Investigation of structural changes of polyacrylonitrile on swelling. Wide-angle X-ray scattering study

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Polyacrylonitrile samples swollen in a system of polymer plus low-molecular-weight substance have been investigated by means of wide-angle X-ray scattering. Nitromethane, pyridine and nitrobenzene have been used as swelling agents. Equilibrium degrees of swelling for these substances have been estimated. Influence of swelling temperature and of kind of swelling liquid on structural changes in polyacrylonitrile has been determined. An explanation of the improvement of order within paracrystalline regions on swelling has been given.

(Keywords: polyacrylonitrile; wide-angle X-ray scattering; supermolecular structure; swelling)

INTRODUCTION

Although polyacrylonitrile (PAN) has been the centre of much attention, literature data concerning the structure of PAN are of rather limited and often of contradictory nature. PAN does not belong to the group of typically amorphous polymers, nor is it a semicrystalline polymer. One group of authors suggest a paracrystalline or lateral ordered structure[1-3], while others assume two-phase[4-13] or three-phase[14-16] structures for PAN. Although PAN single crystals were obtained[17-22], the majority of authors agree as to the lack of longitudinal ordering[1,18,22].

Works concerning the swelling of PAN are far less numerous. The compositions of mixtures that could swell PAN well were theoretically determined[23]. The influence of various organic solvents on PAN fibres was investigated[24].

Andrews *et al.*[14] studied the swelling of PAN films in aqueous I_2/KI solutions. Similar works were carried out at our Institute[25]. Structural changes were observed in PAN swollen in aqueous solutions of dimethylformamide (DMF)[26]. The present work is a supplement to the studies of PAN structure in the swollen state.

EXPERIMENTAL

Sample preparation

Polyacrylonitrile in powdered form was used in the present work. It was prepared by radical polymerization of acrylonitrile (AN) in solution of *N,N*-dimethylformamide (DMF) with azoisobutyronitrile (AIBN) as the initiator at a temperature of 60°C. The polymer was precipitated with boiling distilled water, filtered off and vacuum dried at 60°C. The viscosity-average molecular weight $\bar{M}_v$ of the PAN obtained was equal to about 110000. The configuration was estimated by ^{13}C–{^{1}H} n.m.r. technique using a Varian CFT-20 spectrometer. The polymer was found to comprise nearly equal amounts of the iso- and syndiotactic triads (25% of each) and 50% of heterotactic triads[27].

The samples were swollen by their immersion in some selected swelling liquids.

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 Cu K_α radiation.

D.s.c. measurements were made using the Du Pont Instruments 1090B thermal analyser.

RESULTS AND DISCUSSION

Swelling study

Nitromethane (dipole moment $\mu = 3.02$ D), nitrobenzene ($\mu = 4.01$ D) and pyridine ($\mu = 2.26$ D) were used as swelling liquids. The swelling agents were selected based upon the observations of some authors[28,29], according to whom low-molecular-weight substances offering a high dipole moment have a strong plasticization effect on polyacrylonitrile. On the other hand, this selection depended upon the results of the studies of the equilibrium degrees of swelling for a broad group of swelling liquids.

Figure 1 presents the curves of the changes of the swelling degree with time of swelling (at a temperature of 40°C) for the selected group of swelling agents. Equilibrium degrees of swelling for film PAN samples swollen in nitrobenzene and nitromethane at different temperatures are collected in *Table 1*. The equilibrium degree of swelling is reached after about 10 h in all cases. However, the splitting of the main peak in X-ray traces of PAN at $2\theta = 17°$ (ref. 26) (which is connected with some structural changes in the polymer) already appears after about a few tens of minutes, i.e. before the equilibrium degree of swelling is reached. Moreover, it was found that the changes arrive more quickly with increase of temperature. For example, for the PAN sample swollen in nitromethane at a temperature of 50°C, the evident splitting of the peak at $2\theta = 17.0°$ appears after about 30 min of swelling, whereas for a swelling temperature of

