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Abstract

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ON SOME PROPERTIES OF POLYBENZIMIDAZOLES

The present work gives the results of a comparative study of the properties and structure of polybenzimidazoles synthesized from 3,3′-diaminobenzidine and diphenyl esters of terephthalic and isophthalic acids. These polymers are systems of conjugated double bonds containing nitrogen and may be represented schematically by the following formulas:

$$\left[\text{ −structural unit of polybenzimidazole based on terephthalic acid − }\right]_x, \quad \text{(I)}$$

$$\left[\text{ −structural unit of polybenzimidazole based on isophthalic acid − }\right]_x. \quad \text{(II)}$$

As was reported earlier ($^{1-4}$), polymers of this type possess high thermal stability.

In the present investigation, the structure and properties were studied of polycondensation products obtained by heating the mixture of reagents for 3.5 hours while raising the temperature to 380° and under a vacuum of $4 \cdot 10^{-2}$ mm Hg.

Figure 1 gives the X-ray diffraction patterns of polybenzimidazoles I and II, obtained with Fe $K\alpha$ radiation in a cylindrical camera of radius 2.67 cm. Judging from the character of the X-ray patterns, samples of polybenzimidazole II (based on isophthalic acid) have an amorphous structure. The intense halos in the X-ray patterns, corresponding to an average period $d_1 = 3.97$ Å, indicate that the short-range order is determined by intermolecular contacts.

Samples of polybenzimidazole I (based on terephthalic acid), in contrast to polymer II, are characterized by a crystalline structure with a relatively large number of rather sharp diffraction bands in the X-ray pattern ($d_1 = 4.57$ Å, $d_2 = 3.28$ Å, $d = 1.96$ Å, etc.).

Comparison of the X-ray diffraction patterns of both types of polymers leads to the conclusion that the introduction into the molecular chain of a phenyl group

Fig. 2. IR spectra of polybenzimidazoles

Figure 1: Fig. 2. IR spectra of polybenzimidazoles

with meta substitution, in contrast to para substitution, is the principal factor hindering the packing of molecular units into a crystal lattice. The reason for this is apparently the steric hindrance arising during rotations of the phenyl ring about the lateral ordinary bonds.

Figure 2 shows the infrared absorption spectra of the polymers, obtained on a double-beam IKS-14 spectrophotometer. The spectra contain certain absorption bands common to both polymers, indicating the presence of identical atomic groupings in the units of their molecular chains, as well as bands specific to each polymer.

Figure 3 gives the dependence of the yield of volatile substances on the temperature of heating of the polymers. As is evident from the graphs, both types of polymers possess high heat resistance. It should be noted that polybenzimidazole I (based on terephthalic acid) has higher heat resistance than the type II polymer (based on isophthalic acid).

The main changes in the elemental composition of both types of polymers occur at a temperature of 550°, in accordance with a substantial increase in the yield of volatile substances (Fig. 2). This temperature range corresponds to the beginning of intensive thermal destruction of the polymers.

The X-ray diffraction pattern for both types of polymers does not change substantially up to temperatures close to 500°, which corresponds to preservation of the original structure—crystalline for polybenzimidazole I and amorphous for polymer II.

At 600°, the X-ray diffraction pattern of polybenzimidazole I shows a decrease in the sharpness of the diffraction bands and their shift toward small scattering angles. This indicates disruption of the crystalline packing of the units of neighboring molecular chains and an increase in intermolecular distances. However, a high degree of order in their relative arrangement is still preserved.

Fig. 2. IR spectra of polybenzimidazoles: *1* –initial polybenzimidazole I and the same, heated for 2 h at various temperatures: *2* –450°, *3* –500°, *4* –550°, *5* –600°. *6* –initial polybenzimidazole II and the same, heated for 2 h at various temperatures: *7* –450°, *8* –500°, *9* –550°, *10* –600°

In the X-ray diffraction pattern of polybenzimidazole II at 500°, an analogous shift of the intense halo and its broadening toward small angles are also observed, indicating a decrease in the density of molecular packing of the units. A substantial change in the diffraction pattern of the polymers at higher treatment temperatures, up to 800°, corresponds to a complete transformation of the original structure with a progressive contribution of a carbon structure in the form of stacks of flat layers of aromatic carbon (^{5}).

Fig. 1. X-ray diffraction patterns of polybenzimidazoles.

Figure 2: Fig. 1. X-ray diffraction patterns of polybenzimidazoles.

