A study of conformation, configuration and phase structure of polyacrylonitrile and their mutual dependence by means of WAXS and ^1H BL-n.m.r.

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Polyacrylonitrile (PAN) samples have been investigated using wide-angle X-ray scattering (WAXS) and broad-line nuclear magnetic resonance (^1H BL-n.m.r.). The samples differed as far as their tacticity and amorphous and paracrystalline regions amounts are concerned. Structural changes that occur in the analysed PAN samples when they are annealed are discussed, and both structural similarities and differences are presented. An explanation is given to explain the improvement of order within paracrystalline regions in the polymer with an increased amount of isotactic sequences. An attempt is made at determining the dependence between configuration, conformation and phase structure of PAN.

(Keywords: polyacrylonitrile; broad-line n.m.r.; WAXS; conformation; configuration; phase structure)

INTRODUCTION

Although polyacrylonitrile (PAN) has been the centre of much attention, the structure still remains ill-defined. This is reflected in the literature by the lack of agreement and diversity of interpretations, giving rise to several structural models. A number of authors suggest a one-phase paracrystalline structure of the polymer[1-3]. In other works the possibility of existence of two or three phases is considered. Hinrichsen and Orth[4-7] claim that PAN forms a two-phase system, consisting of areas of different order. Gupta *et al.*[8-10] treat PAN as a conventional semicrystalline polymer. Imai *et al.*[11,12], however, propose a two-phase structure composed of both amorphous and paracrystalline phases, whereas a three-phase structural model was suggested by Andrews *et al.* with two amorphous phases and a crystalline phase[13,14]. Kenyon and Rayford proposed a three-phase model with an amorphous, a paracrystalline and a crystalline phase[15].

The relationship between configuration and crystallinity has been considered by some authors. Hinrichsen and Orth[5] exclusively ascribe the ability to 'crystallize' to syndiotactic chain sequences, with a planar zigzag conformation. Stefani *et al.*[16] have described two crystalline phases in PAN, composed of iso- and syndiotactic sequences which alternate in the chain. Kumamaru *et al.*[17] discovered that PAN molecules can crystallize as a single crystal lamella despite an atactic configuration.

The aim of the work presented here was to investigate the phase structure, conformation and configuration of PAN and attempt to describe possible dependences between them, using wide-angle X-ray scattering (WAXS) and broadline nuclear magnetic resonance (^1H BL-n.m.r.).

EXPERIMENTAL

Sample preparation

Three powdered PAN samples **C**, **A** and **I** were used. Sample **C** was a conventional polymer prepared by radical polymerization of acrylonitrile in dimethylformamide (DMF) solution with azoisobutyronitrile (AIBN) as the initiator at 60°C. The polymer was precipitated from DMF solution with boiling distilled water, filtered off and vacuum dried at 60°C. (This was the same polymer that was used in previous investigations[18,19]. The configuration was estimated by $^{13}C-\{^1H\}$ n.m.r. and the atacticity of PAN–**C** was found[20].

Sample **A** was obtained from sample **C** by swelling in aqueous J_2/KJ solution to about 2000% weight, followed by acetone extraction of the swelling species and drying at 60°C. The polymer was found out to be easily soluble in DMF at room temperature, in contrast to sample **C**. The X-ray diffraction trace of sample **A** presented in *Figure 1a* by the dashed line points to a greater amount of amorphous regions in this sample. As it was suggested previously[19], a greater amount of amorphous regions may result from the disappearance of paracrystalline order on swelling.

Polymerization of an isotactic-rich[22-24] sample (sample **I**) was carried out, according to White's method[21]. An acrylonitrile–urea canal complex was formed at −78°C after 8 days. The complex was irradiated at a dose rate in 0.7 Mr/h for 3 h at −78°C, using Co-60 as the radiation source for γ-ray. The sample was washed with aqueous acetone and extracted with acetone for removal of urea and residual monomer, and then vacuum dried at 60°C.