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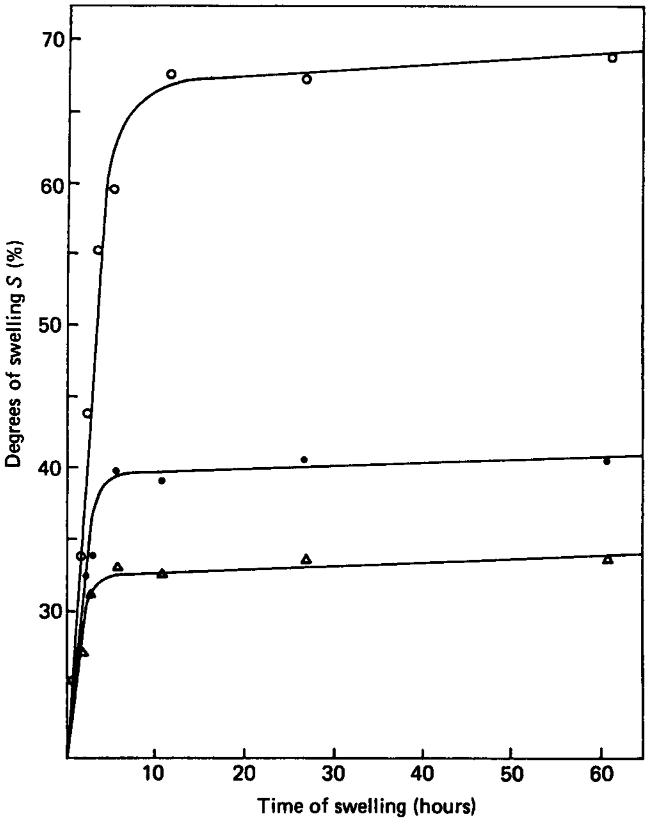

Figure 1 Equilibrium swelling degree curves of PAN vs. time of swelling at a temperature of 40°C for different swelling agents: (○) nitromethane; (●) nitrobenzene; (△) pyridine

Table 1 Equilibrium degrees of swelling (in wt%) for film PAN samples swollen in nitromethane and nitrobenzene at different temperatures

CH_3NO_2		$C_6H_5NO_2$	
t (°C)	*s* (%)	*t* (°C)	*s* (%)
20	30	20	20
40	70	40	40
50	100	50	50
80	120	75	80
90	130	85	90
20[a]	100		

[a] After cooling down

40°C it appears after about twice as long. The rate of structural changes for nitromethane-swollen PAN at 50°C is shown in *Figure 2*.

X-ray study

The main feature of diffractograms of unswollen PAN is the presence of one relatively sharp reflection at $2\theta = 17°$ and of a second, less intense, peak at $2\theta = 29.5°$ which is interspersed by a broad diffuse scattering maximum situated around $2\theta = 25$–$27°$ (refs. 9, 13, 26). According to literature it points to hexagonal lateral packing of chains within more ordered regions[1,2,13,29]. The main peak at $2\theta = 17°$ corresponding to a 5.2 Å lateral repeat distance is interpreted as the (1 0 0) diffraction of a hexagonal lattice formed by parallel close packing of molecular rods ~6 Å in diameter[1,2,29]. In some cases, a splitting of the main peak into two reflections is observed, which indicates orthorhombic packing of PAN molecular rods[2,18,22,26].

In order to describe the structural changes occurring in PAN on swelling, the X-ray traces of the PAN samples swollen at various temperatures and in time periods corresponding to the equilibrium degree of swelling were recorded at room temperature. In all cases X-ray traces were taken for wet samples, i.e. in the presence of a swelling agent. The intensity curves obtained for powdered PAN samples swollen in nitromethane at different temperatures are compared in *Figure 3*. From the comparison there may be seen a tendency for splitting of the peak at $2\theta = 17.0°$ into two reflections corresponding to the lattice distances $d_1 = 5.3$ Å and $d_2 = 5.08$ Å. This splitting, showing that the structure of ordered regions of PAN becomes orthorhombic[2], already appears at swelling temperature near 25°C.

