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Abstract

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ON THE MECHANISM OF THE THERMAL TRANSFORMATION OF POLYACRYLONITRILE

(Presented by Academician V. A. Kargin on 27 VII 1963)

In works [1–3] it was shown that polyacrylonitrile (PAN), upon heat treatment, undergoes changes leading to the appearance in its molecules of conjugated regions and to the emergence of semiconducting properties in the substance. It was suggested that, at the initial stage, this transformation proceeds according to the scheme:

[structural scheme of the transformation of PAN, showing neighboring CH, CH_2, $C \equiv N$ groups converting i

Since the formation of systems of conjugated bonds is accompanied by the appearance of absorption bands in the near-ultraviolet and visible regions of the spectrum, it seemed of interest to use spectral methods to study the nature of this process and to specify the temperature region in which it occurs.

Bearing in mind that the presence of oxygen could not only affect the kinetics of the process but also decisively change its direction, we considered it especially important to carry out the heat treatment under conditions of high vacuum.

The investigations were carried out on PAN films obtained by redox initiation. The molecular weight of the polymer was 270,000. The films were prepared from a solution of PAN in dimethylformamide by slow evaporation of the solvent. Heat treatment was carried out in a special cuvette evacuated to a pressure of 10^{-5}–10^{-6} mm Hg and allowing the absorption spectra to be measured without exposing the sample to air. The initial PAN has no electronic absorption bands over the entire investigated region—in the visible and ultraviolet parts of the spectrum down to 240 mμ. In the infrared region an absorption peak characteristic of the $C \equiv N$ bond is observed. Prolonged treatment of PAN at temperatures below 200° did not lead to the appearance of any absorption bands in the ultraviolet region of the spectrum. On transition to higher temperatures, disappearance of the $C \equiv N$-bond band in the infrared region was observed and simult–

Fig. 1. Spectral curves of the optical absorption of PAN at various stages of heat treatment at 220°.

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Fig. 2. Increase in absorption intensity of PAN during heat treatment. 1 – $\lambda = 580$ mμ, 2 – $\lambda = 540$ mμ

Figure 2: Fig. 2. Increase in absorption intensity of PAN during heat treatment. 1 – $\lambda = 580$ mμ, 2 – $\lambda = 540$ mμ

1 –1 h, 2 –2, 3 –3, 4 –4 h. The curves are reduced to the same value of optical density at the maximum 355 mμ.

Simultaneously, in the ultraviolet region, an electronic absorption spectrum appears that is characteristic of conjugated systems. A significant feature of the emerging spectrum is that, up to a temperature of 250°, the shape and position of its long-wavelength falloff remain unchanged. Figure 1 shows the absorption curves of PAN at different stages of treatment at 220°, normalized to unity at the maximum at 350 mμ. The relative increase in the intensity of the band during heat treatment is shown in Fig. 2. As the temperature is raised, the rate of increase in absorption grows. At 220° the process is practically completed in 10 h, so that the subsequent transition to 250° is not accompanied by additional changes. It should be especially emphasized that in the interval 200-250° the temperature determines only the rate at which the spectrum increases, but not the position of its maxima or the shape of the long-wavelength falloff. Thus, in this region we are dealing with a single process. Transition to a higher temperature (in our experiments, 300°) led to a qualitatively different change in the spectrum. In the region of the maximum at 355 mμ the absorption intensity did not increase. At the same time, on the long-wavelength falloff of the band, in the region 450-600 mμ, a sharp increase in absorption occurred (Fig. 2).

Fig. 2. Increase in the absorption intensity of PAN during heat treatment. 1 – $\lambda = 580$ mμ, 2 – $\lambda = 540$ mμ

The totality of the facts presented shows that, in the heat treatment of PAN, at least two processes should be distinguished: one occurring in the interval 200-250°, and another at higher temperatures. The appearance of an electronic spectrum in the course of the first process shows that regions of conjugated bonds are indeed formed in the polymer. We assume, in agreement with (1), that conjugation proceeds through the nitrile groups. The length of the conjugated segment $(-\mathrm{C}=\mathrm{N}-)_k$ unambiguously determines the position of the absorption band, so that, as such segments lengthen, their spectrum shifts into the long-wavelength region. Therefore, the invariance of the shape and the constancy

of the position of the spectrum apparently allow one to conclude that, at the first stage, there is no successive lengthening of the conjugation chains; rather, some unchanged statistical distribution of conjugated segments by length is established at once.

The reason for the observed phenomena may be as follows. In the polymer molecules there are always regions of regular mutual arrangement of C ≡ N groups. The length of such regions is determined, on the one hand, by the degree of stereoregularity and, on the other, by the conformation of the molecules. The formation of a conjugated system within each such region over its entire length occurs in a comparatively short interval of time, and the process at the initial stage is reduced merely to the quantitative accumulation of conjugated segments, whose distribution by length reflects the distribution of regular regions in the original polymer. Further lengthening of each such segment in the temperature interval 200–250° does not occur. On the contrary, the slight change in the absorption spectrum in the region of short wavelengths should apparently indicate that, during heat treatment, the relative content of short conjugated segments in the substance increases. The long-wavelength shift of the PAN spectrum at temperatures above 250° indicates a further development of the process, which possibly includes the coalescence of the conjugated structures formed earlier.

Further study of the process of the thermal transformation of PAN in oriented samples, as well as in stereoregular polymers, will make it possible to refine our ideas about the mechanism of this process.

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