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Abstract

Full Text

Chemistry

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GAS EVOLUTION AND FORMATION OF DOUBLE BONDS DURING THE RADIOLYSIS OF POLYISOBUTYLENE

When radiolysis of polyisobutylene (PIB) is carried out at the temperature of liquid nitrogen, free radicals accumulate in the polymer that are stable up to the glass-transition temperature of the sample. When the polymer is heated above this temperature, rapid disappearance of the free radicals is observed; however, the mechanism of their disappearance and the role of these reactions in the processes of polymer destruction are still not precisely known. It has been suggested that these reactions may lead to destruction of the polymer chains ([1,2]), to the formation of gaseous products ([2,3]), or to some other changes in the polymer molecules.

In order to test these assumptions, we investigated the processes of gas evolution and formation of double bonds during the radiolysis of PIB over a broad temperature range. Films of industrial PIB, prepared by evaporating dilute solutions of the polymer in carbon tetrachloride, were used as the object of study. The source of ionizing radiation was Co^{60} ($\sim$ 20,000 g-eq Ra) and a linear electron accelerator with an energy of 200 keV. Before irradiation the films were pumped down ($\sim 10^{-5}$ mm Hg) while being heated to 70° for 24 h. The degree of destruction was estimated from viscometric data ([4]). Analysis of the gaseous products was carried out on an MI 1305 mass spectrometer and on a chromatograph. The total amount of evolved gas (G-yield) was determined with a microburet on a Teppler apparatus. In studying the kinetics of gas evolution from films irradiated at −196°, the ampoule with the polymer was placed in a special cryostat with a temperature adjustable from −180 to +50° and connected to the inlet system of the mass spectrometer. IR spectra of the irradiated PIB were recorded on a double-beam spectrometer of the UR-10 type in the region 700–4000 cm^{-1}. Quantitative measurements of unsaturation of the vinylidene type were carried out in a solution of the polymer in carbon disulfide (the absorption coefficient of the 890 cm^{-1} band was taken as 136 ([5])). Recording of IR spectra at low temperature (−165°) was carried out in a specially made cell.

According to mass-spectrometric data, the gas formed upon irradiation of PIB at room temperature contains hydrogen, methane, small amounts of isobuty-

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lene, and traces of ethane. The G-yield of isobutylene is about 0.1 mol/100 eV and increases appreciably only at temperatures above 70°, which is apparently associated with thermal depolymerization of polymer radicals. The total yield of hydrogen and methane* does not depend on the irradiation temperature and is 2.3 mol/100 eV (Fig. 1). The value of G-gas obtained by us is approximately 2.5 times higher than that reported in ([6,7]); apparently, this difference is due to the fact that in the cited works a considerable part of the gas remained dissolved in the polymer. (When pieces of polymer were used, we obtained G-gas values close to those reported in ([6,7]).)

* Before measurement, the ampoule with the sample was heated for 10 h at 70°, and then cooled with liquid nitrogen to freeze out isobutylene.

When the polymer is irradiated above the glass-transition temperature, the gas formed contains about 20% methane (G = 0.46), whereas on passing to the glassy polymer the amount of methane decreases by approximately a factor of two (Table 1).

Table 1

Composition of the gas formed upon irradiation of PIB (dose 8-32 Mrad, analysis at room temperature; the sum $H_2 + CH_4$ is taken as 100%)

Irradiation temp., °C	Methane, mol. %, mass-spectr. analysis	Methane, mol. %, chromatogr. analysis	Hydrogen, mol. %, mass-spectr. analysis	Hydrogen, mol. %, chromatogr. analysis	Irradiation temp., °C	Methane, mol. %, mass-spectr. analysis	Methane, mol. %, chromatogr. analysis	Hydrogen, mol. %, mass-spectr. analysis	Hydrogen, mol. %, chromatogr. analysis
−196	11.0	10.0	89.0	90.0	+25	19.6	20.0	80.4	80.0
−78	11.1	10.0	88.9	90.0	+70	19.5	20.0	80.5	80.0
−30	–	17.0	–	83.0	−196*	11.0	–	89.0	–
0	–	20.0	–	80.0					

* Dose 120 Mrad.