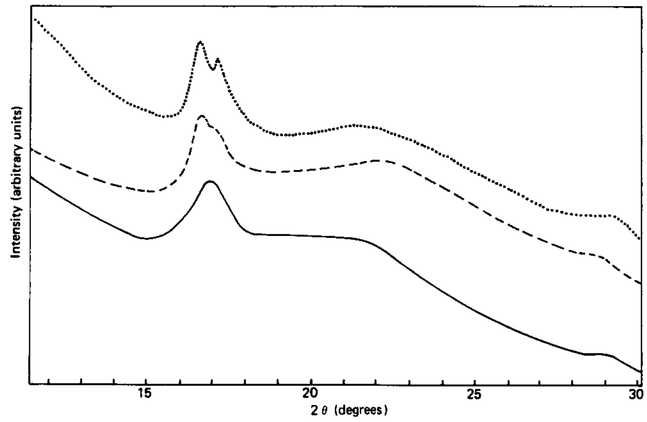

Figure 2 Wide-angle X-ray diffraction traces for the PAN–nitromethane system at 50°C vs. time of swelling—the rate of structural changes: (———) 10 min; (– – –) 20 min; (·····) 30 min

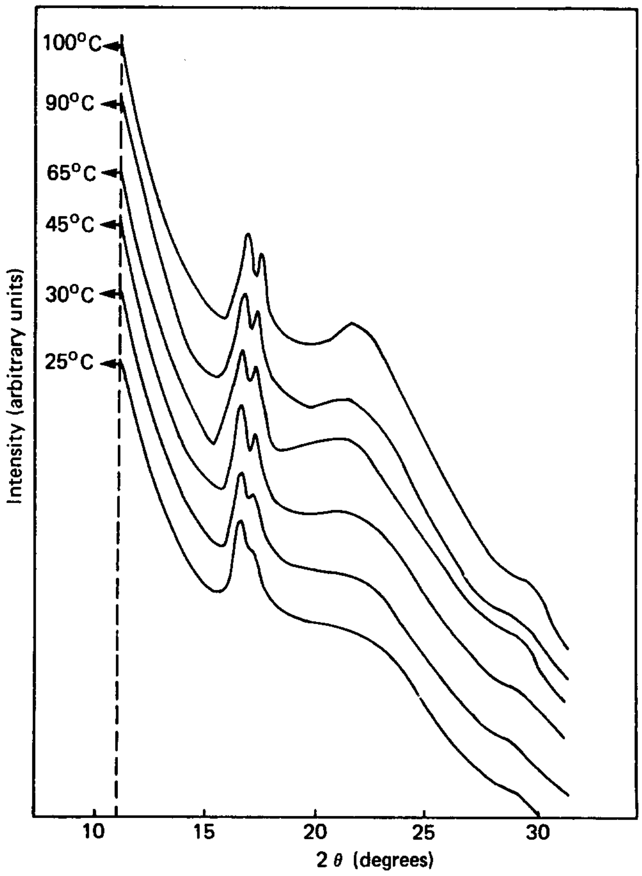

Figure 3 Wide-angle X-ray diffraction traces for the PAN samples swollen in nitromethane at different temperatures

Figure 4 represents the X-ray traces of samples swollen in pyridine at different temperatures. In this case only deformation of the main peak at $2\theta = 17.0^\circ$ is observed.

The intensity curves for PAN samples swollen in nitrobenzene at different temperatures are shown in *Figure 5*. The splitting of the main peak into two reflections appears at a temperature of about 60°C. The positions of these reflections in X-ray traces correspond to the same lattice distances as for the nitromethane-swollen samples.

