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Low-temperature carbonization of polyacrylonitrile and its copolymers

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The low-temperature formation of nucleating centers of carbon structure in polyacrylonitrile and its copolymers has been revealed and characterized using thermal analysis and X-ray diffraction.

The development of new carbon materials is a problem of considerable current interest in polymer chemistry. The thermochemical transformations of polyacrylonitrile (PAN) and the products of PAN carbonization and co-carbonization with other macromolecular compounds find wide application in engineering and industry.[1–4] A retrospective analysis of PAN carbonization conditions performed in a number of publications[1,5–9] shows that the list of regularities[10] related to the mechanisms of transforming PAN into a carbon structure is by no means complete. Recent publications[11–15] indicate that the general pattern of a thermochemical transition of PAN into a carbonized state can be clarified in the process of thorough research.

The aim of this work was to study the mechanism of initiation at the first stage of transforming polyacrylonitrile into carbonizate with the aid of well-known techniques.

Complex thermal analysis is a direct and informative method for recording changes in the structure of organic compounds and, particularly, polymers.

The unique property of PAN as a source material for obtaining carbon compounds with a maximum carbon content at a minimum heat treatment temperature is its capability of forming polycyclic structures at a relatively low temperature. This phenomenon is a result of intramolecular cyclization with the participation of nitrile substituents in an aliphatic polymer chain.

The formation of conjugated polymer cycles containing nitrogen atoms provides sufficient thermal stability of polyacrylonitrile under heat treatment. It is necessary to remove hydrogen atoms in order to preserve the cyclic structure and transform it into aromatic carbon chain compounds. This object is accomplished by introducing oxygen atoms into a PAN chain. PAN can be modified using several procedures for its dehydrogenation after completion of the initial cyclization. They include the introduction of oxygen-containing monomer units into PAN, dosated thermo-oxidative destruction, the introduction of carbon additives with developed surfaces and varying methods of PAN synthesis (changing catalysts, solvents, concentration and diffusion factors). All these operations are aimed at the formation of, first, carbonization nuclei and a turbostratic structure and, second, an oriented carbon structure. The first indications of PAN structural reorganization are phase transitions occurring in the temperature range following PAN cyclization and start of PAN dehydrogenation. These phenomena can be detected by calorimetric methods in the process of PAN sample heating in dynamic mode at a constant rate. The published thermograms of various PAN samples demonstrate thermochemical transformations related to polymer cyclization and destruction under different heating conditions. The results of concomitant qualitative analyses show the presence of the volatile products of cyclization and destruction reactions. The specific character of determining phase transitions and appearance of intermediate metastable compounds require the use of differential scanning calorimetry (DSC) and differential thermal analysis (DTA) combined with thermogravimetric analysis (TGA) and qualitative analysis of structural changes based on several spectral characteristics. The above structural transformations take place in the temperature range of 400 to 550 °C.

Previously,[16–18] exo- and endothermal effects were detected within this temperature range; the shapes of DTA and DSC curves were similar to those observed during the crystallization and melting of organic compounds.

To reveal the nature of this phenomenon, we considered the results of the thermal analysis of commercial PAN samples and polymer samples synthesized in the laboratory, as well as copolymers of PAN with natural macromolecular compounds and carbon nanostructures.[†]

Figure 1 shows the DTA curves of PAN samples synthesized by free-radical polymerization (R-PAN), anionic polymerization (A-PAN) and PAN previously subjected to cyclization (C-PAN). The difference in the structural organization of carbonization nuclei is determined by differences in the structures of the initial samples (which depend on synthesis conditions).

Thus, the structure of R-PAN features wide MWD, low packing density, the presence of branches in a polymer chain and process-related impurities. In A-PAN samples, these defects are absent; the spatial ordering of A-PAN macromolecules facilitates the emergence of nuclei at a lower temperature; the total concentration of these nuclei is considerably higher than that in the case of R-PAN (see temperatures and peak areas in DTA curves *1* and *2*).

