

## Solvent effect in the formation of polyconjugated system during pyrolysis of polyacrylonitrile

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IR spectroscopy and quantum chemistry were used in the studies of structural transformations taking place in polyacrylonitrile films, formed from dimethylformamide and dimethyl sulfoxide upon their IR pyrolysis and convection annealing. Residual solvent was found to affect conditions of the formation of polyconjugated bonds in polyacrylonitrile films.

**Key words:** IR pyrolysis, incoherent interactions, IR spectroscopy, polyacrylonitrile, quantum chemical calculations, AM1 method.

Polyacrylonitrile (PAN) upon pyrolysis forms a number of stable polyconjugated structures possessing a developed surface and high electrical conduction. Further thermal treatment of the polymer results in the formation of a graphite-like carbon matrix.<sup>1–4</sup> Introduction into the polymeric compounds of transition metal salts leads to the PAN-derived carbon-metallic materials, which are efficient catalysts of chemical processes. Properties of such systems depend not only on the nature of metal, which is largely defined by the structure of its valent d-shell, but also on the conditions under which a polyconjugated structure was formed.<sup>5–8</sup>

The so-called IR pyrolysis developed in the recent years is widely used for pyrolysis of PAN, during which the polyconjugated system (PCS) is formed upon IR irradiation at lower temperatures than during convection heating.<sup>9</sup> It was shown,<sup>10</sup> that a sharp acceleration of the rates of chemical reactions during IR pyrolysis is caused by a decrease in the activation energies ( $E_1 \rightarrow E_2$ ) of macromolecules which are in the excited vibration states. IR pyrolysis makes it possible to selectively influence vibration energies of separate functional groups on the macromolecule, that to a certain extent allows one to direct mechanism of structural transformations. An increase in intensity of the IR pyrolysis of PAN leads to the improvement of the graphite-like phase: an increase in the degree of graphitization, a growth in the size of regions of coherent scattering of crystallites, a decrease in the interplanar spacing.<sup>9,11</sup>

In the last 10 years, special attention was paid to the influence of the sample prehistory on physicochemical properties of amorphous glassy polymers. It was noted that

conditions of their formation (concentration of solutions and regime of thermal treatment) affect morphology<sup>12</sup> and gas separation characteristics of films.<sup>12–14</sup> Residual solvents were found to possess a plasticizing character,<sup>15</sup> and for some polymers, on the contrary, an antiplasticization effect as a result of complexation between functional groups of the polymer and the solvent, from which the films are formed.<sup>16</sup> Residual solvents were also shown to influence a mutual arrangement of the fragments of a polymeric chain (its conformational composition) as a result of hydrogen bonding, that affects the distribution of the elements of free volume and gas separation characteristics of films.<sup>17</sup>

The present work is devoted to the studies of influence of hydrogen bonding between molecules of residual solvent and PAN on the conformational structure of the polymeric chain and on the process of PCS formation upon pyrolysis of the polymer.

### Experimental

Polyacrylonitrile with  $M_r = 120\,000$  g mol<sup>-1</sup> (the weight was determined by viscosimetry) was synthesized by radical polymerization in the presence of a redox catalytic system [NaHSO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] according to the known procedure.<sup>9</sup> Formation of PCS was thoroughly studied on the PAN films formed from the solutions in DMF and DMSO standard solvents purchased from Aldrich. Films (5–10 μm thick) were formed from a solution of PAN (wt. 5%).

To study dynamics of spectral changes taking place on heating, film samples were annealed in two ways: by pyrolysis in the laboratory device for pulse photon annealing (IR chamber)<sup>18</sup> and by annealing with a step of 20 °C in the special spectrometer

thermo cell (Bruker) in the temperature range 20–210 °C, which allowed us to record IR spectra during heating "in situ". Pyrolysis of films was carried out with a step of 20 °C in the temperature range 20–200 °C in the laboratory device for pulse photon annealing. KG-220 halogen lamps were used as a source of irradiation, whose irradiation maximum lies in the region 0.9–1.2  $\mu\text{m}$ . A sample of the film in a graphite cassette was fixed by special quartz holders in a cylindrical quartz reactor, whose outer surface was equipped with 15 lamps. Intensity of IR irradiation was controlled by the temperature of heated sample, measured by a thermocouple. The accuracy of temperature adjustment<sup>18</sup> was 0.25 °C. IR spectra after each annealing step were recorded on a Bruker IFS-66v/s vacuum FTIR spectrometer (resolution 1  $\text{cm}^{-1}$ ).

