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Abstract

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ON THE MECHANISM OF RADIOLYSIS OF POLYISOBUTYLENE

The use of EPR in combination with other methods of investigation makes it possible in many cases to obtain highly valuable information on radiation-chemical changes in polymers. In the present work, the accumulation, nature, and possible reactions of free radicals formed upon irradiation of polyisobutylene (PIB) are considered, and certain assumptions are put forward concerning the mechanism of radiolysis of this polymer.

Purified samples of industrial PIB were irradiated in high vacuum ($\sim 10^{-5}$ mm Hg) with γ-rays (Co^{60}; 20,000 g-eqv. radium) or with accelerated electrons (1.6 MeV) at various temperatures. The EPR spectra were recorded on an EPR-2 spectrometer of the Institute of Chemical Physics, Academy of Sciences of the USSR. To determine the absolute concentration of radicals, single crystals of $CuCl_2 \cdot 2H_2O$ with a known content of paramagnetic ions were used.

From Fig. 1, which gives typical curves for the accumulation of radical products in irradiated PIB, it is seen that the amount of radicals formed as a result of irradiation at temperatures below the glass-transition temperature of the polymer ($\sim -65°$) is proportional to the irradiation dose up to comparatively high dose values and is about $0.8 \div 1.5$ radicals/100 eV.

Irradiation above the glass-transition temperature sharply lowers the yield of radicals, which is evidently associated with an increase in the rate of their disappearance as a result of the increased mobility of macromolecules in the polymer.

The EPR spectrum of radicals accumulating at the temperature of liquid nitrogen coincides completely with that published in works ([1,2]) and is a doublet, which can be attributed to only one type of radical: $C(CH_3)_2-\dot{C}H-C(CH_3)_2$ (I), formed as a result of the removal of a hydrogen atom from the polymer molecule. However, the results of investigation of the final products of PIB radiolysis (degradation, gas evolution, formation of double bonds) show that, apparently, in the radiolysis of PIB, in addition to I, radicals of another structure are formed; but because of their higher reactivity they enter into reactions already at low temperatures and cannot be registered by the EPR method at $-196°$ and above.

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

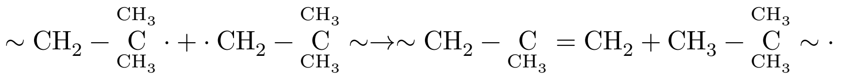
Such radicals may be radicals formed as a result of rupture of the main chain of the polymer:

$$\begin{aligned}&\sim \mathrm{CH_2 - C(CH_3)_2 - CH_2 - C(CH_3)_2} \sim \\ &\quad \rightsquigarrow \sim \mathrm{CH_2 - \dot{C}(CH_3)_2 + \dot{C}H_2 - C(CH_3)_2} \sim\end{aligned} \tag{1}$$

or as a result of abstraction of hydrogen atoms and methyl groups from the polymer molecule:

$$\sim \mathrm{CH_2 - C(\dot{C}H_2)(CH_3)} \sim \quad \text{and} \quad \sim \mathrm{CH_2 - \dot{C}(CH_3)} \sim .$$

Irradiation of PIB at −196° without intermediate warming of the sample leads to the accumulation in the polymer of vinylidene-type double bonds, the number of which does not increase after the disappearance of all frozen macroradicals (^{3}). This result shows that radicals II and III, even at the temperature of liquid nitrogen, enter into a disproportionation reaction:



$$\sim \mathrm{CH_2} - \overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}} \cdot + \cdot \mathrm{CH_2} - \overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}} \sim\rightarrow\sim \mathrm{CH_2} - \underset{\mathrm{CH_3}}{\mathrm{C}} = \mathrm{CH_2} + \mathrm{CH_3} - \overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}} \sim \cdot \tag{2}$$

Hydrogen atoms and methyl radicals formed upon rupture of the $C-H$ and $C-CH_3$ bonds apparently react with saturated polymer chains with formation of hydrogen and methane. The absence of a temperature dependence of the total yield of these products shows that such a reaction proceeds with the participation of "hot" hydrogen atoms and methyl radicals (^{3}). This assumption is also confirmed by the fact that the ratio $CH_4 : H_2$ in PIB irradiated at room temperature corresponds to the ratio of the number of $C-CH_3$ bonds to the number of $C-H$ bonds in the monomer unit of the polymer (^{3}). Consequently, it may be expected that radicals I, IV, and V are formed pairwise near one another in various combinations.

