IR SPECTROSCOPIC CHARACTERISTICS OF POLYACRYLONITRILE COPOLYMER FIBRES

T. A. Belousova

The 1500-1700 cm⁻¹ frequency region in the spectrum of PAN copolymer fibre is structurally sensitive and can be used for the relative characterization of intra- and intermolecular interactions and level of supermolecular structural organization in fibres fabricated in different conditions, in particular, as a function of the nature of the solvent. In the systematic investigation of PAN copolymer fibres, the selectivity of absorption in the indicated frequency region could be analytically useful for further studies to solve both scientific and applied problems.

Polyacrylonitrile (PAN) copolymer fibres are widely investigated in the scientific literature as both final product and as initial (intermediate) stock in fabrication of carbon fibres. IR spectroscopy was used to investigate PAN copolymer fibres primarily for processing into carbon fibre. The goal was to search for spectral criteria for assessing the quality of the fibre which could be used for optimizing the process procedures for its manufacture, implementation of stable spinning, and ensuring reproducible mechanical indexes of the fibre. Fibres made from ternary PAN copolymer containing 93 wt. % basic product — acrylonitrile (AN), 5.7% methyl acrylate, 1.3% itaconic acid, and to a lesser degree fibres with sodium acrylamide-2-methylpropanesulfonate (AMPS) as the third component were primarily investigated. The IR spectra were recorded on a Specord M-80 instrument using the method of suspension of the fibres in liquid petrolatum.

A comparative analysis of the IR spectra of a large number of industrial and laboratory samples of PAN copolymer fibres, both fabricated in precipitation from different solvents and of other samples with a different composition and spinning method, showed that a series of absorption bands of moderate intensity at 1580, 1620, and 1670 cm⁻¹, whose character (number, frequency, relative intensity, degree of resolution) are specific as a function of the conditions of fabrication of the fibres and reproducible, appear in the 1500-1700 cm⁻¹ spectral region. Sections of the spectrum of different PAN fibres with relatively clear spectral characteristics are shown in Figs. 1-3. Leveling of the specific features of the absorption bands in the indicated frequency region in spectra of samples of PAN copolymer fibres fabricated with the method of pulverizing them with KBr and manifestation only in the spectra of similar objects fabricated in the form of a suspension of finely cut fibres in oil (without pulverization) indicates that the important spectral differences are most likely determined by the supermolecular level of structural organization in PAN copolymer fibres precipitated from different solvents and in different conditions. The specific features of the spectra indicated above are characteristic of one narrow frequency region. The bands are monotypic in intensity and have approximately the same extinction coefficient. These findings suggest that they belong to related groups and bonds in the spectra of different samples of PAN fibres.

As for the interpretation of the results obtained, we note that according to the published data [1, p. 48], vibrations of C=O bound by strong intramolecular bonds and C=C, C=N bonds, free and bound, appear in the 1500-1700 cm⁻¹ frequency region. The predominant formation and appearance of conjugated intramolecular chelate bonds in this reason is emphasized [1, p. 221]. The appearance of an ionized carboxyl group is also possible; the salts absorb at 1610-1550 cm⁻¹ (symmetric and antisymmetric vibrations of COO⁻) [1, p. 210]. Resonance is possible between C—O bonds. Ester carboxyl groups joined by a hydroxyl group and H—O—H deformation vibrations appear at 1650-1656 cm⁻¹. In many published studies [2-6] where PAN polymer systems were investigated with IR and UV spectroscopy, the role of the solvent in the appearance of specific
Fig. 1. Section of the IR spectrum of copolymers of PAN with itaconic acid as the third comonomer: 1) fibre fabricated with the thiocyanate method; 2, 3) fibres fabricated from solution in DMAA with LiCl (2) and without LiCl (3) from stock fabricated by the thiocyanate method; 4, 5) fibres fabricated from solution in DMSO (4) and DMF (5); 6) fibres from binary copolymer (with no itaconic acid) fabricated from solution in DMF; 7, 8) fibre fabricated from solution in DMAA with LiCl with “good” (7) and “poor” (8) mechanical indexes; 9, 10) fibres manufactured in Japan; 11) Courtauld fibre (Great Britain).

interactions and the formation of complexes in such systems is noted. In stressing the informativeness of IR spectroscopy in studying polyconjugated structures in PAN copolymers in [6], it is noted that different investigators are actually examining different polymers (homopolymer, copolymers of different composition and method of fabrication, presence or absence of solvent in them) and for this reason, establishing the spectroscopic traits of polyconjugated structures is considered promising. The analysis of such systems is especially important since it is not the free nitrile groups but instead the conjugation sections that are primarily affected in the stage of further processing of PAN fibres (thermooxidation) [7]. The short polyconjugated bonds accelerate formation of naphthyridine structures according to the data in [8].

The analysis of personal and published data suggests that the formation of conjugated intramolecular chelate structures involving the double bonds of C=O, C=C, C=N, and C≡N groups is the most probable. The effect of an intermolecular interaction is also possible. The character of the band of the OH groups in the 3400-3600 cm⁻¹ region also supports the formation of chelate structures; as the published data indicate [1, p. 127], this band becomes broad and weak in the case of