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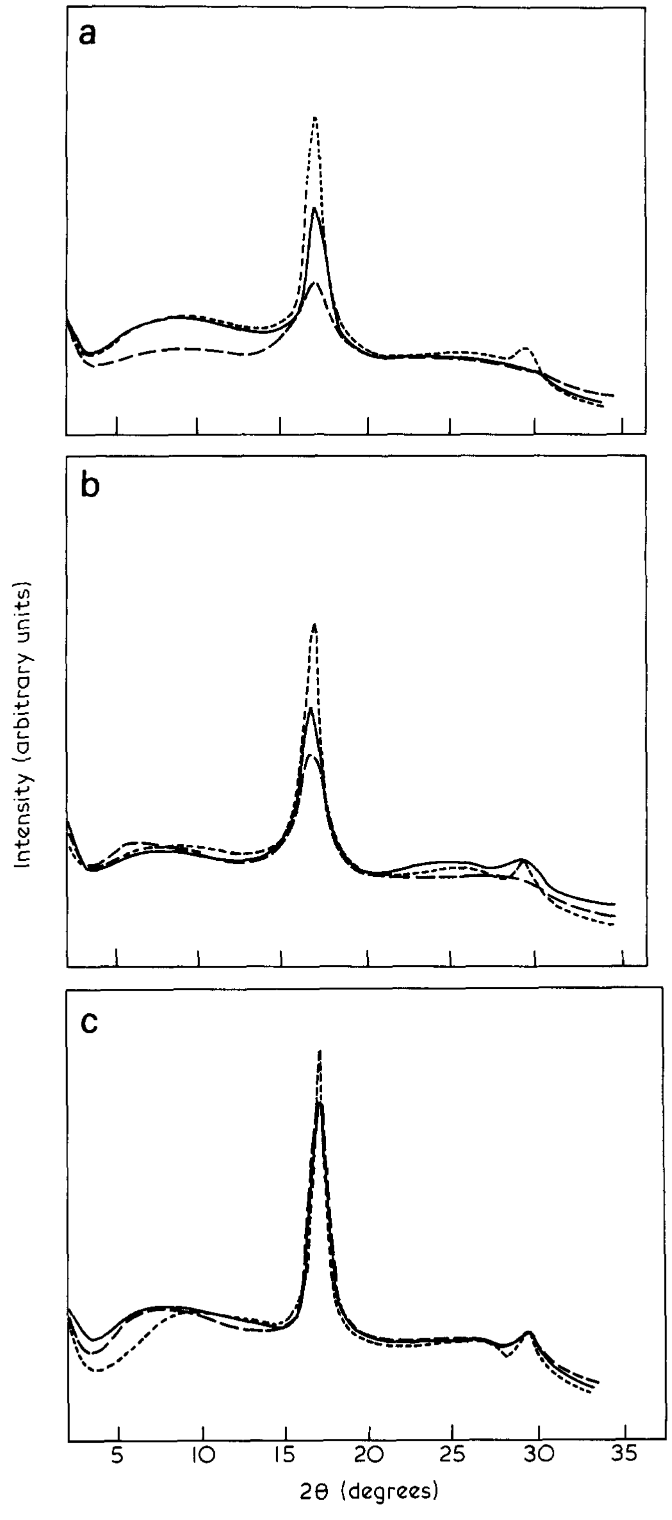

Figure 1 Wide-angle X-ray diffraction traces of the original PAN samples (a) and PAN samples annealed in 1 h at 115°C (b) and at 180°C (c). (– – –) PAN-**A**; (———) PAN-**C**; (·····) PAN-**I**

Measurements

X-ray diffraction traces of the samples under study were recorded within the angle range $2\theta = 2$–$35°$ on a DRON-1.5 diffractometer, using CuKα radiation.

^{1}H BL-n.m.r. measurements were carried out on a broad-line Varian WL-109 spectrometer at a resonance frequency of 30 MHz.

