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Abstract

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THE EFFECT OF STRETCHING AND HYDROSTATIC PRESSURE ON THE ELECTRICAL CONDUCTIVITY OF THERMALLY TREATED POLYACRYLONITRILE

(Presented by Academician V. A. Kargin, March 5, 1963)

Semiconducting polymers obtained by thermal treatment of polyacrylonitrile may be regarded as consisting of regions with a metallic character of electrical conductivity (molecules or parts of molecules with an intact system of conjugated double bonds), separated by potential barriers (intermolecular gaps, as well as sites where conjugation is disrupted), which determine the activation character of the mobility. This model follows from present-day ideas about the properties of long molecules with conjugated double bonds ([1], [2]) and is confirmed for thermally treated polyacrylonitrile by the metallic character of the temperature dependence of the thermoelectromotive force, together with the exponential increase of electrical conductivity with increasing temperature ([3], [4]). In accordance with this model, when a specimen is heated the concentration of current carriers does not change, while the carrier mobility increases according to an exponential law, leading to an exponential decrease in resistance.

Apparently, chemical methods of varying the structure are conceivable for testing this model—for example, methods leading to lengthening of the conjugation chains by increasing the molecular weight, to changes in contacts between molecules by changing the end groups, and so on. However, obtaining molecules with long conjugation chains by direct synthesis is associated with well-known difficulties, while the deterioration of solubility accompanying the lengthening of chains with conjugated double bonds makes it impossible to determine molecular weights. The possibilities for determining the structure of semiconducting polymers are also far from sufficient. For the same reasons, thermal and radiation methods of treatment, which are presumed to lead to an increase in conjugation and to the appearance of crosslinks between molecules, cannot be used.

More reliable are those methods of action that do not lead to an uncontrolled change in structure; in our opinion, such methods include mechanical actions

Fig. 1. Dependence of the resistance of a specimen on hydrostatic pressure. 1 —forward run, 2 —reverse run

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leading to elastic deformation—for example, hydrostatic pressure and longitudinal stretching. Previously we investigated the effect of preliminary stretching on the electrical conductivity of a polymer obtained on the basis of polyacrylonitrile. It was shown that, with increasing degree of stretching, the conductivity increases. If in this case stretching of the fiber leads to straightening of the molecules, to a decrease in the number of barriers per unit length without changing the barriers themselves, then it is logical to suppose that deformation of a semiconducting polymer should affect mainly the barriers between molecules.

In the present work, thermally treated polyacrylonitrile fibers were subjected to hydrostatic pressure and longitudinal stretching. Hydrostatic pressure, by decreasing the distances between molecules, should lead to a lowering of the potential barriers between molecules and, consequently, to an increase in the mobility of the current carriers, which should manifest itself in a decrease in the resistance of the specimens.

Longitudinal stretching, by increasing the distance between molecules, should lead to an increase in the potential barriers and, consequently,

to a decrease in the mobility of the current carriers, and to an increase in the resistance of the specimens.

It should be noted that pressed specimens are unsuitable for such studies, since their resistance depends on the contacts between particles, whereas fibers are monolithic formations. This difference between pressed specimens and fibers is manifested when measuring resistance with alternating current. While the resistance of pressed tablets made of heat-treated polyacrylonitrile depends very strongly on frequency, the resistance of fibers of the same material does not depend on frequency in the range from 0 to $2 \cdot 10^8$ Hz.

Studies under hydrostatic pressure were carried out on individual fibers 3 μ in diameter, and also on bundles consisting of many fibers. To eliminate the influence of contacts, a probe method of measuring resistance was used. The pressure-transmitting medium was D-1A oil.

