Physical Chemistry

Corresponding Member of the Academy of Sciences of the USSR S. N. ZHURKOV, I. I. NOVAK, V. I. VETTEGREN

1964

SovietRxiv

Fig. 1. Change in the IR absorption spectrum of polyethylene upon deformation. 1 —initial, before stretching, 2 —after stretching 7-fold

Figure 1: Fig. 1. Change in the IR absorption spectrum of polyethylene upon deformation. 1 —initial, before stretching, 2 —after stretching 7-fold

Fig. 2. IR spectra of polyethylene. 1 —initial, 2 —after deformation, 3 —after threefold stretching and relaxation, 4 —oxidized at 150°, 5 —irradiated with a quartz lamp

Figure 2: Fig. 2. IR spectra of polyethylene. 1 —initial, 2 —after deformation, 3 —after threefold stretching and relaxation, 4 —oxidized at 150°, 5 —irradiated with a quartz lamp

Abstract

Full Text

Physical Chemistry

Corresponding Member of the Academy of Sciences of the USSR S. N. ZHURKOV, I. I. NOVAK, V. I. VETTEGREN

STUDY OF MECHANOCHEMICAL TRANSFORMATIONS IN POLYETHYLENE BY INFRARED SPECTROSCOPY

It is now known that, under the action of mechanical stresses in polymers, molecular chains rupture, with the formation of macroradicals, the existence of which has been confirmed by the direct method of electron paramagnetic resonance ([1]-[4]). In the presence of oxygen the radicals are oxidized, forming peroxides, which as a result of subsequent reactions are converted into stable compounds. The formation in the polymer of new chemical groups in such transformations should lead to changes in the infrared spectrum: the appearance of new bands or a change in the intensity of bands that existed before the application of mechanical forces.

Fig. 1. Change in the IR absorption spectrum of polyethylene upon deformation.
1 —initial, before stretching, 2 —after stretching 7-fold

Fig. 2. IR spectra of polyethylene.
1 —initial, 2 —after deformation, 3 —after threefold stretching and relaxation, 4 —oxidized at 150°, 5 —irradiated with a quartz lamp

In the present work we used infrared spectroscopy to observe changes in the chemical structure of polyethylene as a result of mechanochemical effects. As

Fig. 3. Change in the IR spectrum of polyethylene upon rupture. 1 —before loading, 2 —after rupture under load

Figure 3: Fig. 3. Change in the IR spectrum of polyethylene upon rupture. 1 —before loading, 2 —after rupture under load

far as we know, similar studies have not been described in the literature.

The experiments were carried out on low- and high-pressure polyethylene in the form of films of different thicknesses. The films were subjected to various mechanical actions: high-elastic deformation, rupture under static and dynamic loading, and scraping of the surface both in air and in liquid nitrogen.

The spectra of the polyethylene samples were recorded before and after mechanical action on an IK-10 spectrometer. In all the mechanical tests listed, changes are observed in the polyethylene spectrum in the region 1700–1800 cm^{-1}.

Figure 1 shows the spectra of polyethylene in the initial state and after stretching 7-fold. It is evident from the figure that, as a result of deformation, a signifi-

the intensity of the absorption bands at 1710, 1735, and 1742 cm^{-1} increased appreciably. According to data from (^{4,5}), these bands correspond to vibrations of the CO bond in acid

$$\mathrm{R{-}C(=O){-}OH},$$

aldehyde

$$\mathrm{R{-}C(=O){-}H},$$

and ester

$$\mathrm{R{-}C(=O){-}OR}$$

groups.

Since the effect we observed is small, it seemed of interest to find conditions under which it could be increased considerably. It turned out that if a deformed polyethylene film is heated at a temperature of 110–115° for 3–4 min, it contracts almost to its initial length. If it is then stretched again and this cycle is repeated many times, the intensity of the bands under study can be greatly increased. Figure 2 shows the spectrum of the initial, once-deformed, and three-times stretched and relaxed polyethylene (curves 1, 2, 3). As can be seen, under these conditions the intensity of the bands increases sharply.