Quantum chemical calculations of models were performed by the AM1 semiempirical method using the MOPAC program package.<sup>19</sup>

## Results and Discussion

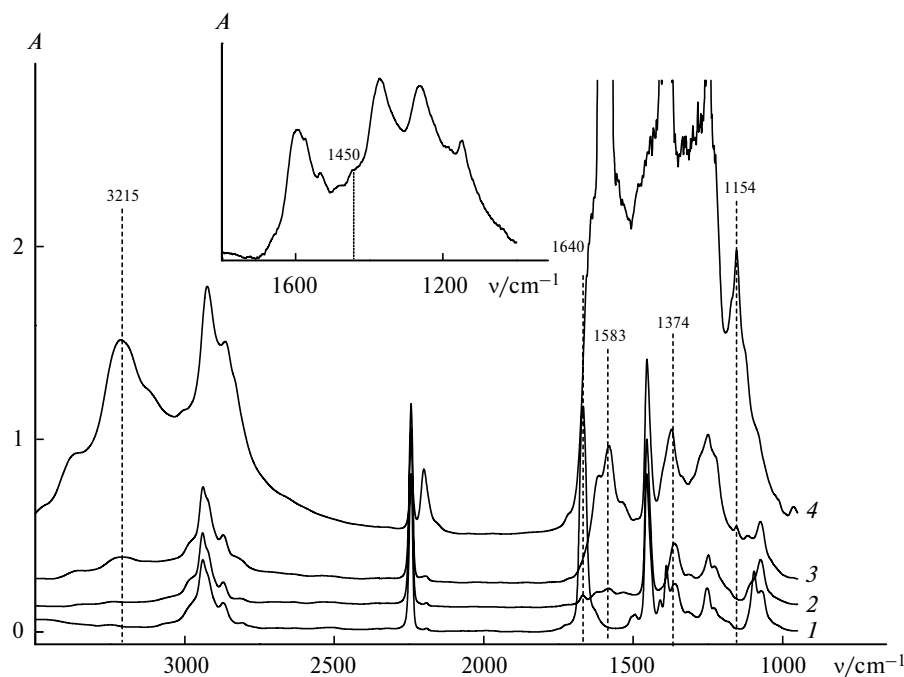
**Formation of polyconjugation in the system PAN–solvent upon IR pyrolysis of film.** Analysis of the IR spectra of PAN films formed from DMF upon step-wise pyrolysis in the IR chamber showed that PCS begins to form in the temperature range 120–140 °C (Fig. 1). The spectrum of the film, pyrolyzed in the IR chamber, recorded at 140 °C exhibits absorption bands at 1583 and 1374  $\text{cm}^{-1}$  from the stretching vibrations of the conjugated bonds  $\text{C}=\text{N}-\text{C}=\text{C}$ , as well as in the region 1200–1100  $\text{cm}^{-1}$  and at 3215  $\text{cm}^{-1}$ . This set of frequencies, characteristic of the aromatic struc-

tures arising upon thermal treatment of PAN, was broadly discussed in the literature.<sup>20</sup>

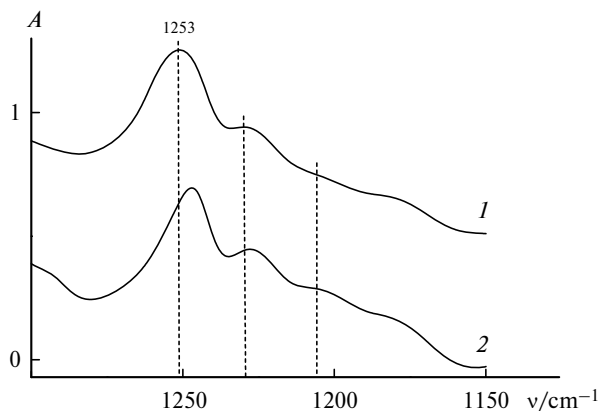
The rise of the thermal treatment temperature causes an increase in intensity of these bands and an insignificant shift of their absorption maxima.<sup>20,21</sup> If the film is heated to 160 °C, the absorption band of the nitrile group splits, which indicates that the terminal CN groups interact with the forming PCS. Analysis of the IR spectra of the IR pyrolyzed PAN showed that the film contains a significant amount of residual DMF: the absorption bands of stretching ( $\nu_{\text{C}=\text{O}}$  at 1640  $\text{cm}^{-1}$ ) and bending vibrations (at 680  $\text{cm}^{-1}$ ) were clearly recorded in the spectrum before the PCS was formed.

