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G. I. DISTLER, P. S. SOTNIKOV, E. I. KORTUKOVA

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Abstract

Full Text

G. I. DISTLER, P. S. SOTNIKOV, E. I. KORTUKOVA

THE INFLUENCE OF THE STRUCTURE OF POLYVINYL ALCOHOL FILMS ON THE MECHANISM OF THEIR PYROLYSIS PROCESS

(Presented by Academician V. A. Kargin, 3 II 1964)

At the present time, the concept of a complex supramolecular structure of high-polymer compounds is generally accepted (^{1}). Different elements of the supramolecular structure must also possess different reactivities. Therefore, analysis of the mechanism of the corresponding structure-sensitive reactions can provide valuable information about the fine structure of polymer systems. As such a reaction, we have investigated, by methods of polarization infrared spectroscopy, the pyrolysis process of polyvinyl alcohol films.

Polyvinyl alcohol films were prepared from a 4% aqueous solution with addition, to a pH equal to 2.25, of a 0.1 N sulfuric acid solution, used as a catalyst in dehydration; orientation of the films was achieved by stretching them threefold. Heat treatment was carried out in air at a temperature of 150°. All measurements were made on a DS-301 infrared double monochromator.

It was established that, during the pyrolysis of unoriented and oriented polyvinyl alcohol films, a dehydration reaction takes place with the formation of conjugated double bonds, the number of which increases with the time of heat treatment. As was to be expected (Fig. 1), in parallel with the increase in the intensity of the absorption bands corresponding to conjugated double bonds (at 3000 cm^{-1}, 1670–1580 cm^{-1}, and 1000 cm^{-1}), there occurs a decrease in the intensity of the absorption bands of the original film, caused by the elimination of water molecules from the polymer chains.

Only the absorption band at 1141 cm^{-1} of oriented polyvinyl alcohol films behaves anomalously: its intensity remains practically constant for some time, and then rapidly decreases until complete disappearance. In the pyrolysis of unoriented films, the intensity of this band begins to decrease immediately.

The interpretation of the 1141 cm^{-1} band, and its crystallinity sensitivity, has long aroused interest and discussion ($^{2-5}$). Liang and Pearson (^{6}) calculated theoretically that a band at 1141 cm^{-1} should be present in the spectrum of crystalline polyvinyl alcohol. However, it follows from their work (although this was not emphasized by the authors) that this band may also appear in the case when the polymer contains no crystals, but only ordered regions with

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

a structure close to that of the unit cell of crystals. Indeed, in the infrared spectra we obtained for unoriented polyvinyl alcohol films there is a band at 1141 cm^{-1} (Fig. 2), whereas diffraction methods fail to establish the existence of crystals in these films. Consequently, the 1141 cm^{-1} band is due both to crystallites formed upon orientation and having the structure determined by Bunn ([7]), which is built of atactic chain segments, and to ordered regions of analogous structure in which only short-range order is realized. The behavior of the 1141 cm^{-1} band during pyrolysis can be explained by the fact that the films also contain other types of order, possessing lower stability toward pyrolysis. For example, these may be randomly arranged regions with isotactic (or other) structure, forming other forms of order. Thus, in works ([8,9]) isotactic polyvinyl alcohol was specially obtained, which did not cause the appearance of the 1141 cm^{-1} band and at the same time was characterized by weak crystallinity.

In addition, owing to packing conditions, there may be chain segments in the polymer that do not participate in the formation of intermolecular order ([10]).

The greatest thermal stability is exhibited by regions with three-dimensional order, formed in oriented films, as follows from the behavior of the 1141 cm^{-1} band. Ordered regions with short-range order of analogous structure in unoriented films do not have this comparatively high thermal stability and, during pyrolysis, begin to break down immediately.

Fig. 1. Changes in the infrared spectrum (for a beam with directions of electric-vector oscillations perpendicular to the orientation axis) of an oriented polyvinyl alcohol film. 1 –initial sample; 2 –pyrolyzed for 20 min at 150°.

Fig. 2. Absorption band at 1141 cm^{-1} in the spectrum of an unoriented polyvinyl alcohol film.

It follows from this that, upon orientation of polyvinyl alcohol films, all ordered regions of this type acquire a three-dimensional structure, or else their stability increases upon orientation. The constancy of the intensity of the 1141 cm^{-1} band at the initial stage of pyrolysis could be explained by the kinetic equilibrium of two processes: 1) an increase in the degree of three-dimensional order during heat treatment, 2) destruction of three-dimensional order as a result of the dehydration reaction. However, this is unlikely, since in unoriented films, where both of these processes are also observed, such kinetic equilibrium is not established–the intensity of the 1141 cm^{-1} band begins to decrease immediately after the start of pyrolysis. It remains to assume that in oriented films other structural formations are pyrolyzed first, and only after their destruction does pyrolysis of the film regions with three-dimensional order begin; this leads to amorphization of the films (disappearance of the 1141 cm^{-1} band and diffuse reflections in X-ray patterns).

Thus, it has been shown that the pyrolysis of polyvinyl alcohol films is sensitive to various elements of the supramolecular structure.

Institute of Crystallography
Academy of Sciences of the USSR

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