For all nitromethane-, pyridine- and nitrobenzene-swollen samples the peak splitting effect disappears on drying, analogously to the case of PAN swollen in aqueous solutions of DMF[26], but for nitrobenzene it happens after a more prolonged time. In X-ray traces of well dried samples one diffraction maximum at $2\theta = 17^\circ$ is observed again (as of unswollen ones). The half-width of this could thus be measured in a conventional way[9]. It was found that the half-width changes with swelling temperature only in the case of nitrobenzene-swollen sample (*Figure 6b*). It decreases from 0.74° to 0.66° between 25°C and 60°C and then remains constant (up to 200°C). At the same time (above 60°C) the peak splitting in the X-ray traces of the wet, nitrobenzene-swollen PAN samples occurs (*Figure 5*).

A temperature dependence of the main peak's half-width for the nitrobenzene-swollen PAN samples and of annealed ones shows some differences (*Figures 6a* and *6b*). The thermal treatment of unswollen PAN leads only to an increase of the size and/or improvement of the hexagonal order of the paracrystalline regions[30]. From a comparison of the change in half-width for the well dried samples (*Figure 6b*) with the behaviour of this peak on swelling (*Figure 5*) it may be stated that:

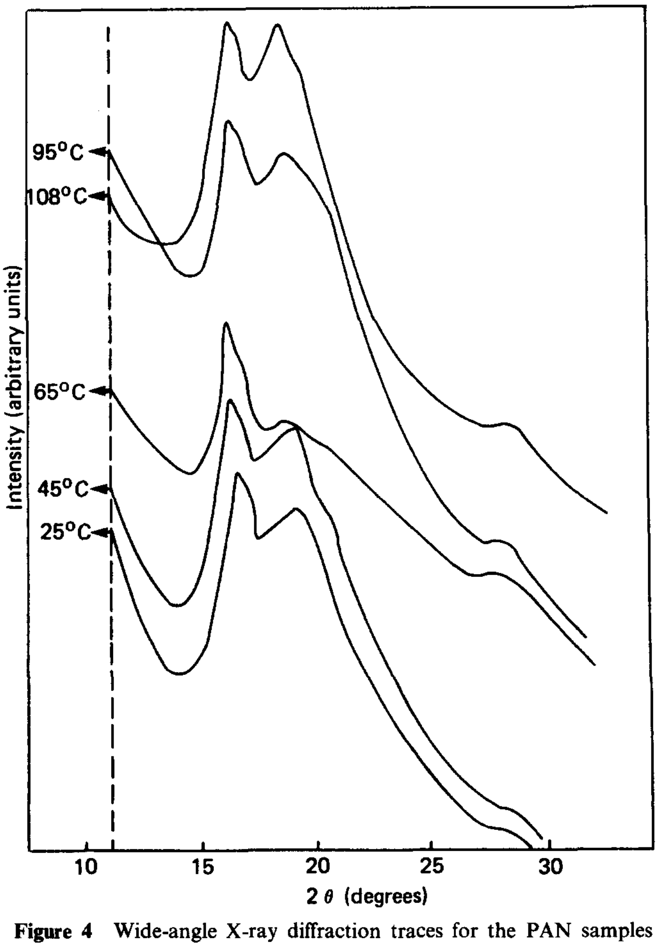

Figure 4 Wide-angle X-ray diffraction traces for the PAN samples swollen in pyridine at different temperatures