High tacticity of A-PAN promotes the prevalence of cyclization processes, as opposed to thermal destruction typical of R-PAN. This fact is proved by the presence of two endothermal

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[†] The commercial sample was an A grade copolymer containing 93% acrylonitrile, 5.7% methyl acrylate and 1.3% itaconic acid (OOO SNV, Saratov) (Technical specifications 2272-001-82666421-2009). The polymer was obtained by radical polymerization in a dimethyl sulfoxide solution or an aqueous solution of sodium thiocyanate.

Laboratory samples were synthesized by anionic polymerization in DMF at –50 °C in an inert atmosphere in the presence of BuLi.

The commercial polymer possesses a low molecular mass (MM) (~20×10^3), a wide molecular-weight distribution (MWD) and a considerable degree of branching, the anionic PAN is a high-molecular-weight narrow-disperse polymer [MM ~ (2–3)×10^6, MWD ≈ 1.08] with a minimum amount of branches.

The commercial PAN sample and chitin, chitosan, cellulose esters and lignins as comonomers were used in the synthesis of copolymers. Copolymerization proceeded according to a radical mechanism in DMF or DMSO. Similarly, carbon nanoadditives (carbon black, thermally expanded graphite, carbon nanofibers and nanotubes) were introduced into PAN solution. Experimental techniques were described elsewhere.[3,16–18]

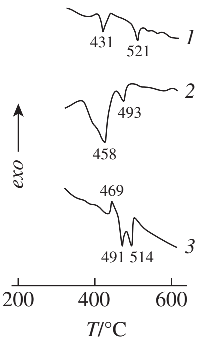

Figure 1 DTA curves for PAN samples in air: (*1*) R-PAN, (*2*) A-PAN and (*3*) C-PAN. MOM derivatograph-C. Sample weight, 50 mg; heating rate, 10 K min^{-1}.

effects at 458 and 493 °C (Figure 1, curve *2*), which are reflective of the melting of iso- and syndiotactic blocks in A-PAN, respectively. These structures can also occur in R-PAN, but their amount is significantly lower (Figure 1, curve *1*). In terms of practical applications, a decrease in the formation temperature of nuclei of a turbostratic structure in the A-PAN samples promotes the acceleration of PAN carbonization and, consequently, increases the amount of carbon residue at the final stages of carbonization (the latter conclusion is verified by the TGA data at 800 °C). Early appearance of carbon structure nuclei is further stimulated by the isothermal annealing of samples. The experiments have demonstrated that heat exposure of an A-PAN sample at 350 °C for 10 h favors the formation of turbostratic structures which melt at 407, 443 and 489 °C.

When the temperature of isothermal exposure is lowered (curve *2*) or increased, structurization is not complete (in the former case), or thermal destruction prevails (in the latter case), Figure 2.

Indirect evidence for the structural reorganization of PAN at 400–600 °C leading to the formation of ordered turbostratic fragments can be seen in the results of X-ray diffraction studies of mineral coal polymorphism.[9] For these coals, the maximum of net ordering is observed at 450–525 °C. Another peculiar feature of the initiation of nuclei generation is the presence of oxygen in the test systems. We found that oxygen present in the reaction system in any form initiates the cyclization and following carbonization of PAN. The thermal analyses of various PAN samples in an inert atmosphere did not reveal polymorphic transformations within the test temperature interval. At the same time, oxygen atoms present in the PAN chain as the elements of comonomer units and oxidized precursors or oxygen adsorbed on the surface of nanoadditives have a beneficial effect on the formation of intermediate oriented carbon structures (the nuclei of turbostratic organized carbon chains).

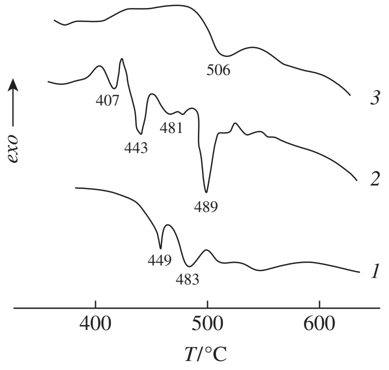

Figure 2 DTA curves for A-PAN powder annealed in nitrogen atmosphere at (*1*) 350 °C for 4 h, (*2*) 350 °C for 10 h and (*3*) 400 °C for 4 h.

