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INTERMOLECULAR STRUCTURE AND SOME ELECTROPHYSICAL PROPERTIES OF POLYVINYL ALCOHOL

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In recent years several attempts have been made to find a connection between the degree of ordering of polymer molecules and the electrophysical properties of a polymer. It has been shown (^{1}) that, in complex polymers with benzene nuclei in the main chain, heating increases the degree of crystallinity and at the same time increases the specific electrical conductivity at room temperature by several orders of magnitude. A group of Japanese investigators (^{2}) attempted to show the influence of the degree of crystallinity on the electrophysical properties of polyethylene. But in these experiments, simultaneously with the change in the degree of crystallinity, the composition of the polymer changed: its oxidation occurred. Therefore, in this case the change in electrophysical properties may be attributed to an equal degree to changes both in the molecules themselves and in their mutual arrangement.

We have found no other works devoted to this question in the literature available to us, although its solution is important for elucidating the mechanism of electrical conductivity in polymers. We have attempted to study the connection between the degree of ordering of macromolecules and electrophysical properties using polyvinyl alcohol (PVA) as an example. Films obtained by the usual method from aqueous PVA solutions were used for the study. From the X-ray pattern (Fig. 1a) it is evident that these initial films possess a definite degree of ordering (crystallinity). The IR spectrum gives the same data. As both methods showed, upon short-term heating of the film to 100° in air, the degree of crystallinity increases considerably (Fig. 1b). When the films are deformed by stretching fourfold at 100°, no noticeable increase in the degree of crystallinity occurs, but a well-pronounced orientation of the crystalline regions appears (see Fig. 1c). Thus, we obtained three types of PVA films, for which the temperature dependence of electrical conductivity was determined. The measurements were carried out in cells in which a vacuum of the order of 10^{-2}–10^{-3} mm Hg was created, using teraohmmeters of the MOM-4 or F-57 type. The temperature of the specimen was measured by a thermocouple. To create contact, a paste made of a gallium-indium alloy was applied through a template to both sides of the specimens in the form of circles with a diameter of ~ 1 cm.

Figure 2

Figure 1: Figure 2

To exclude surface conductivity, an additional experiment was performed. Onto a specimen of PVA film dried in vacuum, in addition to the usual electrodes made of gallium-indium paste, a guard ring of the same paste was applied. The gap between the ring and the electrode was 1-2 mm. Measurements without connecting the ring and with it connected gave identical results. Therefore, subsequent measurements were carried out without the guard ring. Reproducible results for a given film could be obtained only after repeated heating and cooling of the specimen (see Fig. 2). It is evident from the figure that the first heating cycle was accompanied by an increase in electrical conductivity; then the rate of increase decreased, and a minimum is observed on the curve $\lg R$—$1/T$. In subsequent measurements the dependence approaches a straight line more and more, but with each

increases with each cycle. The activation energy remains unchanged. After several cycles reproducible results are obtained—the points for several cycles fall on a single line. A number of control experiments established that neither heating in vacuum alone nor passing an electric current alone leads to such an effect. Evidently, at a temperature close to the softening temperature the viscosity of PVA decreases, the mobility of molecules and impurity ions increases, and under the action of the electric field and vacuum these are removed from the material under study. Holding the conditioned samples in an air atmosphere dried with phosphorus pentoxide does not change their electrical conductivity. Holding the film in moist air, however, led to a very slow decrease in resistance.

Fig. 2. Temperature dependence of the electrical resistance of PVA films during successive measurements

It was observed that when PVA films were heated above the glass-transition temperature, polarization of the sample occurred—the resistance changed severalfold (up to 10 times) when the polarity was reversed. We did not study this rectifying effect in detail. All results reported in the present communication refer to measurements below 85°—the glass-transition temperature of PVA ([3]). Under these conditions no polarization of the samples was observed. The current became established immediately after the instrument was switched on. No changes in the resistance of samples kept under current for a number of hours were observed. All these facts indicate the presence of conduction of the first kind, i.e., not of the ionic type. In all cases the change in electrical conductivity with temperature followed the equation

$$\sigma = \sigma_0 e^{-\Delta E/2kT}.$$

The results of parallel measurements of specific resistance at room temperature show large discrepancies. The values of the activation energy are subject to

Figure 3

Figure 2: Figure 3

Fig. 1. X-ray diffraction pattern of PVA films: a –original; b –subjected to 2-3-minute heating at 100°; c –subjected to fourfold stretching at 100°.