Similar results were also obtained in the radiolysis of other polymers containing side methyl groups (Table 2). According to NMR spectroscopy data ([10]), passage through the glass-transition temperature is accompanied by a change in the segmental mobility of the chains, which in turn should lead to an increase in the activation energy for the detachment of methyl groups from the chain and the abstraction of a hydrogen atom from the molecule by a methyl radical (both of these processes are accompanied by the transition of the corresponding sections of the chain from a tetrahedral configuration to a planar one and, consequently, will be determined by the segmental mobility of the chains ([11])). On the other hand, the rate of diffusion of gases in a glassy polymer is substantially lower

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Fig. 1. Gas evolution from PIB at various irradiation temperatures

Figure 1: Fig. 1. Gas evolution from PIB at various irradiation temperatures

than in a polymer in the highly elastic state. Therefore, taking into account the reduced rate of stabilization of methyl radicals as a result of abstraction of hydrogen atoms from the chain, one may suppose that in the glassy polymer the recombination reaction of a methyl radical with a polymer radical will play a substantial role. All this should lead to an abrupt change in the yield of methane on passing through the glass-transition temperature.

Fig. 1. Gas evolution from PIB at various irradiation temperatures

It is well known that radiolysis of PIB is accompanied only by rupture of polymer chains; the free radicals formed upon irradiation do not combine with the formation of cross-links. Consequently, these radica—

Table 2

Dependence of CH_4/H_2 on irradiation temperature for various polymers

Polymer	Glass-transition temp., NMR method	Irradiation temp., °C	Dose, Mrad	H_2	CH_4	C_2H_6	CH_4/H_2
Polydimethylsiloxane	−93 ([8])	−196	13.8	26.5	72.4	1.1	2.7
Polydimethylsiloxane	−93 ([8])	+25	13.8	19.6	68.8	11.6	3.5
Polyacrylic acid	120 ([9])	+25	13.8	93	7	–	0.075
Polyacrylic acid	120 ([9])	+130	13.8	48.4	47.8	3.8	0.99
Poly-α-methylstyrene	137 ([9])	−78	104	86.8	13.2	–	0.152
Poly-α-methylstyrene	137 ([9])	+137	104	80.5	19.5	–	0.242

are destroyed by some other reactions, which should lead to definite structural changes in the chain, for example, to the splitting off of side groups or to the formation of double bonds. To test this assumption, the kinetics of gas evolution during slow heating of PIB samples irradiated at −196° were investigated, and the IR spectra of these samples were recorded at temperatures below and above the glass-transition temperature. If some fraction of the gas is formed as a result of the reaction of trapped free radicals, then the course of the kinetic curves in

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Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

the region of intense radical destruction should differ from the course of the curves in control experiments (a film irradiated with the same dose but, before examination, rapidly thawed until all free radicals had completely disappeared and then refrozen with liquid nitrogen). From Fig. 2 it is seen that in the glass-transition region of the polymer ($\sim -65^\circ$) the experimental points of the main and control experiments lie satisfactorily on one and the same curve, both for hydrogen and for methane. Experiments with films of different thicknesses (0.1-0.4 mm) lead to analogous results. The results obtained give grounds to consider that hydrogen and methane are formed in the primary acts of radiolysis and that secondary radical reactions do not lead to additional formation of these products.

Fig. 2. Kinetics of evolution of hydrogen and methane from irradiated PIB films.
a —control sample, *b* —main sample

Fig. 3. Unsaturation and scission of main chains at different temperatures

Radiolysis of PIB is accompanied by the formation of unsaturation of two types: $\sim (CH_3)C = CH_2$ (890 and 1650 cm^{-1}) and $\sim CH = C(CH_3)_2$ (830 and 1670 cm^{-1}) ([12,13]). By IR spectroscopy we measured the amount of double bonds of the vinylidene type after irradiation in the temperature interval from -196° to $+150^\circ$. From Fig. 3 it is seen that, independently of the irradiation temperature, 0.86 double bonds are formed for each scission in the main chain of the polymer. Double bonds $\sim CH = C(CH_3)_2$ accumulate in appreciable amounts only upon irradiation above room temperature; however, quantitative determination of unsaturation of this type is difficult. Apparently, double bonds of this type are formed as a result of disproportionation of polymer radicals formed upon scission of the main chain, with participation of a hydrogen atom of the methylene group.