Fig. 1. Accumulation curves of free radicals in PIB irradiated at different temperatures.

Fig. 2. Dependence of the yield of isobutylene G on the temperature of irradiation of PIB. Dose 46 Mrad.

Radicals IV and V, which react already at −196°, may enter into disproportionation reactions without rupture of the main chain of the polymer. Such a reaction should lead to a ratio $G_{\mathrm{C=C}}/G_{\mathrm{destr}} > 1$. However, it was shown earlier (3) that irradiation of PIB at different temperatures always leads to the formation of approximately one double bond for each rupture in the main chain. Disproportionation of such radicals with rupture of the polymer molecule would not change the indicated ratio, but such a reaction requires too complex rearrangements in the molecule and is unlikely to proceed at low temperatures.

Study of the process of disappearance of radicals I, accumulating in the polymer at low irradiation temperatures, shows that their reactions do not lead to the formation of double bonds or to the elimination of methyl groups (3). Apparently, these radicals enter into reactions analogous to those of radicals IV and V, but, because of their lower reactivity (the free valence in radical I is strongly shielded by neighboring methyl groups), they react at higher temperatures.

In works (4,5), upon irradiation of mixtures of low-molecular-weight PIB labeled (C^{14}) in the methyl groups with high-molecular-weight inactive PIB, transfer of radioactive carbon atoms from some polymeric···

molecules to others; moreover, the rate of this transfer increases noticeably at temperatures above the glass-transition temperature of the polymer. It was suggested that the observed result is associated with the occurrence of bimolecular reactions of radicals of types I, IV, and V, accompanied by chain scission and by the transfer of certain groups (for example, CH_3 groups) between polymer chains. However, the data obtained in the present work make it possible to consider these results from another point of view.

It is known that radiolysis of PIB is accompanied by the formation of isobutylene(4). Measurement of the amount of monomer at different temperatures shows (Fig. 2) that the yield of isobutylene is insignificant at low temperatures and increases appreciably only at temperatures above room temperature, apparently as a consequence of the onset of depolymerization of polymer radicals. On the other hand, warming PIB samples irradiated with very high doses ($\sim 10^3$ Mrad) to $\sim -60°$, along with the intense disappearance of polymer radicals, leads to irreversible changes in the initially observed EPR spectrum. The spectrum thus obtained consists of 7 lines of hyperfine structure with additional weaker lines (Fig. 3). An analogous spectrum was obtained by adding ~ 7% isobutylene to a PIB sample irradiated at −196°, followed by holding the ampoule at −78° for 20 h. It may be assumed that the spectrum shown in Fig. 3 corresponds to the radical

$$\sim CH_2 - C\cdot\genfrac{}{}{0pt}{}{CH_3}{CH_3},$$

in which the unpaired electron interacts with the protons of two methyl groups and more weakly with the protons of the methylene group (for geometrical reasons, considered in more detail in works(7, 8))*. Thus, it may be thought that isobutylene molecules, formed during radiolysis or specially introduced into the polymer, add to macroradicals, which leads to the observed changes in the EPR spectrum. From this point of view, the interchain transfer of labeled

Fig. 3. EPR spectrum of PIB irradiated at −180° after warming to −55°. Dose $0.7 \cdot 10^3$ Mrad; spectrum recorded at −180°

Figure 2: Fig. 3. EPR spectrum of PIB irradiated at −180° after warming to −55°. Dose $0.7 \cdot 10^3$ Mrad; spectrum recorded at −180°

carbon atoms can be explained by cleavage reactions and subsequent addition of monomer molecules during radiolysis of PIB. In this case, the temperature dependence of the rate of transfer of labeled atoms(5) will obviously have the same character as the dependence of the rate of formation of isobutylene (Fig. 2).

