Three samples of polyacrylonitrile fibres used for production of carbon fibres were investigated by x-ray diffraction, differential scanning calorimetry, and thermogravimetry. It was found that spinning of polyacrylonitrile fibre with the thiocyanate method ensures a smaller crystallite size, while the composition of the copolymer affects the thermogravimetric parameters.

The interest in polyacrylonitrile (PAN) textile fibre has recently decreased markedly, primarily due to competition from cheaper polyester fibres. At the same time, PAN fibres remain the basic raw material for production of high-strength, high-modulus carbon fibres (CF). A wide assortment of PAN fibres that differ both in the textile structure and linear density and the production methods and composition of the copolymer is being manufactured for these purposes [1]. The results of studying the structure of three samples of industrial PAN fibres obtained by wet spinning and differing in the composition of the acrylonitrile copolymers and solvent used are examined here (Table 1).

We know [1] that as a function of the production history, PAN can have a different supramolecular (crystal) structure — from totally amorphous to monocristalline. At the same time, the matrix effects observed in conversion of PAN fibre into CF require unconditional attention to the crystallite parameters and amorphous layers in PAN fibres.

The crystal structure of samples of PAN fibres was investigated on a Thermo ARL X-TRA powder diffractometer (CuKα-radiation, λ = 1.54.18 Å, Peltier semiconductor detector). The x-rays for determining the crystallite parameters were made in the angle range of 2θ = 10-60° at the rate of 1°/min with accelerating voltage of 45 kV and current strength of 44 mA. The diffraction patterns obtained are shown in Figs. 1-3. The crystallite size was determined with the Scherrer equation and the angle of disorientation was determined with the Wolff-Bragg equation [2]. The crystallite parameters of these samples reported in Table 2 suggest that spinning of PAN fibre using an aqueous salt solution as solvent results in much smaller crystallites than in fibres spun from solution in organic solvents. At the same time, the composition of the copolymer has almost no effect on crystallite formation in spinning of PAN fibres.

The difference in the degree of orientation of the crystallites is due to the features of plasticizing and thermal drawing of PAN fibre during production. It is only possible to note that spinning the fibre from the binary copolymer ensures much greater orientation of the crystallites for a smaller size.

Since PAN fibres undergo heat treatment in controlled conditions for production of carbon fibre, it was useful to first study the physical processes that take place in the fibres in different stages of heating in the region of the glass transition temperatures.

The studies were conducted on a Netzsch DSC 204 differential scanning calorimeter. The 4-6-mg sample was heated at the rate of 10 K/min. The curves in Figs. 4-6 characterize the heat release in heating the samples and the composite parameters are reported in Table 3.

A comparison of the characteristic temperatures for the region of inflection of the calorimetric curve suggests the determining effect of the solvent used in spinning the fibre on the glass transition process. In the case of organic solvents, the glass transition takes place at relatively lower temperatures than in using an aqueous salt solution as the solvent. As noted previously [3], based on the Flory—Huggins lattice model, the glass transition temperature should be directly proportional to the energy required for changing the segmental mobility.

A comparison of the data reported in Tables 2 and 3 suggest that despite the smaller crystallite size in spinning from salt solution, the mobility of the PAN molecules in the amorphous phase is less than the mobility of the PAN molecules in the fibre spun from a solution in an organic solvent.

This result is confirmed by comparing the heat capacity, one of the important characteristics of the structure of polymer fibres. We know that the various differences in the properties of polymers are determined by the reciprocal position of the molecular chains, their flexibility, and the intermolecular interaction energy. The values of the heat capacity are directly dependent on the flexibility of the molecular chains and their aggregates, and they are lower the greater the rigidity of the polymer chains [3]. Actually, fibres spun from salt solution have a lower heat capacity than fibres spun from an organic solvent, which confirms the greater rigidity of their segments.

At the same time, the width of the glass transition temperature region is not very dependent on the type of fibre, respectively 22.8, 21.3, and 24°C for samples 1, 2, and 3. This can be attributed to the effect of the spinning conditions only in the initial period of devitrification, which confirms the decisive significance of the structural factor related to the features of the spinning process in comparison to the structure of the macromolecule (presence of a third comonomer).

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TABLE 1. Basic Characteristics of PAN Fibres

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Type of copolymer</th>
<th>Type of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Binary</td>
<td>Organic</td>
</tr>
<tr>
<td>2</td>
<td>Ternary</td>
<td>Salt solution</td>
</tr>
<tr>
<td>3</td>
<td>Ternary</td>
<td>Organic</td>
</tr>
</tbody>
</table>

*The numbers of the samples in the following tables and figures correspond to the numbers of the samples in Table 1.

TABLE 2. Crystallite Parameters in Samples of PAN Fibres

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Crystallite size, nm</th>
<th>Angle of disorientation, deg</th>
<th>Degree of orientation of crystallites</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>30.2</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>57.7</td>
<td>84</td>
</tr>
<tr>
<td>3</td>
<td>9.7</td>
<td>64.8</td>
<td>84</td>
</tr>
</tbody>
</table>

Fig. 1. X-ray pattern of PAN fibre, sample 1.

Fig. 2. X-ray pattern of PAN fibre, sample 2.
When PAN is heated to higher temperatures, thermochemical transformations that lead to weight loss begin together with physical processes. The thermogravimetric studies were conducted on a Netzsch STA 449 C Jupiter Tensor 27 at a heating rate of 10 K/min in continuous dry air flow medium. The results are reported in Table 4.

A comparison of the temperatures corresponding to the weight loss by the PAN fibre samples suggests the greater effect of the composition of the copolymer than the spinning conditions on these indexes. This result is due to the effect of incorporating a third active comonomer of the itaconic acid type in the copolymer on the change in the mechanism of oxidation of PAN fibre. The third comonomer is the active site that serves as the initiating section of the beginning of the oxidation process. In accordance with the kinetics of solid-phase processes [1], thermal oxidation of PAN macromolecules does not begin in the units of the active comonomer but takes place randomly, beginning in random units of the polymer molecule.

For this reason, incorporation of an active comonomer significantly decreases the initial temperature of this process and shifts it to the region of lower temperatures. Correspondingly, a decrease in the process temperature is accompanied by relatively lower weight losses in the fibre.

In summarizing the results of the comparative studies of PAN fibres with different composition of the acrylonitrile copolymer and spinning conditions, we can draw the following conclusions.

A qualitative change in the type of solvent (organic or aqueous salt solution) has a marked effect on the size of the crystallites that appear when the polymer precipitates. The crystallites in the fibre spun from an organic solvent are 60-66% larger than in the fibre spun from salt solution.

An analysis of the size of the glass transition temperature region and heat capacity values shows that the rigidity of the uncrystallized segments of the polymer chains in PAN fibre spun from an aqueous salt solution is greater than the rigidity of the chains in fibres spun with an organic solvent.
The data on the thermogravimetric changes in heating these fibres confirm the activation effect of the third comonomer, manifested by a decrease in the initial weight loss temperature and the corresponding decrease in the weight loss of the fibre in oxidation.

REFERENCES