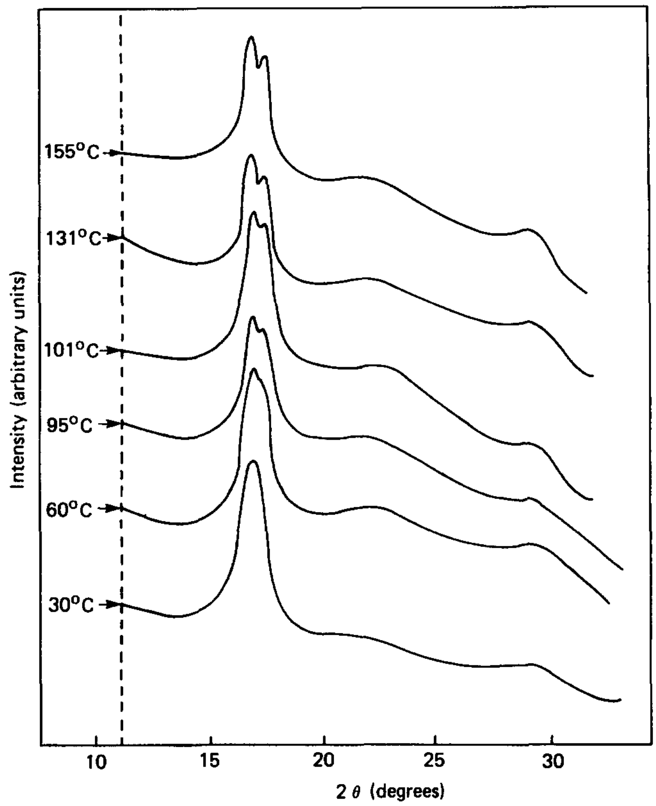

Figure 5 Wide-angle X-ray diffraction traces for the PAN samples swollen in nitrobenzene at different temperatures

(a) at swelling temperatures up to 60°C the same process as for unswollen annealed polymer takes place[30];

(b) swelling at elevated temperatures (above 60°C) causes a reorientation of the chains and formation of an orthorhombic structure, which is reflected by the tendency for splitting of the main peak.

Based upon the method of calculation of the T_g range of paracrystalline regions[9,30], the upper limit of T_g for the nitrobenzene–PAN system can be estimated (for estimating the lower one it is necessary to record some X-ray traces at temperatures below 25°C). The T_g value obtained from this method ($\sim 80^\circ$C) is in very good agreement with that obtained from d.s.c. measurements (81.5°C).

The other interesting feature of X-ray traces of swollen PAN samples is a growth of the amorphous 'hump' with swelling temperaure and its shift from the original value of $2\theta \sim 26^\circ$ to $2\theta \sim 22^\circ$ for nitromethane-swollen sample (*Figure 3*) and to $2\theta \sim 19^\circ$ in the case of pyridine-swollen one (*Figure 4*). For nitrobenzene-swollen samples this effect is not so marked (*Figure 5*). The observed phenomenon of the hump's growing and shifting is probably connected with the intensive penetration of the swelling liquid into the amorphous regions of the polymer, resulting in increase of the interchain distances. Such an explanation can be confirmed by analysis of ^{1}H braod line n.m.r. spectra in which a narrow component corresponding to the swollen amorphous regions is present; moreover the amount of this component increases with swelling temperature[31].

Summarizing, it can be noticed that, for both PAN–nitromethane and PAN–nitrobenzene, temperature ranges exist, depending on the low-molecular-weight substance used, within which swelling causes a defined

