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Abstract

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INVESTIGATION OF SOME PHYSICAL PROPERTIES OF THE CONDENSATION PRODUCTS OF *o*-DIHYDROXYBENZENE WITH FORMALDEHYDE

In many recent works, special attention has been devoted to the study of the distinctive physical properties and to the synthesis of polymers containing conjugated bonds in the main polymer chain. The distinctive properties of such polymers are associated with the degree of conjugation and with the delocalization of π-electrons along the molecular chain ($^{1-5}$). The electrical properties of polymers may depend not only on the degree of conjugation in the polymer molecule, but also, to a significant extent, on the structure of the polymer as a whole (^{6}), on the degree of its crystallinity (^{7}), and on the ordering of the molecules (^{8}).

Among these polymers, those are of particular interest in which the polyconjugated chain includes the groups $-CH_2-$, $-CH_2-CH_2-$($^{8-10,12}$), $-NH-$(^{11}), $-N{=}N-$(^{13,14}), and the group $-OCH_2-CH_2O-$(^{15}); especially interesting is the influence of the latter on the mobility of π-electrons in the conjugated chain, on the structure of the polymer, and, along with this, on changes in the semiconducting properties of the polymers.

In works (^{10,11}) it was shown that the introduction of these bridges between benzene nuclei does not lead to complete rupture of the conjugation chain; exchange interaction exists. It proved curious that introducing into the polymer a short bridge consisting of one methylene group between benzene nuclei not only does not increase the activation energy of the polymer conductivity, but, on the contrary, decreases it in comparison with a polymer in which conjugation exists throughout the entire macromolecule.

The authors of works (^{8,9}) explain this phenomenon by the fact that the degree of crystallinity of the polymer increases with the introduction of methylene groups separating the benzene nuclei, since the flexibility of the molecular chain increases. The increase in the degree of crystallinity and in the packing density of the macromolecules facilitates electronic transitions between macromolecules to such an extent that this effect outweighs the decrease in conjugation caused by the separation of the benzene nuclei by the methylene group.

The study of the electrophysical properties of such polymers has only just begun.

Fig. 1. EPR spectra of resin III at different heating temperatures: a—140°, b—185°, c—300°

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In this connection we prepared a resin based on *o*-dihydroxybenzene (pyrocatechol) and formaldehyde and investigated the changes in some of its physical properties under the influence of heat treatment.

Synthesis of resins. We prepared samples of resins of the resite type, condensed on the basis of *o*-dihydroxybenzene and formaldehyde under different conditions. The resins obtained are infusible and insoluble in organic solvents; without melting, they slowly disappear in a flame. The color ranges from dark brown to black.

Magnetic properties. To record EPR spectra, the resin samples were heated in a stream of dry purified nitrogen over the temperature range from 20 to 450° C. In the spectra of all the resins examined, single symmetrical singlets without hyperfine structure were found, with a width between the points of maximum slope of 1-9 oersteds. The lines (Fig. 1) were described with a high degree of accuracy by the Lorentz formula. The concentrations of paramagnetic centers were determined by comparison with standard samples of the stable radical DPPH, whose signal can likewise be assigned to a Lorentzian form.

The spectra recorded show that all resin samples are characterized by a signal with a *g*-factor corresponding to a free electron, typical of polymer chains with conjugated bonds.

The spectra recorded at the temperature of liquid nitrogen for different samples and different heating temperatures gave lines without hyperfine structure; the character of the spectrum did not change, while the absorption intensity increased. This indicates that the paramagnetic state for these resins is the ground state, not an excited one, i.e., electron unpairing does not occur as a result of thermal excitation. Grinding the resins in an agate mortar also does not affect the magnitude of the absorption, i.e., the absorption is not due to "broken bonds" ([17]). After the samples had stood for six months, the intensity of the absorption effect did not change. Thus, in the systems studied, polyconjugated bonds at a certain degree of polycondensation, the ground state of the molecules becomes paramagnetic.

Fig. 1. EPR spectra of resin III at different heating temperatures:
a—140°, *b*—185°, *c*—300°

Fig. 2. Dependence of the concentration of paramagnetic particles on the heating temperature of the resins

For all heated resin samples, a strong increase in the number of paramagnetic particles near 200° is characteristic, and at 350° they showed maximum absorp-

Fig. 2. Dependence of the concentration of paramagnetic particles on the heating temperature of the resins

Figure 2: Fig. 2. Dependence of the concentration of paramagnetic particles on the heating temperature of the resins

Fig. 3. Broadening of paramagnetic absorption bands for various resins: 1 —resin sample I, 2 —resin sample II, 3 —resin sample III

Figure 3: Fig. 3. Broadening of paramagnetic absorption bands for various resins: 1 —resin sample I, 2 —resin sample II, 3 —resin sample III

tion (Fig. 2), with the concentration of unpaired electrons reaching 10^{20} E_e/g. Comparison of the EPR spectra of different resins and of the curves for the dependence of the concentration of unpaired electrons on the heating temperature shows that, for resins which by their condensation conditions are highly cross-linked (resin I), the initial concentration of paramagnetic particles is considerably higher than for the other resins; the less cross-linked the molecule, the lower the initial concentration of paramagnetic particles. A similar picture has been described in works (${}^{19-21}$). The change in the width of the absorption band with increasing heating temperature is also quite illustrative. Thus, for resin I, which is built from strongly cross-linked molecules that change little during heating, no broadening of the absorption band is observed. For the other two resins, the width of the absorption band changes (Fig. 3).

