THERMAL TRANSFORMATIONS OF POLYACRYLONITRILE FIBRES WITH DEEP DEGREES OF CONVERSION

M. T. Azarova, V. M. Bondarenko, and G. I. Savchenko

It was shown that oxidative dehydrogenation with primary formation of C= C double bonds and then C = C conjugated bonds is the basic chemical reaction in the early stages of thermal stabilization of PAN fibres. A hypothesis was advanced concerning the nature of the appearance of oxygen-containing functional groups. A correlation was found between the amount of oxygen added to the fibre and its density.

Oxidative thermal stabilization of polyacrylonitrile (PAN) fibres is the most important stage in production of carbon fibres (CF), where PAN fibre acquires new qualities, becoming nonmelting, noncombustible, insoluble in most solvents, and suitable for subsequent high-temperature processing. The chemical structure of the product formed is not known, and any proposed model is hypothetical, since the transformation of PAN is the consequence of not one, but several parallelly occurring reactions. This situation significantly hinders the interpretation of the results obtained and simultaneously explains the difference in the published opinions.

As we noted previously [1], changing the conditions of conducting the experiment, in particular, studying the thermal transformations of PAN fibres in an oxygen-containing, and not an inert medium, has allowed many investigators to criticize the widespread concept of the predominant occurrence of cyclization of the polymer chain in PAN, resulting in the formation of a heteroaromatic polycyclic system. The model of global cyclization proposed by Houtz in 1950 [2] and then confirmed by Grassie in systematic studies [3] has continued to be critically investigated. Both those who consider formation of azomethine compounds to be the basic reaction and consequently consider intermolecular cross-links to be important [4] and those who practically denied cyclization and suggested that a conjugated polyene chain is formed [5, 6] are opponents of this model.

The difficulty in the occurrence of this process in atactic PAN fibres and in fibres based on copolymers of acrylonitrile in which the regularity of arrangement of nitrile groups is also perturbed could serve as additional evidence against the hypothesis of predominant cyclization. The problem of the participation of oxygen in the transformations, on one hand considered a catalyst of cyclization and on the other hand as an inhibitor which prevents migration of a proton to a nitrile group nitrogen or absorbs the free radicals formed, is very intricate.

The study described here is the logical continuation of the previous study in [1] in which the radical character of thermal transformations of PAN regardless of its chemical structure was demonstrated by independent methods of investigation. It was shown that this mechanism is realized in the initial stages of heating PAN homopolymers and copolymers by accumulation of free radicals and subsequent evolution of the reaction according to a chain-transfer mechanism.

If this hypothesis is true and transformation of PAN passes through formation of hydroperoxides, then a consequence of this process should be the formation of a polyconjugated chain as the evolution of oxidative dehydrogenation.

IR spectroscopy, which was also used in the present study, is the classic method of investigating the chemical structure of polymers in general and PAN in particular. We investigated the changes in the IR spectra of unoriented PAN films and films drawn by 900% after heating in air at 145-190°C. The samples were treated with heat in a fixed position in the holder used for taking the IR spectra.

The spectra of the films were recorded at room temperature on a UR-10 spectrophotometer with the minimum scanning rate and slit program 4. A polarizer made of a stack of selenium plates was used. The dichroism of the 2240 cm⁻¹ band...
observed in the IR spectra of the polymers was defined as the ratio of the optical densities in perpendicular $D_\perp$ and parallel $D_\parallel$ polarization of the electric emission vector ($d = D_\perp/D_\parallel$).

The following basic absorption bands were observed in the spectrum of the PAN film before heating: 1070 cm$^{-1}$ (skeletal vibrations of C≡N bonds), 2865 and 2930 cm$^{-1}$ (stretching vibrations of C−H bonds). The basic bands were strongly polarized. Heating the films caused new bands to appear in the spectrum corresponding to 807, 1600, 1670, 1720, and 2210 cm$^{-1}$, which were distinctly observed in both ordinary and in polarized radiation.

An examination of the change in the intensity of the different absorption bands as a function of the duration of heating at 145°C (Fig. 1) suggests that the intensity of the 1600 cm$^{-1}$ band, assigned to both vibrations of C−N bonds and to C−C bonds in different studies, increases most rapidly. Since the rate of the change in the 2240 cm$^{-1}$ band is much lower, the 1600 cm$^{-1}$ band can be assigned to C=C bond stretching vibrations with a high degree of probability, and the previously advanced hypothesis in [7, 8] concerning the predominant occurrence of oxidative dehydrogenation reactions with formation of a conjugated polyene chain should thus be confirmed. The 2210 cm$^{-1}$ band in the spectrum of the samples investigated probably reflects vibrations of a nitrile group conjugated with a C=C bond.

 Increasing the temperature of heating the film to 160°C causes an increase in the peak intensities of all absorption bands (Fig. 2), but the rate of the increase in the intensity of the 1600 cm$^{-1}$ absorption band remained maximum, while the rate of the decrease in the 2240 cm$^{-1}$ band significantly lagged behind. It should be noted that the change in the 2240 cm$^{-1}$ band was frequently anomalous: its intensity in the initial stage of heating could not only decrease, but also increase slightly. This phenomenon can partially be attributed to a change in the conformation of the molecular chains and an increase in the mobility of the nitrile groups due to breaking of initially existing hydrogen bonds or, as noted in [9], due to perturbation of dipole—dipole pairs of polar groups. From this point of view, it is not totally correct to precisely calculate the decrease in the concentration of nitrile groups with the curves of the change in the 2240 cm$^{-1}$ absorption band, and only an examination of the relative changes in the spectra is possible.