Fig. 1. Dependence of the resistance of a specimen on hydrostatic pressure. 1 —forward run, 2 —reverse run

Figure 1 shows the dependence of resistance on the magnitude of hydrostatic pressure for one of the measured specimens. As can be seen from the figure, the resistance decreases practically linearly with increasing pressure. Upon gradual release of the pressure, the curve is reproduced completely within the experimental error. This dependence has a similar form for all the specimens studied;

Figure 2

Figure 2: Figure 2

moreover, the resistance of all specimens at a pressure of 8 thousand kg/cm^2 is 30–45% lower than at atmospheric pressure. We attribute the decrease in resistance with increasing pressure, i.e., with decreasing distance between molecules, to an increase in the mobility of the carriers due to a lowering of the potential barriers. If, indeed,

$$U = U_0 \exp\left(-\frac{\Delta E}{kT}\right),$$

as is assumed in the model, and if, in first approximation, $\Delta E = \Delta E_0 - aP$, then

$$R = R_0 \exp\left(-\frac{aP}{kT}\right), \tag{1}$$

where P is pressure, R_0 and ΔE_0 are the resistance and activation energy without pressure, and a is a constant. The magnitude of the effect observed experimentally indicates that, within the range of applied pressures, $aP/kT < 1$; consequently, relation (1) can, with sufficient accuracy ($\sim 5\%$), be replaced by the relation

$$R = R_0 \left(1 - \frac{aP}{kT}\right), \tag{2}$$

which agrees satisfactorily with the experimental curve shown in Fig. 1.

The investigation of the change in fiber resistance under longitudinal stretching involves considerable difficulties. Since the effect is manifested in a change in the third significant digit of the resistance value, especially stringent requirements are imposed on the constancy of the specimen temperature during deformation, on the quality of the contacts, etc.

Stretching of the fibers was carried out by bending the insulating substrate on which the specimen was fixed. The values of the relative deformations used by us lay in the range $0.3 \div 1.5 \cdot 10^{-3}$. Constancy of temperature during deformation, with an accuracy better than 0.1°, was achieved by careful thermostating of the oil in which the

the experiment was carried out and was monitored with a thermocouple moving together with the deformable substrate. The change in resistance during deformation was recorded with a high-ohmic EPPV-60 potentiometer. In accordance with our assumption, the resistance of the fibers increases upon stretching.

Figure 3

Figure 3: Figure 3

Fig. 2. Dependence of the increase in resistance on relative deformation

Figure 2 shows the dependence of the change in resistance of one of the specimens on the magnitude of the relative deformation. As is seen from the figure, the change in resistance is proportional to the relative deformation. The value of the strain-sensitivity coefficient m (the ratio of the relative change in resistance to the relative deformation ε) for some specimens reached 10–13, whereas the strain-sensitivity coefficient associated with the change in geometrical dimensions upon stretching should be of the order of 2.

Figure 3 gives the temperature dependences of the strain-sensitivity coefficient for two specimens. As follows from the figure, the strain-sensitivity coefficient is practically independent of temperature.

If it is assumed that, upon stretching, the barrier height is $\Delta E = \Delta E_0 + b\varepsilon$, then

$$R = R_0 \exp\left(\frac{b\varepsilon}{kT}\right), \tag{3}$$

where R_0 is the resistance of the unstretched specimen, and b is a constant.

From the maximum value of $dR/d\varepsilon$ observed in the experiment, it follows that $b\varepsilon/kT \cong 10^{-2}$, i.e., (3) may be replaced by

$$R = R_0 \left(1 + \frac{b\varepsilon}{kT}\right), \tag{4}$$

Fig. 3. Dependence of the strain-sensitivity coefficient on temperature for two specimens

and, owing to the smallness of $b\varepsilon/kT$, the change in resistance under deformation is

$$\Delta R = dR = R_0 \frac{b\varepsilon}{kT},$$

which agrees with the experimental dependence presented in Fig. 2, while the temperature dependence of the strain-sensitivity coefficient should obey the expression

$$m = \frac{\Delta R}{R} \Big/ \varepsilon = \frac{b}{kT}.$$

However, an increase in temperature from 290 to 340°K should lead to a decrease in m by $\sim 15\%$, which lies within the error of the measurements.

Thus, the experimental results obtained in the present work confirm our assumptions concerning the mechanism of electrical conduction in the polymer semiconductors studied by us.

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