RESULTS AND DISCUSSION

PAN phase structure

In order to describe structural changes that PAN samples undergo on annealing as well as to prove differences in structure between them, X-ray diffraction traces were recorded of both the original samples and the samples annealed in 1 h at various temperatures within the range 60°–200°C (for samples **A** and **I**) and 100°–200°C for sample **C**. All the diffractograms were recorded at room temperature.

Figure 1a compares X-ray diffraction traces of the original samples, for which the maximum temperatures of thermal treatment during sample preparation were taken as their annealing temperatures. For samples **A** and **I**, this was the drying temperature, 60°C, but for sample **C** the temperature was 100°C, since the latter had been boiled in water before drying. *Figures 1b* and *1c* present X-ray diffraction traces of the three PAN samples annealed at temperatures 115°C and 180°C, respectively.

Diffractograms of all the PAN samples show the presence of two relatively sharp reflections at $2\theta = 17°$ and $2\theta = 29.5°$, which in accordance to literature indicates a hexagonal, lateral packing of chains[1,2]. It is worth noting that the reflection at $2\theta = 29.5°$ is only seen for sample **I** in the whole range of annealing temperatures. This reflection becomes visible for sample **C** only after annealing at temperatures above 105°C, whereas for sample **A** this reflection is seen above 120°C.

Half-breadth measurements (full breadth at half height intensity) of the main reflection at $2\theta = 17°$ were carried out, and the relative amounts of the more ordered regions estimated from the diffractograms (in accordance with the literature[1,2] where they are considered as paracrystalline regions with lateral order). The amounts of these regions were obtained by the simple method first applied by Hendus[25] to polyethylene and adapted to PAN by Hinrichsen[6]. According to this method the intensities at $2\theta = 11°$ and $2\theta = 21°$ as well as at $2\theta = 21°$ and $2\theta = 32°$ (after subtraction of background scattering) were connected by straight lines. The ratio of the area between these lines and the scattering curve to the total area was taken as the relative amount of paracrystalline regions. The amounts of the paracrystalline regions estimated by the method of Hendus–Hinrichsen are about 27% for the original samples **C** and **I** and about 22% for the original sample **A**. These values may bear a serious error and are merely of approximate meaning.

Figure 2 presents half-breadth changes of the main reflection as a function of the sample annealing temperatures. Half-breadth measurements of this reflection are for the original samples **A**, **C** and **I**, 1.1°, 0.7° and 0.5°, respectively, which may indicate[26] the greatest perfection of the structure in the isotactic-rich PAN and/or the greatest sizes of the paracrystalline regions in this polymer.

A two-step decrease of the value of the main reflection's half-breadth is observed for sample **A**. The first step drops from 1.1°–0.8° in a relatively narrow annealing temperature range 60°–110°C. Above 110°C there is a further decrease of breadth (0.5° for an annealing temperature of 200°C) with a simultaneous increase in the amount of paracrystalline regions to about 34%.

The drop of the half-breadth for the reflection at $2\theta = 17°$ for sample **I** is markedly smaller (from 0.5° to