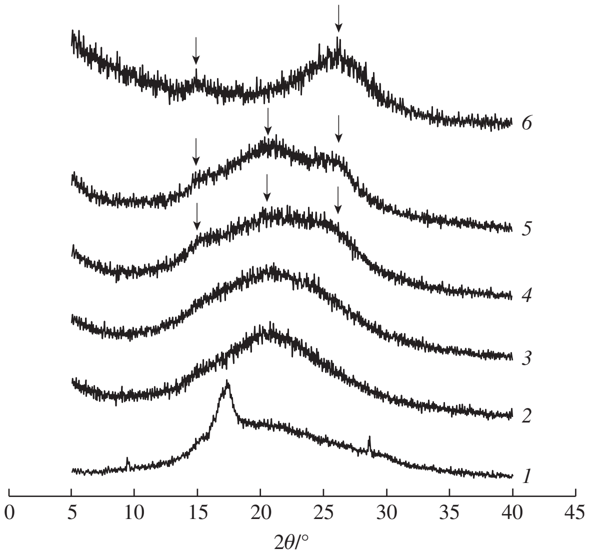

Figure 3 Diffractograms of polymer samples: (*1*) PAN + 0.005% CNT, initial state; (*2*) PAN + 0.005% CNT heated up to 450 °C with further annealing (cooling); (*3*) heating at 470 °C; (*4*) heating at 500 °C; (*5*) heating at 520 °C; and (*6*) heating at 520 °C with further annealing for 30 min at 500 °C.

The conclusions based on the above thermal analysis and the data on low-temperature carbonization of PAN copolymers with natural polymers[16–18] and nanostructural additives were verified[3] by X-ray diffraction measurements of the samples subjected to dynamic and isothermal heating within a temperature range of 450–520 °C. Figure 3 gives the diffractograms of samples, which demonstrated the most pronounced effects at 450–520 °C. These are PAN containing 0.005% carbon nanotubes in the initial state (curve *1*) and polymers heated up to 450, 470, 500 and 520 °C with the following annealing (curves *2*–*5*, respectively). In the diffractogram of the initial composition, an intense reflection at $2\theta = 17.4°$ is observed; this peak corresponds to the interplanar distance of 5.1 Å. Two weak reflections at $2\theta = 9.5°$ ($d = 9.4$ Å) and 28.6° ($d = 3.1$ Å) and a weak reflection (shoulder) at $2\theta = 15.5°$ are also present. The intense reflection at $2\theta = 17.4°$ corresponds to pure PAN.[19] The appearance of other reflections in the diffractogram (curve *1*) can be apparently attributed to the influence of CNTs on the structure of the composite film.

Sample heating to 450 °C (Figure 3, curve *1*) followed by annealing leads to the disappearance of reflections corresponding to a crystalline state of PAN. In the diffractogram, an amorphous halo at $2\theta = 21°$ can be seen accompanied by a weak reflection at $2\theta = 16°$. Heating at higher temperatures (470 and 500 °C) resulted in the diffusion of the halo with retaining the weak reflection at $2\theta = 16°$. Finally, the heating of this composite up to 520 °C (curve *5*) led to the appearance of reflections at $2\theta = 15$, 22 and 26° to indicate the formation of a new crystalline structure in the PAN-CNT composition. Note that annealing at 500 °C for 30 min led to dramatic changes in the X-ray diffraction pattern (curve *6*). The diffractogram showed only a weak halo at $2\theta = 15°$; a reflection at $2\theta = 26°$ became more intense; these observations indicate the destruction of an intermediate crystalline structure, which was detected as an exothermal peak in the DTA curve (Figure 1), and the formation of a turbostratic carbon structure.

Thus, the complex study of the thermal transformations of PAN and its copolymers at the stage of low-temperature carbonization by thermal and X-ray analysis supports our previous suggestions concerning the mechanism of initiating the formation of nuclear carbon structures from polyacrylonitrile. The revealed phenomenon belongs to thermotropic phase transitions accompanying PAN structural reorganization at the initial carbonization stage.

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