Fig. 3. Change in the IR spectrum of polyethylene upon rupture. 1 —before loading, 2 —after rupture under load

Fig. 4. IR spectra of dispersed polyethylene. 1 —before dispersion, 2 —after planing in nitrogen

Figure 4: Fig. 4. IR spectra of dispersed polyethylene. 1 —before dispersion, 2 —after planing in nitrogen

Fig. 4. IR spectra of dispersed polyethylene. 1 —before dispersion, 2 —after planing in nitrogen

Using these data, an estimate was made of the volume concentration of carbonyl groups formed in the process of polyethylene deformation (Table 1). In the calculation, the absorption coefficients given in work (^{6}) were used.

Table 1

Concentration of groups $(1 \cdot 10^{18}\ \mathrm{cm}^{-3})$ **(low-pressure polyethylene)**

Sample	R–C(= O)–OH	R–C(= O)–H	R–C(= O)–OR
Undeformed	0.8	3.9	1.6
Stretched by 600%	1.9	8.1	3.2
3-times deformed and relaxed	9.2	54.0	26.9

These data show that the high-elastic deformation of polyethylene is not a purely rheological process, since it is accompanied by destruction of macromolecules and a change in the chemical composition of the polymer.

Along with investigating the effect of deformation, the influence of fracture on the chemical composition of polyethylene was also traced.

Of considerable interest is the fact that the intensity of the bands at 1710, 1735, and 1742 cm^{-1} increases upon rupture of the specimen under the action of static and dynamic

loads. These experiments were carried out on highly oriented polyethylene, whose strain at rupture did not exceed 15%. Figure 3 shows the spectra of an oriented polyethylene film before failure and of one ruptured under a static load of 9 $\mathrm{kg/mm}^2$. This fact shows that even in this case, when the deformation of the polymer is small, mechanochemical transformations take place in it.

Similar changes in the spectrum were also found when polyethylene was ground at room temperature. In this case, however, doubts arise as to whether the observed effect is connected with thermal destruction caused by heating of the polymer. To clarify this, experiments were carried out on planing polyethylene in liquid nitrogen. Under these conditions, owing to good heat removal, self-heating of the polymer is excluded.

Figure 4 gives the spectrum of a polyethylene sample prepared from shavings obtained in liquid nitrogen. It is evident from the figure that under these conditions as well there is a considerable increase in the intensity of the absorption bands in the region 1700-1800 cm^{-1}.

Thus, mechanical actions—stretching and fracture—lead to the decomposition of polyethylene and to the appearance of new chemical groupings, which are recorded by the change in the infrared spectrum in the region 1700-1800 cm^{-1}.

This shows that the method of infrared spectroscopy makes it possible to observe subtle effects of the action of mechanical forces on polymers. Such possibilities open the way to a detailed study of mechanochemical transformations underlying the phenomena of rupture, fatigue, and deformability of polymeric materials.

In conclusion it should be noted that there is a difference between the spectra obtained as a result of mechanochemical transformations and the spectra of the same polyethylene subjected to thermal and radiation destruction. As is seen from Fig. 2 (curves 4, 5), during thermal and radiation oxidation the intensity of the absorption band at 1718 cm^{-1}, which corresponds to ketones of the structure

$$\mathrm{R{-}C(=O){-}R},$$

increases strongly, whereas during deformation and fracture the intensity of this band practically does not change. The reason for these differences is still not clear at present.

Physico-Technical Institute named after A. F. Ioffe
Academy of Sciences of the USSR

Received
27 IV 1964

CITED LITERATURE

1. S. N. Zhurkov, E. E. Tomashevskii, V. A. Zakrevskii, *Fiz. tverd. tela*, **3**, 2843 (1961).
2. S. E. Bresler, S. N. Zhurkov et al., *ZhTF*, **24**, 358 (1959).
3. P. Yu. Butyagin, A. A. Berlin et al., *Vysokomolek. soed.*, **1**, 865 (1959).
4. S. L. Aggarwal, O. J. Sweeting, *Chem. Rev.*, **57**, 665 (1957).
5. F. M. Rugg, J. J. Smith, R. C. Bacon, *J. Polymer Sci.*, **13**, 535 (1954).
6. A. L. Gol' denberg, L. N. Pirozhnaya et al., in: *Molecular Spectroscopy*, Leningrad, 1960.