The solvent desorbs from the film during IR pyrolysis at 120–140 °C, resulting in the disappearance of the DMF spectral signs. However, existence of the incoherent interactions (complexes with hydrogen bonding) in the system DMF–PAN is indicated by the shift of the absorption maximum and the change in the profile of the absorption band of bending vibrations  $\delta_{\text{C}-\text{C}-\text{H}}$  at 1250  $\text{cm}^{-1}$  in the spectrum of PAN (Fig. 2). In the initial PAN film containing residual DMF, this absorption band was found at 1253  $\text{cm}^{-1}$ , after the IR pyrolysis to 120 °C and desorption of the solvent, the absorption maximum displaces to 1247  $\text{cm}^{-1}$ .

Similar studies were carried out for PAN films formed from DMSO (Fig. 3). In this case, PCS is formed only at 180 °C during IR pyrolysis of PAN film (is characterized by splitting of the band of the CN group and strong absorption in the region 1600–1200  $\text{cm}^{-1}$ ), that is 40 °C



**Fig. 1.** Fragments of the IR spectra of the PAN film formed from a DMF solution (1) and heated in the IR chamber at 120 (2), 140 (3), and 160 °C (4). In the insertion: a magnified fragment of the IR spectrum of the surface.



**Fig. 2.** Fragments of the IR spectra of the PAN film formed from a DMF solution before (1) and after pyrolysis in the IR chamber at the sample temperature of 120 °C (2).

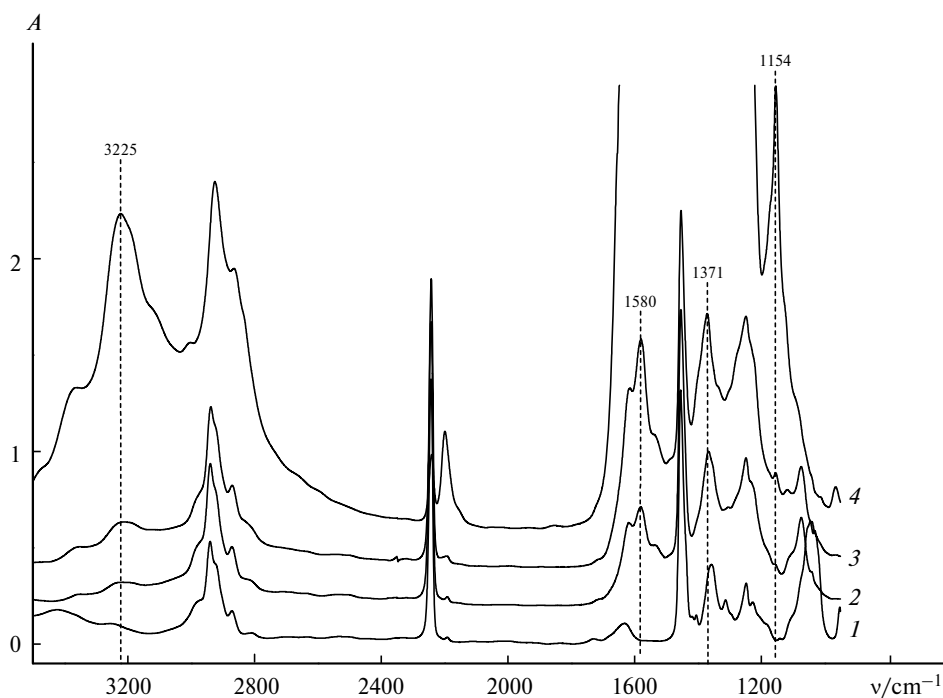
higher than for the system with DMF. The difference in the temperatures for formation of PCS indirectly indicates that the initial structuring of the system (before formation of conjugated bonds) can be affected by incoherent interactions. Such interactions lead to the changes in electron density on the atoms of functional groups as a result of changes in their surrounding, including those caused by the formation or disintegration of noncovalent bonds.

