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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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ACTION OF UV LIGHT ON FREE RADICALS IN γ-IRRADIATED POLYPROPYLENE

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As we established earlier (1), irradiation with visible and ultraviolet light of polymers in which radicals have previously been formed by γ-irradiation leads to changes in the original form of the e.p.r. spectra. These changes must be associated with transformations and recombination of radicals under the action of light. It should be noted that these effects are observed even at the temperature of liquid nitrogen. It seemed essential to clarify the nature of the transformations of radicals that lead to a change in the form of the e.p.r. spectra. This communication presents data concerning phototransformations of radicals formed by γ-irradiation of polypropylene.

Polypropylene in the form of transparent films was irradiated with Co^{60} γ-radiation at a dose rate of ~ 500 rad/sec, at various temperatures. Illumination of the irradiated films was carried out both outside the resonator and in the resonator of a radiospectrometer (type RE1301). The light source was a DRSh-250 lamp.

Fig. 1. *a* —e.p.r. spectrum of allyl radicals (2) at 77° K; *b* —e.p.r. spectrum of alkyl radicals (1) at 77° K, obtained after irradiation of allyl radicals (2) with UV light

Under the action of γ-radiation at 77°K in polypropylene under vacuum conditions, alkyl radicals are initially formed

$$-\mathrm{CH}_2 - \dot{\mathrm{C}} - \mathrm{CH}_2 - \qquad \begin{array}{c} | \\ \mathrm{CH}_3 \end{array} \tag{1}$$

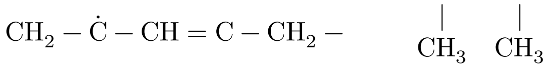
(Fig. 1*b*), whose e.p.r. spectrum consists of 8 h.f.s. lines (2,3). Illumination with unfiltered light at 77° K does not cause disappearance of these radicals; only

Fig. 2

Figure 2: Fig. 2

the ratio of the h.f.s. components in the e.p.r. spectrum changes somewhat.

At room temperature in polypropylene, radicals of the allyl type are recorded, apparently of the following structure



$$\mathrm{CH_2-\underset{\displaystyle CH_3}{\overset{\cdot}{C}}-CH=\underset{\displaystyle CH_3}{C}-CH_2-}$$

(2)

whose e.p.r. spectrum at 77° K consists of 9, and at room temperature of 17, h.f.s. lines (3) (Fig. 1*a*). Irradiation with visible light (BS-7 filter) and ultraviolet (UFS-1 filter) does not affect the spectrum or the number of these radicals. However, under the action of unfiltered light, which contains a small amount of ultraviolet with short wavelengths, at 77° K a change occurs in the shape of the e.p.r. spectrum: the 9-line spectrum is converted into an 8-line one. This change shows that the allyl radical (2) (Fig. 1*a*) is converted under the action of short UV into the alkyl radical (1) (Fig. 1*b*). In this case the total number of radicals does not decrease.

It is known that polypropylene does not absorb ultraviolet light. Since the observed transformation of radicals is caused by ultraviolet light with wavelengths $\lambda \leqslant 2500$ Å, it is likely that the light is absorbed by the allyl radical itself. Double bonds in a number of substances absorb light in the wavelength range 1800-2000 Å (4). However, an unpaired electron localized on a double bond can shift the absorption by the double bond into a longer-wavelength region (5).

For the transformation of an allyl radical into an alkyl radical, according to the data of (6,7), 15-20 kcal/mol are required. Overcoming such a potential barrier is provided by the energy of the light absorbed by the radical. The mechanism of the transformation of the allyl radical into an alkyl radical apparently consists in the fact that the unpaired electron of the allyl radical (which, under the action

Fig. 2. *a*—EPR spectrum of peroxide radicals in polypropylene at 77° K; , —stages in the transformation of peroxide radicals in polypropylene under the action of ultraviolet light at 77° K into alkyl radicals (3)

of ultraviolet radiation, is in an excited state) migrates along the polypropylene chain; in this process a "jump"of an atomic hydrogen occurs between neighboring carbon atoms.

