Crystalline Structure of Polyacrylonitrile–Iodine Complex

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SYNOPSIS

The existence of structural order is found in the polyacrylonitrile (PAN)–iodine complex obtained by immersing PAN film in an aqueous solution of I_2/KI. We provide an interpretation for the key features of this structural order and for the structural change of PAN by iodine sorbing. The observed diffractions suggest that iodine penetrates into the crystalline phase of PAN at relatively low iodine concentrations and are intercalated between PAN molecular cylinders in the form of polyiodine columns that are composed mainly of I_5^- (most likely the I_2/I_3^- complex). Pseudohexagonal crystals of PAN are expanded uniaxially by replacement of PAN molecular cylinders by the polyiodine columns. The intercalated polyiodine column layers are arrayed parallel with PAN chain layers in the crystalline phase. The results led to a proposal of an intercalation model for the crystalline structure of the PAN–iodine complex. The crystalline structures are expected to exist with two different types of the polyiodine layers. The crystalline transition between these structures occurs by thermal mobility of PAN chains. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In our previous article,[1] it was reported that iodination of oriented polyacrylonitrile (PAN) film produces a significant change in the structural order of PAN. Generally, the penetrated iodine in polymer–iodine complexes was viewed as a pertubation of the structures of the parent polymers with which the iodine ions formed charge-transfer complexes. Moreover, it was reported that iodine sorption changed the crystalline structures of some polymers, such as polyacetylene,[2-4] poly(vinyl alcohol),[5,6] and nylon 6.[7-9]

The observation of the structural change in the PAN–iodine complex, analogous to the above-mentioned polymers, is of interest in view of the peculiar crystalline structure of PAN. The structural information of the complex is not only needed in order to interpret the electronic properties of the complex, but also has great significance especially in elucidating the typical structure of high molecular weight PAN.

Wide-angle X-ray scattering was used mainly to investigate the crystalline phase of the complex.

However, broad X-ray diffractions observed only on the equator severely constrain structural work on the complex as much as on the pure PAN. These diffractions can originate from complex regions with substantially different iodinated levels, rather than in one phase, making interpretation of it more difficult.

In this article, we discuss the structures of the crystalline phase and thermal crystalline transitions of the oriented PAN–iodine complex film and suggest a structure for the polyiodine column and possible structural models in the crystalline phase of the complex.

EXPERIMENTAL

Materials Preparation

PAN homopolymer was prepared in a dimethyl sulfoxide/water solution by suspension polymerization. The intrinsic viscosity of the polymer was measured in dimethyl formamide solution at 35°C. The viscosity-average molecular weight was 9.2×10^5, and the molecular weight dispersity, 1.81. The polymer was dissolved to make 4% dimethyl formamide solution, from which PAN film was cast on glass plates. Uniaxial orientation was achieved by stretching the

film by a factor of 7 at 120°C. The stretched PAN films were immersed in the aqueous I_2/KI solutions of different concentrations at 27°C over 24 h for equilibrium sorption. The iodinated PAN films were then dried between filter papers in a vacuum oven at 60°C for 24 h.

The degree of iodination (I/M) was calculated by $(A_m/A_i) \times [(W_i - W_0)/W_0]$, where I is maximum number of iodine atoms sorbed in the sample, M, the number of monomer units in the sample; A_i, the atomic weight of iodine; A_m, the molecular weight of the repeat unit; and W_i and W_0, the weight of the film before and after iodination.

Characterization

Wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) measurements were carried out using Ni-filtered and graphite-mono-chromated CuKα radiation. The WAXS photographs were obtained on a flat film using a Laue camera with a sample-to-film distance of 35 mm and exposure time of 150 min at 37.5 kV and 20 mA. The diffraction profiles were obtained in a parafocus and transmission mode of a Rigaku diffractometer. High-temperature X-ray diffractions were continuously recorded in a step size of 0.02° at each designated temperature for investigating the crystalline phase transition. Differential scanning calorimetry analysis (DSC) was carried out using a heating rate of 10°C/min under an atmosphere of N_2 gas.

RESULTS AND DISCUSSION

Changes from the Structure of PAN

Figure 1 shows X-ray diffraction photographs of the pure PAN film and the iodinated PAN films taken with an incident beam normal to the film plane. Figures 2 and 3 show changes in the equatorial and meridional X-ray diffraction profiles as a function of I/M, respectively. With an increasing I/M value up to 0.13, all reflection lines take a similar form to that of the pure PAN, i.e., the diffraction positions are not changed, but the intensities decrease gradually with increasing the iodine content, and then finally disappear.

