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Formation of Oriented Structures during Radiation Polymerization of Vinyl Monomers on Fibers

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Whereas most natural fibers are formed in an oriented state during the process of their growth, direct methods for obtaining oriented synthetic polymers are still unknown. Therefore, the preparation of oriented polymer structures directly in the course of monomer polymerization is one of the important problems of modern polymer chemistry ([1]).

In the present work an attempt has been made to approach the solution of this question, proceeding from the assumption that favorable conditions for the formation of oriented structures exist during the polymerization of monomers from the gas phase on the surface of already prepared oriented fibers and films. In this case the oriented macromolecules of the fiber or film should serve as a kind of "matrix," directing the growth of the chain molecules of the new polymer formed in the adsorption layer. To test this assumption, experiments were carried out on the radiation polymerization of acrylonitrile on kapron fiber by irradiating the latter in the presence of monomer vapor. The radiation method of initiation was chosen as the most universal one, and also because, with such initiation, the surface of the fiber is altered to the least extent.

The polymerization was carried out in a two-chamber glass apparatus, analogous to an apparatus previously used for graft radiation polymerization of vinyl monomers on the surface of mineral particles ([2]). A sample of fiber (filament kapron fiber for cord was taken) was placed in one chamber, which was a thin-walled ampoule. Into the second chamber, communicating with the first, the monomer was poured; before the experiment it had been distilled and thoroughly dried with calcium chloride; in addition, a certain amount of calcium chloride was placed in the reaction apparatus. The apparatus was evacuated while the monomer was frozen and the fiber heated at 80° to a residual pressure of 10^{-4}–10^{-5} mm Hg. Irradiation was carried out on a radiation x-ray unit with a demountable tube of the TRTs-3a type (80 kV, 200 mA); the dose rate was about $3 \cdot 10^{15}$ eV/cm$^3 \cdot$ sec, and the irradiation time was 3–6 hr. The temperature of the fiber during irradiation was 80°, and the temperature of the monomer 40° (vapor pressure 200 mm Hg). The weight gain of the fiber as a result of polymerization of acrylonitrile on it amounted in different experiments

Fig. 1. Portion of the IR polarization spectrum of polyacrylonitrile obtained from the vapor phase on capron fiber.

Figure 1: Fig. 1. Portion of the IR polarization spectrum of polyacrylonitrile obtained from the vapor phase on capron fiber.

to 15–33 wt. %. To study the orientation of the polyacrylonitrile formed on the fiber, the method of IR spectroscopy was used. IR absorption spectra in polarized light were recorded on a Hilger H-800 instrument with a sodium chloride prism and a selenium polarizer. The fibers were laid parallel to one another and placed in an immersion medium (hexachloropropylene or vaseline oil). In all cases perpendicular dichroism was found for the valence vibrations with frequency 2235 cm^{-1} (the group $-C \equiv N$), the sign of which coincides with the sign of the dichroism in pure oriented

of oriented polyacrylonitrile fiber obtained by the usual method. The dichroism value of polyacrylonitrile (0.83–0.87) obtained on capron fiber by radiation polymerization of the monomer from the vapor phase unequivocally indicates its orientation. One of the characteristic IR spectra obtained is shown in Fig. 1. For comparison, experiments were carried out on radiation polymerization of acrylonitrile from the gas phase on unoriented capron fiber and on oriented fiber from the liquid phase by irradiating the fiber wetted with monomer. In these cases no dichroism was detected. Apparently, molecules of the liquid monomer exert a disorienting influence on the process of macromolecular growth occurring on the fiber.

Thus, the results of the investigation, performed using the polycaproamide–acrylonitrile system as an example, confirmed the assumption of directed growth of macromolecules during their formation on an oriented fiber under conditions of irradiation of the latter in the presence of monomer vapors. At present, studies are being conducted to determine the possibility of obtaining oriented structures of various polymers using both chemical and natural fibers as a "matrix."

Fig. 1. Portion of the IR polarization spectrum of polyacrylonitrile obtained from the vapor phase on capron fiber. (15.7 wt. % polyacrylonitrile relative to the weight of the fiber, dose rate $3 \cdot 10^{15}$ eV/cm$^3 \cdot$sec, exposure 6 h, temperature 80°, monomer vapor pressure 200 mm Hg); $E_\perp$, $E_\parallel$—the electric vector is oriented respectively perpendicular and parallel to the fiber axis.

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