After heating this same polypropylene sample, for example at 313° K for 5-10 min, a spectrum consisting of 9 hfs lines, belonging to the allyl radical (2) (Fig. 1a), is again recorded. The number of radicals also does not change in this case. Thus, under the action of ultraviolet light and heating, a reversible migration of the free valence along the polypropylene macromolecule occurs. The same change in the spectrum, but considerably slower, is observed during storage even at the temperature of liquid nitrogen, i.e., migration of the free valence occurs even at such low temperatures. The established reversible change in the EPR spectra upon illumination and heating, caused by the reversible transformation alkyl radical ⇄ allyl radical, thus confirms the view we expressed earlier concerning the role of migration of the free valence in the mechanism of the principal effects occurring during γ-irradiation of polymers: the formation of double bonds, destruction of the chain, and formation of "crosslinks."

Another type of transformation of stabilized radicals in γ-irradiated polypropylene, observed by us upon illumination, is the transformation of peroxide radicals into alkyl radicals. Peroxide radicals were obtained by oxidation of alkyl radicals (heating at 173–193° K after irradiation at 77° K) and allyl radicals (irradiation at room temperature in air or irradiation at 77° K followed by heating in air at room temperature). Ultraviolet light (UFS-1 filter) at 77° K causes changes in the form of the EPR spectrum, which is presented in Fig. 2.

At the first moment of ultraviolet illumination, the spectrum of another radical (Fig. 2) is superimposed on the spectrum of the peroxide radical (Fig. 2a). With further irradiation, the spectrum of the peroxide radical disappears, and there remains

EPR spectrum consisting of 4 hfs components (Fig. 2b). The splitting between the lines of the hfs spectrum is 24 ± 0.5 Oe, i.e., it coincides with the splitting between the components of the hfs spectrum of the alkyl radical (1) (^{3}).

Apparently, as before, the light is absorbed by peroxide radicals. It may be assumed that UV light causes isomerization of the peroxide radicals (^{8}): the free valence in the excited peroxide radical attacks the C–C bond in the same molecular chain. For example,

$$\begin{aligned} &-\mathrm{CH(CH_3)-CH_2-C(CH_3)(\dot{O}-O)-CH=C(CH_3)-CH_2}- \\ &\xrightarrow{h\nu} -\mathrm{CH(CH_3)-CH_2-O-O-\dot{C}(CH_3)-CH=C(CH_3)-CH_2}- \end{aligned} \tag{3}$$

Radical (3) decomposes with rupture of the main polymer chain; in this process a radical on O and a carbonyl group are formed, i.e.,

$$-\mathrm{CH(CH_3)-CH_2\dot{O}+C(=O)(CH_3)-CH=C(CH_3)-CH_2}- \tag{4}$$

The radical formed apparently isomerizes into an alkyl radical

$$-\mathrm{CH(CH_3)-\dot{C}(H)-OH} \tag{5}$$

Fig. 3. EPR spectrum of radicals obtained after heating to 300° K
polypropylene containing radicals (5) at 77° K in vacuum

Figure 3: Fig. 3. EPR spectrum of radicals obtained after heating to 300° K polypropylene containing radicals (5) at 77° K in vacuum

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The interaction of the unpaired electron with equivalent α- and β-hydrogens in the alkyl radical (5) should give an EPR spectrum consisting of 4 hfs lines with the binomial component ratio $1 : 3 : 3 : 1$. The spectrum obtained has a close ratio of hfs lines—$1 : 2.5 : 2.5 : 1$.

From the mechanism considered it follows that, in the process of conversion of peroxide radicals into alkyl radicals, destruction of the macromolecule occurs, accompanied by the formation of carbonyl and hydroxyl groups. Other possible mechanisms for conversion of the peroxide radical do not ultimately give the observed EPR spectrum.

When polypropylene containing radicals (5) is heated in vacuum at 210° K, additional hfs components appear in the EPR spectrum, whose intensity increases with increasing temperature. During heating, recombination of radicals (5) also occurs. After heating at $t^\circ \geq 238^\circ$ K, the EPR spectrum measured at 77° K consists of 9 hfs lines (Fig. 3), i.e., upon heating the alkyl radical (5) is converted into the allyl radical (2).

If heating is carried out in air, then conversion of radical (5) back into a peroxide radical occurs. Upon repeated irradiation with UV light, the peroxide radical is again converted into the alkyl radical (5).

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