When the I/M increases over 0.33, more striking changes are observed on the equator and meridian. The new reflection spots begin to appear after the (100) reflection of pure PAN disappears and become gradually sharp with increasing iodine content. In a study of other polymer systems, some researchers[10]

believed that these reflections, denoting 8 Å spacing, came from the pseudohexagonal iodine lattice formed in the amorphous regions. These new reflections, however, are scarcely found in unoriented PAN film. Hence, these reflections are not attributed to iodine lattice formed in the amorphous region. These indicate that iodine can penetrate into the PAN crystalline phase and be arranged regularly with PAN chains in the lateral direction to the axis of the PAN molecular cylinder. The penetration of iodine seems to take place uniformly through the whole crystalline phase of PAN, since the new reflections are not found with the (100) reflections of PAN and are found only after the (100) reflection disappears completely.

Figure 4 shows the SAXS meridional intensity profiles for the pure PAN film and the iodinated PAN films. The pure PAN film has a relatively distinct diffraction peak. It is an extraordinary case in that a distinct long-spacing structure is verified for the PAN homopolymer except in the case of solvent-swollen or heat-stabilized PAN. The origin of the SAXS peak is a periodic fluctuation in the electron density of the phase boundary, which is typically identified with the presence of crystallites. The long spacing of the periodicity is estimated as about 158 Å from λ/π, where λ is the wavelength and π is the scattering angle.

With increasing iodine content, the amorphous region is gradually filled with the iodine of higher electron density so that the scattering intensity of the periodic electron density weakens and broadens and, at last, is buried in background scattering. However, it does not strengthen again even though the iodine content increases more. If the iodinated PAN film had an inverted structure of the electron density that is caused by iodines accumulating in the amorphous phase, the scattering intensity should increase again. This means that the amorphous phase of the complex intermixes indiscretely with the crystalline phase penetrated by iodine.

Polyiodines in the Crystalline Phase

Figure 5 shows the meridional X-ray diffraction of the PAN–iodine complex film and indicates the appearance of two diffraction peaks at $2\theta = 28.8°$ and 18.8°. The corresponding space of this peak is 3.1 and 4.7 Å. These diffuse meridional reflections are attributed to polyiodines in which the atoms form a linear lattice of about 3 Å periodicity. This kind of reflection has been observed in other systems as well.[5,9,11,12] The Mössbauer effect[13] and X-ray diffraction data[4] also have shown that I_5^- and I_3^- ions
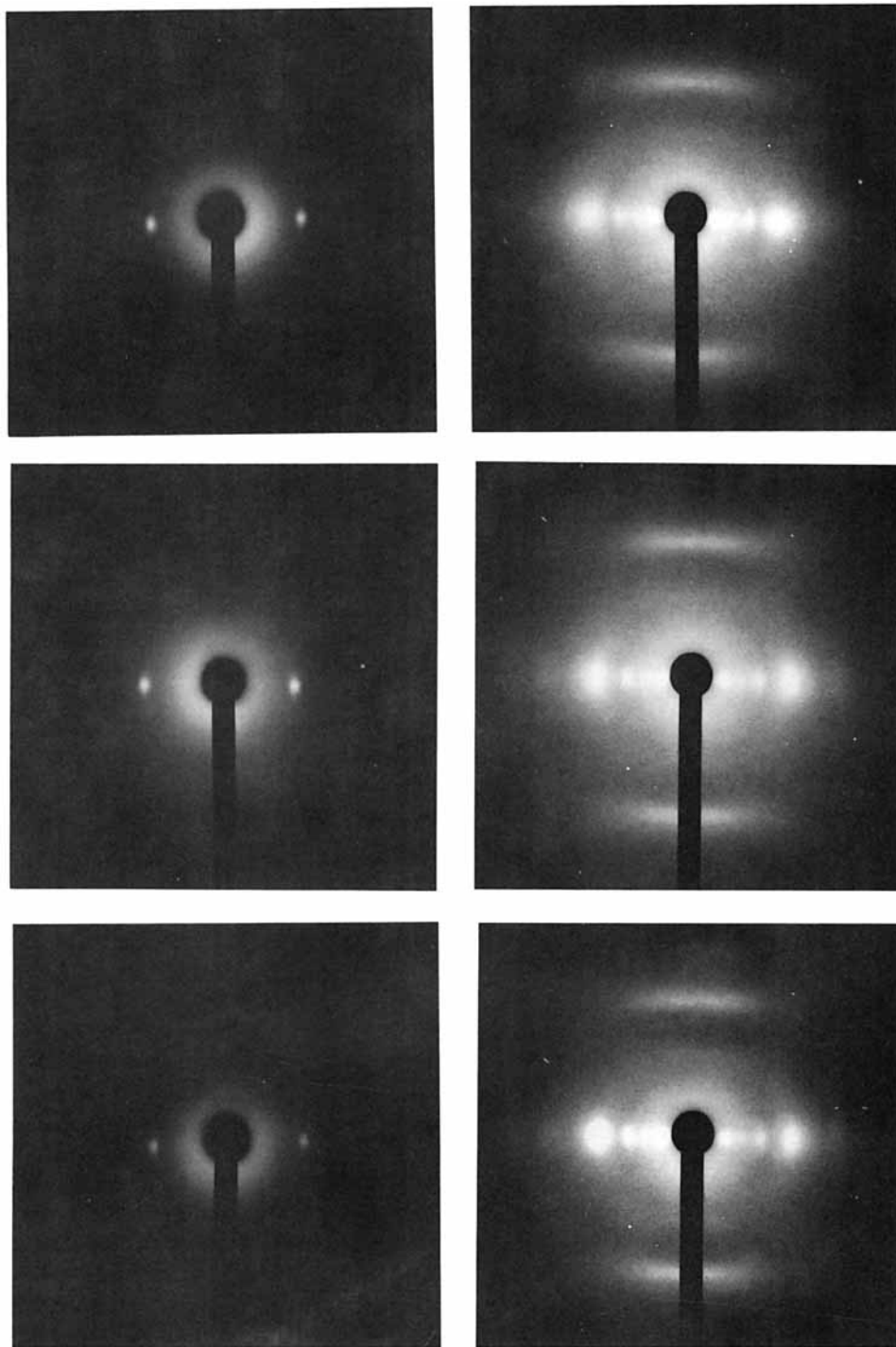
Figure 1   X-ray diffraction photographs of the PAN–iodine complex according to iodine content: left top (pure); left middle (I/M = 0.01); left bottom (I/M = 0.13); right top (I/M = 0.33); right middle (I/M = 0.62); right bottom (I/M = 0.77).