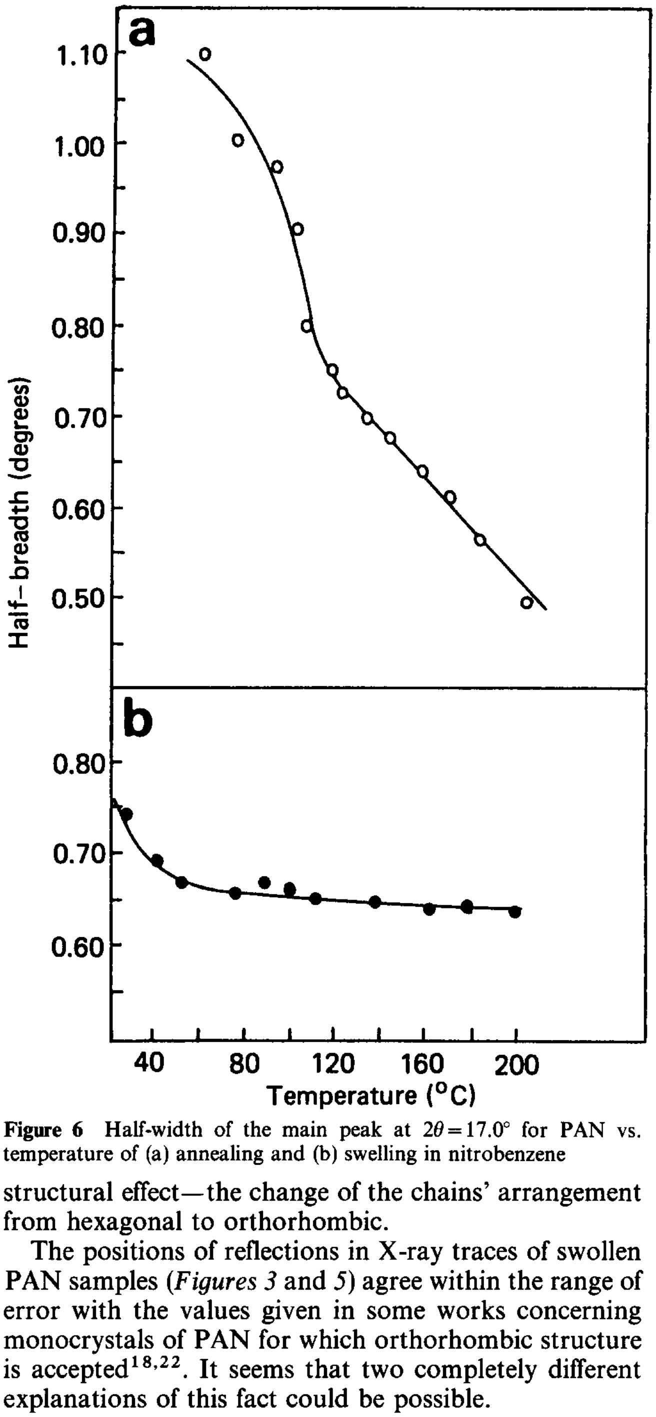

Figure 6 Half-width of the main peak at $2\theta = 17.0°$ for PAN vs. temperature of (a) annealing and (b) swelling in nitrobenzene

structural effect—the change of the chains' arrangement from hexagonal to orthorhombic.

The positions of reflections in X-ray traces of swollen PAN samples (*Figures 3* and *5*) agree within the range of error with the values given in some works concerning monocrystals of PAN for which orthorhombic structure is accepted[18,22]. It seems that two completely different explanations of this fact could be possible.

The lack of displacement of the reflections from theoretical positions calculated for an orthorhombic network could be evidence against the swelling of the paracrystalline regions as a foreground process (one explanation). With some exceptions, ordered regions of a polymer at temperatures well below the melting point are generally inaccessible to most penetrants. But in our opinion, in the case of PAN the possibility of swelling of paracrystalline areas cannot be rejected. In such a case the agreement between the theoretical and experimental positions of the reflections could indicate that the diameter of the PAN molecular rod (thought of as a molecule fitting within a cylinder of about 6 Å in diameter[1,2,29]) is smaller. The decrease of diameter would be possible if some conformational changes took place. The smaller the diameter, the more free space between the chains, so that the swelling agent could easily penetrate into paracrystalline regions (the other explanation). The possibility of changing the arrangement of the chains from hexagonal to orthorhombic as a swelling effect may be treated as an example of a polymorphic transformation. Moreover, some similarities of the PAN chain alignment in the paracrystalline regions to mesomorphic-type structures can be found.

CONCLUSIONS

Swelling of polyacrylonitrile (PAN) in some low-molecular-weight substances offering a high dipole moment causes change of the structure of the paracrystalline areas from hexagonal to orthorhombic, which is reflected in the X-ray traces by the splitting of the main reflection at $2\theta = 17°$. The observed structural effect takes place in defined temperature ranges depending on the swelling agent used.

The rate of structural changes increases with swelling temperature.

The lack of displacement of the reflections from the theoretically calculated positions indicates either that only the amorphous part of the polymer undergoes swelling or that some conformational changes are necessary for swelling of paracrystalline regions to take place.

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