Figure 3: Fig. 1. X-ray diffraction pattern of PVA films: a –original; b –subjected to 2-3-minute heating at 100°; c –subjected to fourfold stretching at 100°.

smaller fluctuations. We carried out a statistical treatment of the results of determining $\lg\sigma_{25^\circ}$ and ΔE for each kind of film. The data from this treatment are given in Table 1. The reliability of the difference between the mean values was determined from the factor t (4).

It turned out that there is no reliable difference between ΔE for films with different degrees of crystallinity; nor was any influence of the orientation of the macromolecules on the values of ΔE detected. The same phenomenon is observed for $\lg\sigma_{25^\circ}$, but in the case of annealed films there is a reliable difference at $t_{0.95}$ and an absence of it at $t_{0.98}$. Evidently the decrease in $\lg\sigma_{25^\circ}$ here is connected with loss of water during heat treatment.

These data concern the study of electrical conductivity in the direction perpendicular to the orientation axis of the macromolecules. Therefore a series of experiments was set up with the direction of current along the orientation axis. The scheme for applying electrodes of gallium-indium paste in this case is shown in Fig. 3. For comparison, a series of experiments was carried out by the same method with unoriented films. The results of the statistical treatment showed that there is no reliable difference between the mean data of these two series of experiments. Thus, according to the existing classification (5), PVA can essentially be assigned to organic semiconductors. The mechanism of electrical conductivity is probably,

Fig. 3. Scheme of applying electrodes and a guard ring during measurements with the direction of current parallel to the plane of the film

axis of stretching

conducting paste

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Fig. 1. X-ray diffraction pattern of PVA films.
a –original, *b* –subjected to 2-3-minute heating at 100°,
c –subjected to fourfold stretching at 100°.

is analogous to polyamides and proteins, where special importance is attached to charge transfer through bridges of hydrogen bonds. In the case of PVA we were unable to discover a relationship between the electrophysical properties and the mutual arrangement of the molecules. No anisotropy of the electrophysical properties was found in specimens with oriented macromolecules. Probably, in

Table 1

No.	Type of film	Number of experiments	Mean value $-\lg\sigma^{\circ}_{25}$ ($\Omega^{-1}\cdot$ cm^{-1})	Dispersion $S^2_{\lg\sigma}$	Dispersion of the mean square $S_{\lg\sigma}$	Mean value ΔE (eV)	Dispersion $S^2_{\Delta E}$	Dispersion of the mean square $S_{\Delta E}$
A. Direction of current perpendicular to the plane of the film								
1	Initial	17	12.254	0.326	0.138	2.0	0.13	0.007
2	Subjected to crystallization at 100°	7	12.772	0.146	0.146	1.75	0.33	0.22
3	Stretched fourfold at 100°	6	12.461	1.790	0.355	2.04	0.11	0.13

No.	Type of film	Number of experiments	Mean value $-\lg\sigma^{\circ}_{25}$ ($\Omega^{-1}\cdot$ cm^{-1})	Dispersion $S^2_{\lg\sigma}$	Dispersion of the mean square $S_{\lg\sigma}$	Mean value ΔE (eV)	Dispersion $S^2_{\Delta E}$	Dispersion of the mean square $S_{\Delta E}$
B. Direction of current parallel to the plane of the film								
4	Initial	7	12.106	0.549	0.280	2.78	0.108	0.124
5	Stretched	7	12.750	0.231	0.033	3.08	0.052	0.086

polymers of this type the electrophysical properties are determined only by the short-range order and by the nature of the chemical bonds. Charges are transferred not only along the chain of the macromolecules, but also across them. The separate segments, and not the entire macromolecule, are responsible for electrical conductivity.

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