were present in an iodinated phase of polyacetylene. A study[14] by Raman spectroscopy has shown that I_5^- was formed predominantly rather than I_3^- in such heavily doped nylon 6.

The number of iodine atoms in the polyiodine column of the PAN–iodine complex was estimated by using a Laue function[15] for a linear lattice given by
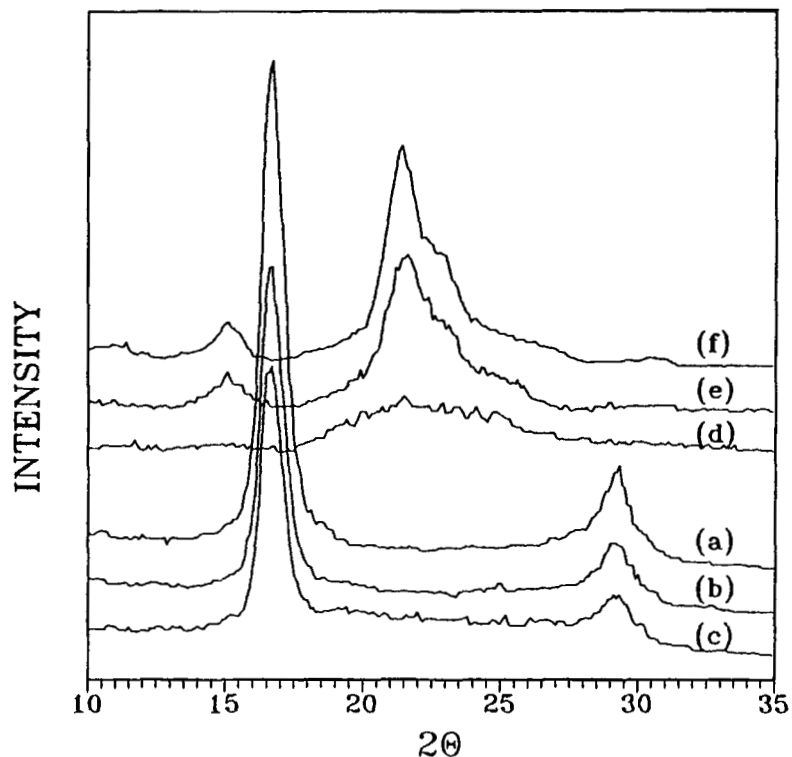
Figure 2 Equatorial X-ray diffraction profiles (parafocus mode) of the pure PAN and the iodinated PAN films: (a) $I/M = 0$; (b) 0.01; (c) 0.13; (d) 0.33; (e) 0.62; (f) 0.77.

