Soviet-era science, translated into English

Chemistry

A. S. Kuz' minskii, M. B. Neiman, T. S. Fedoseeva,

1962

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196201.33029

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

Chemistry

A. S. Kuz’ minskii, M. B. Neiman, T. S. Fedoseeva,
Ya. S. Lebedev, A. L. Buchachenko, V. F. Chertkova

Study of Transformations of Free Radicals in γ-Irradiated Polyisoprenes

(Presented by Academician V. N. Kondrat’ ev, 21 V 1962)

The development of a three-dimensional structure in linear polymers leads to a fundamental change in their physicochemical and mechanical properties. Much attention in the literature is devoted to questions of structuring (vulcanization), but data on the initial and intermediate reactions leading to the crosslinking of molecular chains are extremely limited. The initial stages of structuring, as a rule, are associated with the formation and destruction of free radicals; the study of the structure and properties of these radicals makes it possible to approach closely the study of the mechanism of the structuring reaction.

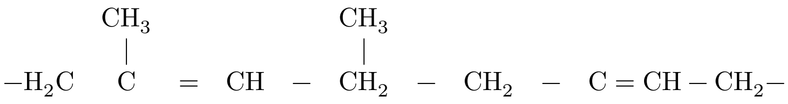
The method of electron paramagnetic resonance (EPR) is the only method that provides direct information on the structure and properties of free radicals. Recently this method has found broad application in the study of polymer radicals (1). However, almost all investigations in this area concern crystalline polymers or amorphous polymers with a high glass-transition temperature (plastics) (2, 3). Transformations of free radicals in elastomers have been studied very little by the EPR method because of their short lifetimes (4).

In the present work the nature and kinetic properties of free radicals formed in polyisoprenes under the action of γ-radiation, and their role in the structuring process, have been studied. Cis- and trans-polyisoprenes* were chosen as the objects of investigation.

The crystalline structure of trans-polyisoprene should promote trapping of free radicals; therefore all kinetic investigations relate to this polymer. The EPR spectra of the irradiated polymers were recorded on an EPR-2 spectrograph in the form of the first derivative of the energy-absorption curve (5). The change in the concentration of free radicals with time was determined from the change in the amplitude of the first derivative of the EPR absorption line. In trans-polyisoprene irradiated with a Co^{60} source with doses from 10 to 50 Mrad at room temperature in vacuum, formation of free radicals was observed; their spectrum is shown in Fig. 1a.

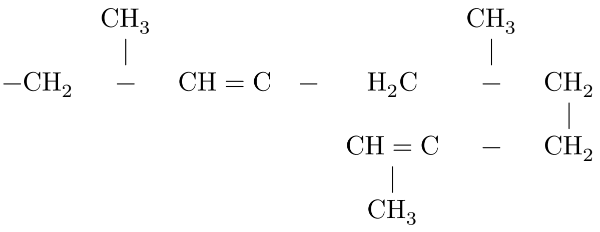
* Trans-polyisoprene (gutta-percha)

SovietRxiv



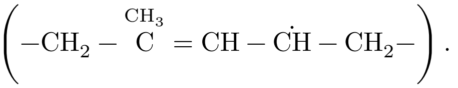
$$-H_2C\ \ \overset{CH_3}{C} = CH - \overset{CH_3}{CH_2} - CH_2 - C = CH - CH_2-$$

represents a polymer with a degree of crystallinity of 55-60%. Cis-polyisoprene –



(natural rubber). An amorphous isomer with a glass-transition temperature of 83°. The specimens were prepared in the form of films 70 μ thick.

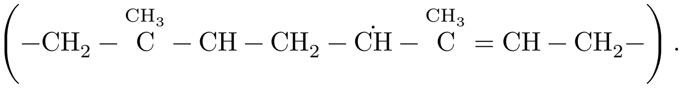
It may be assumed that it belongs to a radical formed by the abstraction of hydrogen from an α-methylene group, by analogy with allylic radicals in Teflon (6) and polyethylene (7). The magnitude of the splitting between components is $\sim$ 14 Oe. In general this is characteristic of splittings in hydrocarbons on β-protons, but in the case of a radical of such a structure there should be observed a doublet of octets



$$\left(-CH_2-\overset{CH_3}{C}=CH-\dot{C}H-CH_2-\right).$$

Fig. 1. EPR spectra of a trans-polyisoprene radical irradiated at room temperature. (a)–spectrum of an alkyl radical, (b)–spectrum of a peroxide radical.

On the other hand, abstraction of hydrogen from the neighboring CH_2- group is possible; then a triplet of quintuplets should be observed



$$\left(-CH_2-\overset{CH_3}{C}-CH-CH_2-\dot{C}H-\overset{CH_3}{C}=CH-CH_2-\right).$$

It is not possible at present to draw a final conclusion about the structure of the radical from the available spectrum. When samples are irradiated at −196°, the spectrum of trans-polyisoprene is a broad singlet, which can be explained by the superposition of spectra of radicals formed as a result of rupture of the polymer chain or abstraction of hydrogen from other groups. The spectrum of the alkyl radical of trans-polyisoprene changes into the spectrum of a peroxide radical, as shown in Fig. 1b, if air is introduced at room temperature into an ampoule containing a film of irradiated trans-polyisoprene. In cis-polyisoprene irradiated at room temperature in vacuum with doses up to 25 Mrad, no EPR spectrum is observed, which can be explained by the rapid recombination of the radicals formed, owing to the internal mobility of the molecular chains.