Table 1

Change in resin composition upon heating

Preliminary heating temperature (for 1 hour, in °C)	C	H	O
Unheated resin	60.93	5.41	33.66
110	60.83	4.75	34.42
225	68.41	3.70	27.89
360	72.87	3.43	24.60
450	84.51	3.37	12.12

Infrared spectra.

Comparison of the infrared spectra of a resin sample successively cured at temperatures from 20 to 360° shows that near 200° the intensity of the absorption bands attributed to —OH groups decreases sharply, which is associated with the process of further resin condensation and a decrease in the number of methylol and phenolic hydroxyls.

For the insoluble fractions of the resins, as well as for resins cured in the IR spectra, a significant increase in the general absorption background with smoothing of individual absorption bands is observed, which is characteristic of polyconjugated systems that usually possess semiconductor properties.

~~**Fig. 3.** Broadening of paramagnetic absorption bands for various resins: *1* —~~ resin sample I, *2* —resin sample II, *3* —resin sample III

Fig. 4. Change in resistance as a function of the heating temperatures of a sample of resin II: *I* —unheated, *II* —heated to 700°

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Figure 4: Fig. 4. Change in resistance as a function of the heating temperatures of a sample of resin II: I —unheated, II —heated to 700°

Electrical properties. The electrical conductivity of resin III was measured at temperatures from 20 to 700°. The measurement was carried out on direct current using samples prepared from a monolithic piece of resin. The temperature dependence of the specific electrical conductivity follows the exponential law $\sigma = \sigma_0 e^{-E/kT}$. The electrical conductivity of the unheated sample at room temperature was 2.6×10^{-7} $\text{ohm}^{-1} \cdot \text{cm}^{-1}$, and at 700° 8.5×10^{-4} $\text{ohm}^{-1} \cdot \text{cm}^{-1}$. From the conductivity curve for the uncured (unheated) sample (curve *I*, Fig. 4) it is evident that the conductivity increases sharply as heating proceeds and moisture and volatile pyrolysis products are removed, and then remains constant. Near 200° the resin cures intensively; further condensation and formation of a spatial structure take place, accompanied by the release of water (see Table 1—the C content increases, while H and O decrease), which is in good agreement with the IR spectral data. As the crosslinking proceeds, the conductivity increases, and when crosslinking is completed, the conductivity becomes constant.

For a sample previously heated to 700°, a gradual increase in conductivity is observed.

Heat treatment. When samples are heated in air or in a stream of nitrogen to 700°, the color of the sample changes from brown to black. The results of elemental analysis, as a function of the heating temperature in a stream of nitrogen, are given in Table 1.

From comparison of the conductivity curves with the curves of broadening of the resonance absorption bands it is clear that near 200° both the conductivity (curve *I*, Fig. 4) and the width of the absorption band (curves *2*, *3*, Fig. 3) change strongly. This indicates that in the temperature region around 200° there is a significant change in the degree of conjugation.

For resin I, the most highly crosslinked one, only the initial concentration of paramagnetic particles is significantly higher, and with increasing temperature it changes in the same way as for the other resins.

The cause of the observed phenomena evidently consists in the fact that, at early stages of curing, separate polyconjugated regions are formed that are isolated from one another and not united into a single system of polyconjugation. They consist of weakly connected conjugated regions; their electrical and magnetic properties are determined by the behavior of individual, weakly interacting unpaired electrons within such a region and by the energy barriers between such regions.

As a result of heat treatment, further fusion occurs and a single condensed structure is formed, i.e., a three-dimensional region of regularly conjugated molecules is formed with collectivization of the electrons and their strong interaction. In addition, during heat treatment there occurs a process of partial oxidation of the resin with formation of semiquinones and conversion of structure (a) into structure (b), stabilized by a more developed and regular polyconjugation and by delocalization of the unpaired electron throughout the entire volume; this, evidently, also determines the magnetic and electrical properties of these formations.

(a)
[[chemical structural scheme: polycondensed o-dihydroxybenzene-formaldehyde structure with phenolic OH groups and methylene bridges]]

$$\longrightarrow$$

(b)
[[chemical structural scheme: partially oxidized semiquinone-containing polyconjugated structure with quinonoid O groups, OH groups, methylene bridges, and delocalized unpaired electrons]]

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