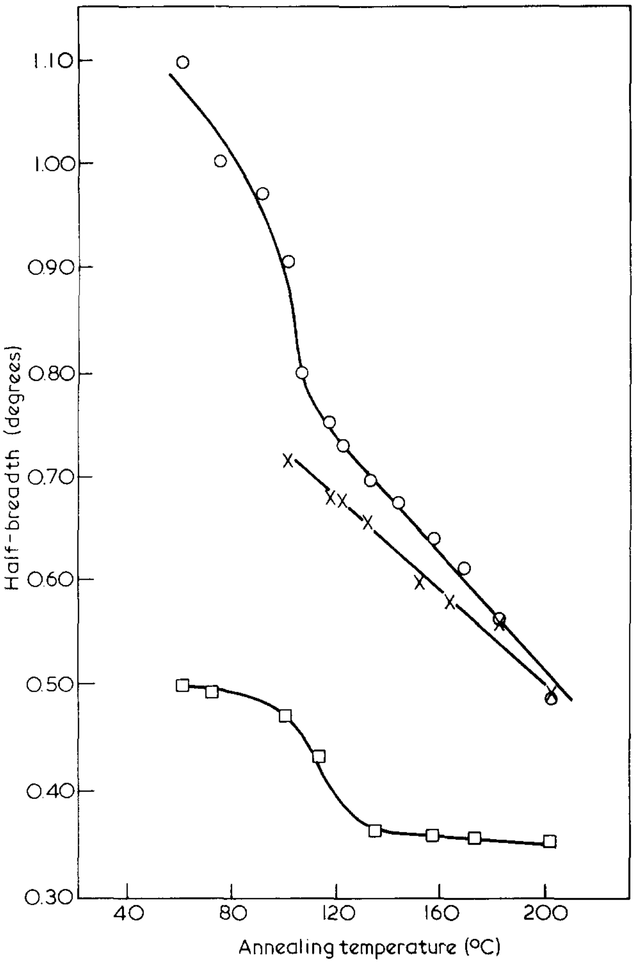

Figure 2 Full breadth at half-height intensity of the main reflection at $2\theta = 17°$ as a function of annealing temperature for PAN samples. (○) PAN-A; (×) PAN-C; (□) PAN-I

about 0.35° with an annealing temperature range of 60°–200°C), however, it also shows a two-step nature, although it is not so distinct. The final value of the half-breadth settled at 140°C. The amount of paracrystalline regions increased from about 27–34%.

A continuous decrease of the half-breadth value from 0.7°–0.5° within annealing temperature range 100°–200°C is observed for sample **C**. On the basis of the nature of the other two curves (for samples **A** and **I**) it cannot be discounted that in this case we would deal with a two-step decrease of the half-breadth, but within a temperature range broader than the analysed one. The increase of paracrystalline regions amount is similar to the one of sample **I**.

The values of both half-breadths and paracrystalline regions amounts are equal for samples **A** and **C** above 180°C. The half-breadth values reach 0.5° only at these temperatures (as in the case of the original sample **I**). The final breadth for sample **I** (about 0.35°) was not obtained for samples **A** and **C** at any of the annealing temperatures applied.

The two-step nature of the half-breadth decreases in the main reflection of the PAN samples examined (*Figure 2*) cannot be interpreted unanimously[26]. However, it seems that during the first step there is an improvement in the paracrystalline regions, and during the second step further improvement is accompanied by an increase in the size of these regions. This may be supported by the fact that the temperature range between these two steps (at about 110°C) is near to the lower limit of T_g from the BL-n.m.r. method (see later).

The values of the paracrystalline regions, calculated from X-ray diffractograms of samples above 110°C are in agreement with the Gaussian component calculated from ^{1}H BL-n.m.r. lines above T_g. For sample **C** this value reaches 30% (in ref. 18 an estimated value of the Gaussian components is given, which is lower than the value presented in this paper; based on more detailed calculations). The value for a component with a different tacticity (sample **I**) was also about 30%.

The agreement of the Gaussian component's (from the ^{1}H BL-n.m.r. lines of the samples with various tacticities) with the values of paracrystalline regions of these samples (calculated from X-ray diffractograms) would appear to agree with the phase heterogeneity of PAN assumed in our previous work. Moreover, it may also solve the problem of non-unanimous interpretation of the complex shape of the n.m.r. lines at temperatures above 115°C[18].

From the discussion presented in this paper the conclusion may be drawn that the possibility of the growth of paracrystalline regions amount is not dependent on PAN tacticity. However, the degree of perfection for these regions, which is higher for a polymer with an increased amount of isotactic sequences, evidently depends on the tacticity.

