Bengough and H.W.Melville, Proc.Roy.Soc., A230, 429 (1955).
54. P.Yu.Butyagin and A.A.Berlin, Vysokomol.Soed., 1, 865 (1959).
55. S.N.Zhurkov, E.E.Tomashevskii, and V.A.Zakrevskii, Fiz.Tverd.Tela, 3, 2841 (1961).
56. S.N.Zhurkov, V.A.Zakrevskii, and E.E.Tomashevskii, Fiz.Tverd.Tela, 6, 1912 (1964).
57. E.N.Zhurkov, A.Ya.Savostin, and E.E.Tomashevskii, Dokl. Akad.Nauk SSSR, 159, 303 (1964).

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