To test the assumption of the possibility of formation of double bonds in the polymer as a result of interaction of two polymer radicals with one another, IR spectra were recorded of PIB films irradiated with accelerated electrons at -196°, before their heating and then after complete disappearance of all radicals. From Fig. 4, 1, 2 it is seen that already at low temperature absorption bands appear in the regions 890 and 1650 cm^{-1}, characteristic of vinylidene bonds, and heating of the polymer to -45° (Fig. 4, 1, 2) does not lead to an increase in absorption in these regions.

Thus, the data obtained show that the destruction of free radicals in PIB at

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Fig. 4. Infrared spectra of PIB (spectra recorded at −165°, layer thickness 0.1 mm). 1 –unirradiated film, 2 –irradiated at −196° with a dose of 400 Mrad, 3 –film after irradiation heated to −45°.

Figure 4: Fig. 4. Infrared spectra of PIB (spectra recorded at −165°, layer thickness 0.1 mm). 1 –unirradiated film, 2 –irradiated at −196° with a dose of 400 Mrad, 3 –film after irradiation heated to −45°.

temperatures above the glass-transition temperature is accompanied neither by the formation of gaseous products nor by the appearance

in the polymer. The latter is somewhat unexpected, since the usual pathways for the disappearance of free radicals are either their combination with one another, which in the present case would lead to crosslinking of the polymer, or their disproportionation (abstraction by one radical of a hydrogen atom from the α-carbon atom of another radical), which should have led to the formation of a double bond in the chain. The data available in the literature ([12,14]) give grounds to believe that, in the radiolysis of PIB, the crosslinking reaction practically does not occur, while the results obtained in the present work show that the disproportionation reaction also does not proceed (at least, according to the usual scheme). In this connection it must be borne in mind that the usual disproportionation of radicals formed upon abstraction of hydrogen atoms from methyl or methylene groups of the polyisobutylene molecule is impossible, since these radicals have no hydrogen atoms at the α-carbon atoms. It is possible that, in this case, saturation of the free valences of the radicals occurs as a result of the abstraction by one radical of a hydrogen atom from a methylene or methyl group, with the simultaneous formation of cyclopropane or cyclopentane rings:

Fig. 4. Infrared spectra of PIB (spectra recorded at −165°, layer thickness 0.1 mm). **1** –unirradiated film, **2** –irradiated at −196° with a dose of 400 Mrad, **3** –film after irradiation heated to −45°.

$$\sim CH_2{-}C(CH_3)_2{-}CH_2{-}C(CH_3)(\dot{C}H_2) \sim + \sim CH_2{-}C(CH_3)(\dot{C}H_2){-}CH_2{-}C(CH_3)_2 \sim \longrightarrow \begin{array}{c} \diagup C \\ CH_3 \end{array} \begin{array}{l} CH_2 - CH_2 \\ \\ CH_2 \end{array}$$

Attempts to detect cyclopropane and cyclopentane groups by the infrared spectroscopic method, however, proved unsuccessful because of the strong absorption by C–H groups in the same region in which cyclopentane derivatives absorb (1450 cm^{-1}) ([15,16]); and from the absorption at 1020 cm^{-1} one cannot judge with certainty the formation of cyclopropane rings, owing to the insignificance of the change in the intensity of this line upon thawing the sample.

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REFERENCES

1. Yu. D. Tsvetkov, Yu. N. Molin, V. V. Voevodskii, *Vysokomolek. soed.*, **1**, 1805 (1959).

2. A. Todd, *J. Polym. Sci.*, **42**, 223 (1960).

3. A. R. Shultz, *J. Polym. Sci.*, **35**, 369 (1959).

4. M. Fox, P. J. Flory, *J. Phys. Chem.*, **53**, 197 (1949).

5. J. L. Binder, H. C. Ransaw, *Anal. Chem.*, **29**, 503 (1957).

6. V. L. Karpov, Session of the Academy of Sciences of the USSR on the Peaceful Uses of Atomic Energy, July 1–5, 1955. Publishing House of the Academy of Sciences of the USSR, 1955, p. 3.

7. I. Ya. Petrov, V. L. Karpov, Proceedings of the First All-Union Conference on Radiation Chemistry, Publishing House of the Academy of Sciences of the USSR, 1958, p. 279.

8. H. Kusumoto, I. J. Lawrenson, H. S. Gutowsky, *J. Chem. Phys.*, **32**, 724 (1960).

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