On the basis of the enthalpy and entropy of melting points calculated by Krigbaum and Tokita[27]; Bohn *et al.*[1] found that PAN consists of stiff chains with weak intermolecular forces. This can be explained by a random character of nitrile groups locations. Thus, a higher degree of perfection of the paracrystalline structure in isotactic PAN seems to be produced by an increased regularity of nitrile groups.

The amorphous polymer obtained by Joh *et al.*[11,12] proved to have a predominantly isotactic configuration. However, in their opinion, the configuration is not responsible for the amorphousness. This is because the X-ray diffractogram of isotactic PAN formed in the urea canal complex is similar to the diffractogram of an atactic polymer. The possibility of obtaining from an atactic PAN a polymer with an increased amount of amorphous regions (sample **A**), may also be a confirmation of this opinion. Moreover, Kumamaru *et al.*[17] were able to obtain single crystals of this polymer in spite of an atactic configuration.

Taking into account the results presented here as well as the conclusions of the authors quoted above, it may be stated that in the case of PAN there is no relationship between the tacticity on the one hand and the phase structure and ability to 'crystallize' on the other. Nevertheless, configuration does exert an influence on the degree of perfection of paracrystalline regions – these are characterized by a higher perfection in the case of an isotactic polymer.

Conformation and configuration of PAN

A previous analysis of sample **C**[18] (using ^{1}H BL-n.m.r. based on the estimated value of the amount of a two-proton system), assumed the existence of a specific conformation in iso- and heterotactic triads. The conformation was characterized by a mutual approach of protons from H–C–CN groups to a distance of about 1.5 Å. However, a more detailed analysis carried out here, based on n.m.r. absorption lines, showed that the amount of this component has a higher value, close to the theoretical value of about 22%. This was calculated using the assumption that proton proximity is possible in syndiotactic sequences.

In order to verify the possibility of adapting our conformational model to all PAN chain sequences independently of their configuration, ^{1}H BL-n.m.r. lines of the isotactic-rich polymer (sample **I**) were recorded within a wide temperature range. Numerical analysis of n.m.r. lines showed that the n.m.r. temperature characteristics were very similar to sample **C**[18], therefore they have not been presented graphically. It is noteworthy that the value of the component originating from high proton proximity for a rigid lattice of isotactic-rich PAN is similar to the amount value of this component for an atactic polymer sample. Therefore, the possibility of the model's spreading on all sequences, in spire of their tacticity, seems to be supported.

It was also found out that the T_g range (calculated on the basis of the temperature dependency of the n.m.r. line widths) is situated within the same limits of 120°–160°C for both samples **I** and **C**. This is the same for both components representing the amorphous and paracrystalline regions. The results (in the previous section) indicate that the increase of paracrystalline regions takes place above the same temperature (near to the lower limit of T_g from the n.m.r. method), independently of the polymer's tacticity. As was shown previously[18], the conformation is the main factor responsible for the T_g value of PAN, thus the similarity of conformation in sequences with various tacticity may also be proved by the agreement of the T_g ranges for the two samples.

Moreover (as mentioned above), the lack of difference in activation temperature of motions which are typical for glass transition in paracrystalline and amorphous regions, indicates that the conformation of PAN chains sequences is similar in both of these regions.

The results of the present investigation are compatible with the model accepted by Bohn *et al.*[1] They supposed that the steric and dipolar intramolecular interactions determined the irregular helical conformation regardless of tacticity. On the other hand, Miyachi and Andrews[14] on the basis of Bohn's model, underlined an inherent tendency to assume a helical conformation even by macromolecules in the amorphous phase.

CONCLUSIONS

(a) PAN forms a heterogenous system, composed of amorphous and paracrystalline regions. Both the phase structure and the ability to 'crystallize' do not show dependence of chain configuration. The degree of perfection of paracrystalline regions is higher in the case of a polymer with an increased amount of isotactic sequences.

(b) On the basis of the presented results we accept the same conformational model for chain sequences of various tacticity both in amorphous and paracrystalline regions.

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