The influence of solvents on the structure of forming conjugation can be confirmed by the difference in positions of characteristic absorption bands of the resulted

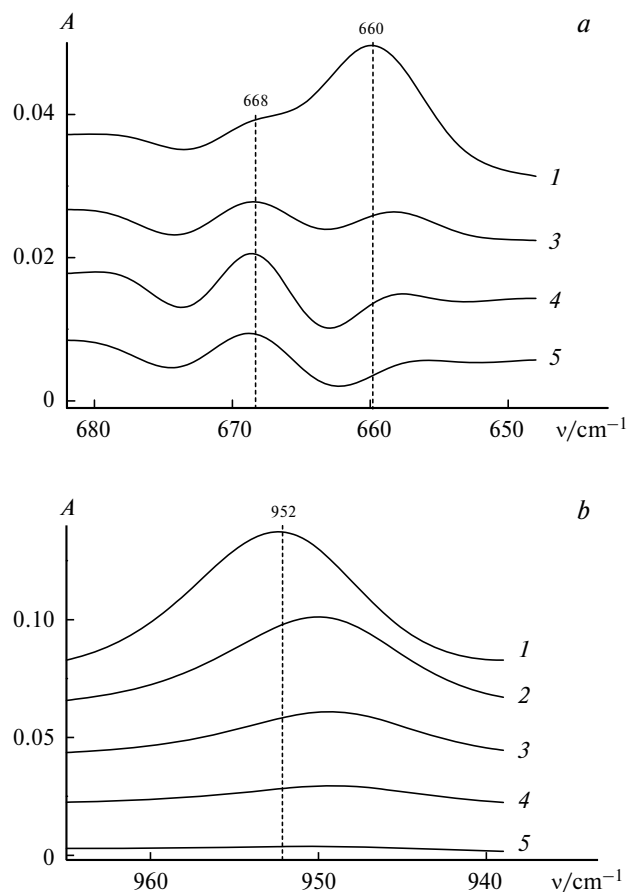
PCS in films formed from different solvents and heated to the maximum temperature (see Fig. 1 and 3). Thus, the absorption band of the formed NH groups in the system PAN–DMF has the maximum at 3215  $\text{cm}^{-1}$ , whereas in the system PAN–DMSO this band is displaced toward the short-wave region, to 3225  $\text{cm}^{-1}$ , that can correlate with the length of the conjugated section of a polymeric chain.

**Formation of polyconjugation in the system PAN–solvent upon convection heating of films.** It is known<sup>9,20</sup> that the mechanism of formation of conjugated structures upon IR irradiation of PAN does not differ from the mechanism of thermal transformations, only dynamics changes. Therefore, for the in detail studies of the initial step in the formation of PCS and, especially, for the studies of complexation processes with residual solvent, we recorded IR spectra of the films in the systems PAN–DMF and PAN–DMSO upon their convection heating to 200 °C in a high-temperature unit of FTIR spectrometer. In this case, all the structural changes in the systems occurred at higher temperatures as compared to the IR pyrolysis. The beginning of the formation of PCS was detected at 200 °C, that is 80 °C higher than in the case of IR pyrolysis.

Analysis of the spectra of the film heated in the spectrometer unit showed that the absorption band of DMF consists of two modes: one is attributable to the free residual DMF and ceases to be registered at the solvent boiling point (153 °C), whereas the other is due to the bonded solvent and is registered even on convection heating of the



**Fig. 3.** Fragments of the IR spectra of the PAN film formed from a DMSO solution (1) and heated in the IR chamber at 140 (2), 160 (3), and 180 °C (4). In the insertion: a magnified fragment of the IR spectrum of the surface.