Fig. 2. Dependence of the reciprocal value of the relative concentration of radicals on time for different irradiation doses at 20°.
(1)–$47 \cdot 10^6$, (2)–$37 \cdot 10^6$, (3)–$20 \cdot 10^6$, (4)–$10 \cdot 10^3$ r.

The spectrum of cis-polyisoprene irradiated at $-196°$ is a broad singlet, which, upon gradual thawing, changes into a spectrum analogous to the spectrum of trans-polyisoprene irradiated at room temperature; moreover, at temperatures of 14°, 16° the EPR spectrum is still observed.

In order to study the kinetic properties of free radicals of trans-polyisoprene, we investigated the dependence of the radical concentration on dose and the kinetics of their decay at room temperature in the dose range 10–50 Mrad, in which the degree of crystallinity remains constant and does not depend on the radiation dose.

In samples irradiated at $-196°$, the total concentration of free radicals is higher than in samples irradiated at room temperature. When the films are thawed to room temperature, the radical concentration decreases by approximately a factor of 3. This decrease in concentration may be caused by rapid recombination of radicals in the amorphous part of the sample. At room temperature the rate of radical decay is low and depends on the magnitude of the dose.

Fig. 3. Dependence of the number of cross-links on the radiation dose

Fig. 4. Dependence of K, the rate of radical decay, on the number of cross-links.
(1) –dose $10 \cdot 10^6$, (2) –dose $20 \cdot 10^6$, (3) –dose $37 \cdot 10^6$, (4) –dose $47 \cdot 10^6$ r

Figure 2 presents the dependence of the reciprocal of the relative radical concentration on time at room temperature in the dose interval 10–50 Mrad. The character of the kinetic curves indicates that the process of free-radical decay in vacuum is described by a second-order equation and apparently corresponds to radical recombination

$$R \cdot + R\cdot \rightarrow \text{stable product.}$$

The slopes of the straight lines differ for different doses; moreover, the higher the irradiation dose, the lower the recombination rate of the radicals. This difference in decay rates is apparently due to the presence of additional steric obstacles arising in the amorphous part of the polymer under the action of γ-irradiation.

We calculated the values of the effective rate constants for radical decay as a function of the irradiation dose:

SovietRxiv

Irradiation dose, $r \cdot 10^{-6}$	10	20	37	47
K_{eff}, $\text{sec}^{-1} \cdot 10^4$	6.25	4.33	3.34	2.74

To relate the rate of radical decay to the density of the spatial network, we determined the degree of cross-linking in the polymer by the Flory-Rehner method ([8]) in the dose interval from 10 to 50 Mrad. It was shown that even at doses of 10 Mrad a sparse network is formed—about 600 isoprene units between two neighboring cross-links. As follows from Fig. 3, with increasing dose the number of cross-links in the polymer increases (at a dose of 150 Mrad saturation is reached, and the number of isoprene units between two cross-links decreases to 1.2).

With an increase in the number of cross-links, the mobility of the molecular chains should apparently decrease as a result of increased intermolecular interaction; as a result, the possibility of radical recombination also decreases, i.e., the rate of decay is lower the denser the spatial network. The existence of a correlation between K, the rate and the number of cross-links (Fig. 4) also confirms the validity of this conclusion.

The present work opens broad possibilities for studying the influence of spatial networks on the stability of radicals, as well as for elucidating the role of stable and trapped radicals in the processes of structuring and degradation, which are among the most important processes in polymer chemistry and technology. It has been established that, upon irradiation of trans-polyisoprene at room temperature with doses of 10-150 Mrad, free stabilized radicals are formed. Their concentration has been determined in the dose interval from 10 to 60 Mrad, depending on the irradiation conditions.

It has also been established that, in the dose interval of 10-150 Mrad, the number of cross-links per 1 g of polymer increases, and the rate of radical disappearance in this interval decreases with increasing density of the spatial network.

Scientific Research Institute
of the Rubber Industry

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
25 V 1962

REFERENCES

1. Yu. N. Molin, Yu. D. Tsvetkov, V. V. Voevodskii, *Vysokomolek. soed.*, **1**, No. 12, 1805 (1959).

2. S. Ohnishi, M. Kashiwagi et al., Abstracts of reports at the Conference on the Use of High-Energy Sources in Industry, Warsaw, September, 1959.

3. Yu. D. Tsvetkov, L. S. Lebedev, V. V. Voevodskii, *Vysokomolek. soed.*, **1**, No. 10, 1519 (1959).

4. Takao Keiō, J. Farad. Soc., **55**, 1211 (1959).

5. N. N. Bubnov, A. G. Semenov, *Pribory i tekhn. eksp.*, No. 1, 59 (1959).

6. Ya. S. Lebedev, Yu. D. Tsvetkov, V. V. Voevodskii, *Optika i spektroskopiya*, **8**, issue 6, 811 (1960).

7. Yu. N. Molin, N. Ya. Buben et al., *DAN*, **123**, 882 (1958).

8. P. L. Flory, *J. Chem. Phys.*, **11**, 521 (1943).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.