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### Abstract

### Full Text

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# ON THE PYROLYTIC METHOD FOR THE SYNTHESIS OF BLOCK COPOLYMERS

*(Presented by Academician V. A. Kargin, 9 VIII 1963)*

Many studies have been devoted to obtaining block copolymers by means of mechanochemical reactions ($^{1,2}$). The basis of these reactions is the interaction of free radicals formed during the mechanical cracking of polymer chains.

It seemed to us very interesting to use, for the synthesis of block copolymers, the interaction of radicals formed during the thermal destruction of two or several polymers, since it was known from works ($^{3,4}$) that the thermal destruction of many polymers proceeds by a free-radical mechanism. By applying moderate heating, i.e., by causing slight thermal decomposition of a mixture of two polymers, we could expect that recombination of the polymer radicals formed under these conditions would lead to the production of new types of polymeric materials. The following processes were studied: (a) interaction of a polymer with reactive oligomers (for example, epoxy resins), (b) interaction of two polymers.

**Fig. 1.** Kinetics of gas evolution during thermal destruction of polyethylene *(1)*, polyisobutylene *(2)* and their mixture *(3)*. $T = 220^\circ$

**Fig. 2.** Kinetics of gas evolution during thermal destruction of polyethylene *(1)*, epoxy resin ED-15 *(2)* and their mixture *(3)*. $T = 220^\circ$

As objects of study, the following mixtures (1:1) were chosen: nitrile rubber SKN-26 and epoxy resin ED-15; low-pressure polyethylene and resin ED-15; polyethylene and polyisobutylene (mol. wt. 200,000).

Thermal destruction of the initial samples and their mixtures was carried out in the apparatus described in ($^{3}$). In doing so, the mildest experimental conditions were selected, corresponding to slight evolution of volatiles and absence of any change in the color of the sample. On the basis of these considerations, pyrolytic synthesis of SKN-26 and ED-15 was carried out at 250° for one hour, and that

Fig. 3. IR spectra of nitrile rubber SKN-26 (1), epoxy resin ED-15 (2), polyethylene (3), and polyisobutylene (4).

Figure 2: Fig. 3. IR spectra of nitrile rubber SKN-26 (1), epoxy resin ED-15 (2), polyethylene (3), and polyisobutylene (4).

Fig. 4. IR spectra of block copolymers based on nitrile rubber SKN-26 and epoxy resin ED-15 (1), polyethylene and polyisobutylene (2), polyethylene and epoxy resin ED-15 (3).

Figure 3: Fig. 4. IR spectra of block copolymers based on nitrile rubber SKN-26 and epoxy resin ED-15 (1), polyethylene and polyisobutylene (2), polyethylene and epoxy resin ED-15 (3).

of polyethylene with ED-15 and polyethylene with polyisobutylene at 220°, also for one hour.

Under these conditions, as we established, the thermal destruction of samples of polymers and their mixtures was characterized by low values of the activation energy of the process, $E = 15$–$20$ kcal/mole. Figs. 1 and 2 show the kinetics of gas evolution during the thermal destruction of polymers and their mixtures. In all cases, lower gas evolution is observed during the joint destruction of two polymers than for the initial samples. After

**Fig. 3.** IR spectra of nitrile rubber SKN-26 (1), epoxy resin ED-15 (2), polyethylene (3), and polyisobutylene (4)

**Fig. 4.** IR spectra of block copolymers based on nitrile rubber SKN-26 and epoxy resin ED-15 (1), polyethylene and polyisobutylene (2), polyethylene and epoxy resin ED-15 (3)

the pyrolytic synthesis had been carried out, the resulting block copolymers were subjected to extraction, after which films $10\,\mu$ thick were pressed from them for recording the IR spectra.

Table 1 presents the results of extraction of one of the components of the polymer mixture before and after heating. These data show that joint heating of two polymers leads to a considerable decrease in the solubility of one of the starting products.

Figure 3 shows the IR spectra of the initial polymers, recorded on a Hilger H-800 IR spectrometer with a NaCl prism in the region 700–2400 cm$^{-1}$.

The characteristic bands of these compounds[5,6] are given in Table 2.

Figure 4 presents the spectra of the block copolymers. As is evident from the figures, in the spectra of all products subjected to pyrolytic synthesis, bands characteristic of both components are observed. In the spectra of block copolymers containing ED-15 resin, the intensity of the 916 cm$^{-1}$ band, characteristic of vibrations of epoxy groups, decreases substantially. This indicates that the thermosynthesis of SKN-26 and ED-15, as well as of polyethylene with ED-15, takes place through the interaction of SKN-26 and polyethylene with the epoxy groups of ED-15.

**Table 1**

| Polymer mixture (1 : 1) | Solvent | Solubility, % before heating | Solubility, % after heating |
|---|---|---|---|
| SKN-26 + ED-15 | Cyclohexanol : ethylene glycol (2 : 1) | 50 | at 250° 10.2 |
| Polyethylene + ED-15 | Acetone | 50 | at 220° 16 |
| Polyethylene + polyisobutylene | Benzene | 50 | at 220° 7.3 |

Thus, from the experimental data obtained it may be concluded that joint heating of polymers (in the absence of oxygen)

**Table 2**

| Initial products | Frequency, $cm^{-1}$ | Interpretation | Initial products | Frequency, $cm^{-1}$ | Interpretation |
|---|---|---|---|---|---|
| Polyethylene | 721731 | Deformation vibrations of $CH_2$ groups in the plane of molecular symmetry | Rubber SKN-26 | 1460 | Deformation vibrations of $CH_2$ groups |
| Polyethylene | 1460 | Deformation vibrations of $CH_2$ groups | Rubber SKN-26 | 2237 | Valence vibrations of C N groups |

| Initial products | Frequency, $\mathrm{cm}^{-1}$ | Interpretation | Initial products | Frequency, $\mathrm{cm}^{-1}$ | Interpretation |
|---|---|---|---|---|---|
| Polyisobutylene | 122713611383 | Deformation vibrations of isopropyl and tertiary butyl groups | Epoxy resin ED-15 | 823 | Out-of-plane deformation vibrations of CH groups of the benzene ring |
| Polyisobutylene | 1460–1470 | Deformation vibrations of $CH_2$ groups | Epoxy resin ED-15 | 916 | Vibrations of epoxy groups at the end of chains |
| Rubber SKN-26 | 915965 | Out-of-plane deformation vibrations of 1,2 and 1,4 groups | Epoxy resin ED-15 | 1040 | Vibrations characteristic of aromatic ethers |
| Rubber SKN-26 |  |  | Epoxy resin ED-15 | 15101615 | Planar vibrations of C=C groups in the benzene ring |

leads to the formation of block copolymers through recombination of polymer radicals formed during thermal destruction of the samples.

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