In the IR spectra of both polymers heated at 500°, all the main absorption bands are present. The bands specific to both polymers also remain practically unchanged. This indicates preservation of the molecular chains of the polymers. At higher temperatures, changes in the spectrum are observed that characterize substantial transformations of the molecular chains associated with processes of thermal destruction and synthesis. The changes in the spectrum in the region of 700-900 cm^{-1} (Fig. 2), characterized by transformation of the types of substitution and condensation of aromatic rings and imidazole groups, due to reac-

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Fig. 1. X-ray diffraction patterns of polybenzimidazoles. 1 –for the initial polybenzimidazole I and for the same material heated for 2 hours at temperatures: 2 –500°, 3 –600°, 4 –650°, 5 –700°, 6 –800°; 7 –for the initial polybenzimidazole II and for the same material heated for 2 hours at temperatures: 8 –500°, 9 –600°, 10 –650°, 11 –700° and 12 –800°.

tion and crosslinking of the molecular chains. It should be noted that the relative intensity of the band at $\sim 840\ \text{cm}^{-1}$ of the para-substituted phenylene groups in polybenzimidazole I, as well as of the band at $\sim 700\ \text{cm}^{-1}$ of the meta-substituted phenylene groups, increases upon heating to high temperatures (600°). Apparently, the transformation of the units at high temperatures proceeds primarily through the imidazole, and not the phenylene, groups.

The values of the specific resistance upon heating were studied by the capacitor-discharge method for the initial polymers, and by a probe method for the products of their thermal treatment. From the temperature dependence, the activation energies of conductivity ΔE were determined. The results of these measurements are given in Table 1. Both polymers are characterized by semiconducting properties and have a negative temperature coefficient of resistance.

For polybenzimidazole I treated at 500° for two hours, the values of ρ and ΔE remain unchanged. This confirms the preservation of its initial structure. For polybenzimidazole II, under the same treatment conditions, a significant increase in ΔE is observed in comparison with the initial polymer. This is consistent with the relatively lower heat resistance of polymer II, for which structural transformations arise at lower temperatures, in contrast to polybenzimidazole I.

Fig. 3. Dependence of the yield of volatile substances on the heating temperature of polybenzimidazoles: *I* –for polybenzimidazole I, *II* –for polybenzimidazole II.

A detailed comparative study of the kinetics of the evolution of volatiles during

Fig. 3. Dependence of the yield of volatile substances on the heating temperature of polybenzimidazoles: I —for polybenzimidazole I, II —for polybenzimidazole II

Figure 3: Fig. 3. Dependence of the yield of volatile substances on the heating temperature of polybenzimidazoles: I —for polybenzimidazole I, II —for polybenzimidazole II

thermal decomposition under isothermal conditions for both types of polymers reveals characteristic differences in the kinetic characteristics.

Table 1

Electrophysical characteristics of the initial and heated polybenzimidazoles

	Polybenzimidazole I	Polybenzimidazole I	Polybenzimidazole II	Polybenzimidazole II	Polybenzimidazole II	Polybenzimidazole II
	initial	heated 2 h at 500°	initial	heated 2 h at 500°	heated 2 h at 600°	heated 2 h at 800°
ρ, $\Omega \cdot$ cm	$3.0 \cdot 10^{13}$	$2.44 \cdot 10^{13}$	$1.8 \cdot 10^{13}$	$7.5 \cdot 10^{13}$	$3.2 \cdot 10^{8}$	6.3
ΔE, eV	0.84	0.84	0.64	1.2	0.56	0.36

The process of thermal decomposition is satisfactorily described by the equation for the rate of a first-order reaction up to a degree of decomposition $\alpha = v_t/v_0 = 0.7$, where v_t is the yield of volatiles over time τ and v_0 is the yield of volatiles after two hours' exposure at 800°.

Polybenzimidazole I is characterized by higher values of the apparent activation energy $\Delta E_1 = 43.1$ kcal/mol and of the pre-exponential factor in the Arrhenius equation $K_0 = 1.1 \cdot 10^9$, compared with polybenzimidazole II, for which $\Delta E_2 = 37.2$ kcal/mol and $K_0 = 2.8 \cdot 10^7$.

It should be assumed that the higher temperatures of the onset of intensive destruction of polybenzimidazole I noted by us, corresponding to its greater thermal stability in comparison with polymer II, are determined by the increased value of the activation energy of the destruction process.

Taking into account the similarity of the types of bonds in the molecular units of both polymers, there are grounds to suppose that the difference in the activation energy of the thermal destruction process is determined by the contribution to this quantity, for polybenzimidazole I, of the heat of disordering of its crystalline lattice.

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