Fig. 3. EPR spectrum of PIB irradiated at −180° after warming to −55°. Dose $0.7 \cdot 10^3$ Mrad; spectrum recorded at −180°.

It has been shown experimentally that no crosslinks are formed in PIB(6, 9), i.e., radicals I, IV, and V do not enter into recombination reactions. Therefore, taking into account all that has been said above, it may be assumed that their most probable reactions will be disproportionation with the formation of five- or three-membered rings, as is proposed in (3).

Consequently, the destruction of PIB proceeds by reaction (1) in the primary acts of radiolysis, with subsequent disproportionation of radicals II and III according to (2). Since the number of pairs of radicals formed by reaction (1) does not depend on the irradiation temperature, the experimentally observed(5) temperature dependence of the rate of destruction of PIB should apparently be explained by a change in the ratio of the rates of disproportionation and recombination of radicals II and III at different temperatures. If one takes into account that the volume occupied by the system in the transition state of the disproportionation reaction is greater than that of the recombination reaction, and that

* A more detailed interpretation of this spectrum will be published in the near future.

Since disproportionation requires a greater intensity of thermal intramolecular motions in the polymer, it may be expected that the rate of disproportionation will increase as the free volume and intramolecular motions increase.

When the temperature is raised from −196° to the glass-transition temperature, only the vibrational component of the free volume increases, as a result of the gradual thawing of thermal motions in the polymer. Therefore, it may be expected that a significant fraction of radicals II and III will recombine in the "cage," and that the rate of destruction of PIB will depend only weakly on temperature. When the glass-transition temperature of the polymer is reached, the free volume of the system increases sharply not only as a consequence of the thawing of segmental motions in the polymer, but also as a result of an increase in the number of vacancies (10,11), which leads to a sharp increase in the rate of disproportionation of radicals II and III and, consequently, to the same increase in the rate of destruction (5). It is evident that an increase in the intensity of intramolecular motions in PIB will also promote the course of the disproportionation reaction of polymer radicals with participation of a methyl hydrogen atom, which will lead under these conditions to the accumulation of double bonds of the type $\sim \mathrm{CH} = \mathrm{C(CH_3)_2}$, detected upon irradiation of PIB above 25° by IR spectroscopy from the absorption band at 830 cm^{-1} (3).

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REFERENCES

1. Yu. D. Tsvetkov, Yu. N. Molin, V. V. Voevodskii, *Vysokomolek. soed.*, **1**, 1805 (1959).
2. G. M. Zhidomirov, Yu. D. Tsvetkov, Ya. S. Lebedev, *Zhurn. strukturn. khim.*, **2**, 696 (1961).
3. E. N. Teleshov, A. S. Teleshova et al., *DAN*, **154**, No. 6 (1964).
4. In Shen-Kan, E. N. Teleshov et al., *Acta chim. Sinica*, **26**, 157 (1960).
5. A. N. Pravednikov, E. N. Teleshov et al., *J. Polym. Sci.*, **58**, 1039 (1962).
6. P. Alexander, R. M. Black, A. Charlesby, *Proc. Roy. Soc.*, **A232**, 31 (1955).
7. R. J. Abraham, H. W. Melville et al., *Trans. Farad. Soc.*, **54**, 1133 (1958).
8. D. J. E. Ingram, M. C. R. Symons, M. G. Townsend, *Trans. Farad. Soc.*, **54**, 409 (1958).
9. Y. Okada, *J. Appl. Polym. Sci.*, **7**, 1791 (1963).
10. Ya. I. Frenkel, *Kinetic Theory of Liquids*, Academy of Sciences of the USSR Press, 1945.
11. K. Gerhard, *Koll. Zs.*, **190**, 1 (1963).

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