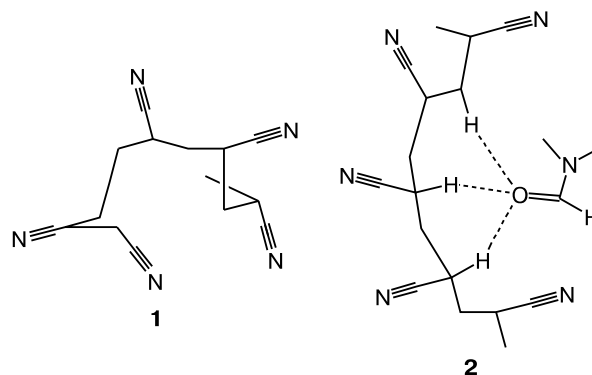
**Fig. 4.** Fragments of the IR spectra of the starting PAN film (1) and heated in the spectrometer thermo cell at the sample temperature of 110 (2), 150 (3), 170 (4), and 200 °C (5). The films are formed from DMF (a) and DMSO (b) solutions.

film to 200 °C (Fig. 4, a). No such spectral changes are observed for the film formed from DMSO, the solvent is completely removed from the film upon heating to 190 °C (Fig. 4, b). No polyconjugated system is formed from DMSO upon heating of the film in the spectrometer thermocell.

To sum up, analysis of the spectral data showed that there are interactions of the polymeric chain with the solvent in the system PAN–DMF. No such interactions were found experimentally for the system PAN–DMSO. To clarify the nature of interaction of PAN with DMF and evaluate its influence on the conformational structure of PAN polymeric chain, we carried out quantum chemical calculations for certain models.

**Quantum chemical calculations.** To perform calculations, we have chosen and optimized a structural model of PAN consisting of five elementary units, in which the dihedral angles between the CN groups initially are equal to  $\sim 90^\circ$  (1). With such a choice of the structure 1, we can neglect the influence of terminal groups, whereas the calculated geometric, energy, and electron characteristics of

interactions with internal units correspond well to the real processes in the polymer.



The quantum chemical simulation showed a possibility of existence in the systems under study of complexes of various nature, that enabled us to clarify interpretation of the experimental data. Formation of complex 2 is indicated by the AM1 calculations of structural, electron, and energy characteristics with hydrogen bonds between the H atoms at the C atom of the PAN main chain and the O atom in DMF: the complexation energy  $\Delta E = 24 \text{ kJ mol}^{-1}$ , the hydrogen bond distances  $l = 2.264, 2.316, 2.345 \text{ \AA}$ , which are less than Van der Waals radii of these atoms, the changes in charges on the atoms involving into the hydrogen bonding  $\Delta q_{\text{H}_{\text{trt}}} = 0.028, \Delta q_{\text{O}} = 0.062$ , the dihedral angle  $\text{N}=\text{C}-\text{C}=\text{N}$  after complexation  $11.5 \text{ deg}$ . A partial change in the charge is observed on the H atom of the  $\text{CH}_2$  group ( $\Delta q_{\text{H}} = 0.024 \text{ e}$ ). An increased number of DMF molecules hydrogen-bonded with the polymeric chain increases the complexation energy, that is in good agreement with the high temperatures of desorption of the bonded form of DMF from the PAN films.

It is known that formation of PCS does not take place simultaneously within the whole polymeric chain, rather it involves only those sections, where the CN groups are the most ordered. Structural analysis of the PAN model before and after complexation showed a decrease and equalization of the dihedral angles  $\text{N}=\text{C}-\text{C}=\text{N}$  between the neighboring planes  $\text{C}-\text{C}=\text{N}$  in the system PAN–DMF.

Thus, the calculated data illustrate the role of solvents in the formation of the ordered structure of PAN. The energy of hydrogen bonding explains the increase in the temperature of complete desorption of residual DMF from the film with respect to its boiling point. In this case, the bound in the complex  $\text{H}_{\text{trt}}$  atoms are not involved in the initial step of the formation of PCS and interfere with the conjugation of adjacent  $\text{CH}_2$  groups: the absorption band at  $1450 \text{ cm}^{-1}$  ( $\delta_{\text{CHH}}$ ) remains in the IR spectra of PCS formed from the system DMF–PAN, *i.e.* structural defects will be present in PCS. Formation of polyconjugated bonds in PAN films depends on the method of thermal treatment and the nature of the solvent, from which the starting film was founded. A solvent capable of forming

complexes with PAN, with hydrogen bonds is actively involved into the formation of initial structure of the polyconjugated system in PAN, ordering the CN groups along the polymeric chain and facilitating formation of conjugated units in the course of pyrolysis, at the same time, it causes arising of defects in PCS in the initial step of formation.

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