$$L^2(S) = (\sin N\pi S \cdot C/\sin \pi S \cdot C)^2$$

Here, S is the scattering vector; C, the c-axis vector; and N, the number of iodines. From the diffraction width ($\Delta\beta$), 4.8×10^{-2} Å^{-1}, N was estimated as 5, which is certainly similar to the results in the other polymer–iodine complex systems mentioned above. Therefore, these polyiodine sequences composed
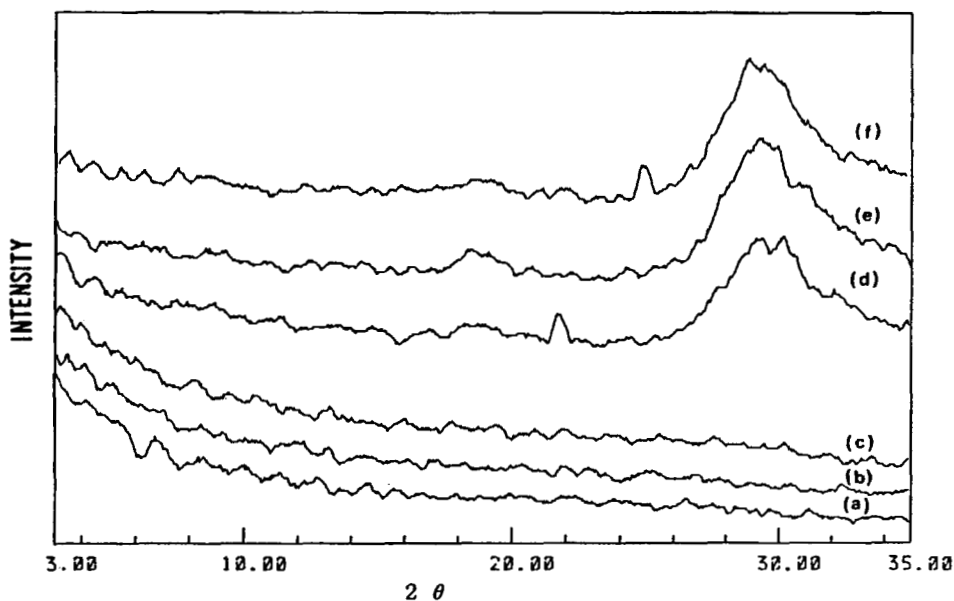

Figure 3 Meridional X-ray diffraction profiles (parafocus mode) of the pure PAN and the iodinated PAN films: (a) $I/M = 0$; (b) 0.01; (c) 0.13; (d) 0.33; (e) 0.62; (f) 0.77.
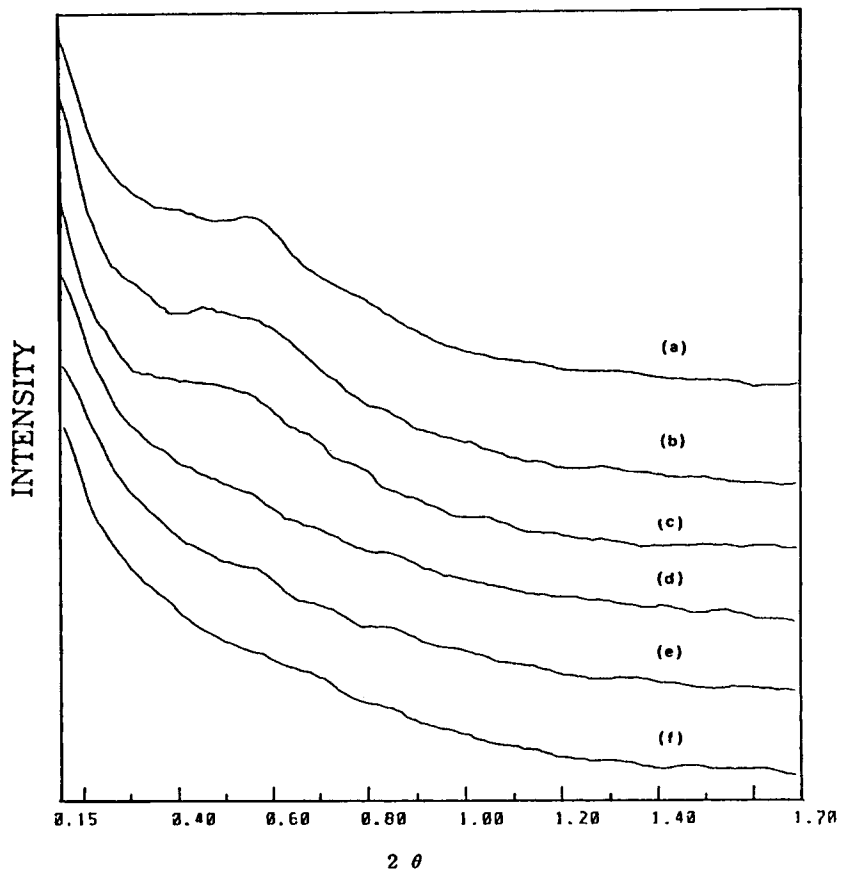
Figure 4   SAXS meridional profiles of the pure PAN and the iodinated PAN films: (a) $I/M = 0$; (b) 0.01; (c) 0.13; (d) 0.33; (e) 0.62; (f) 0.77.
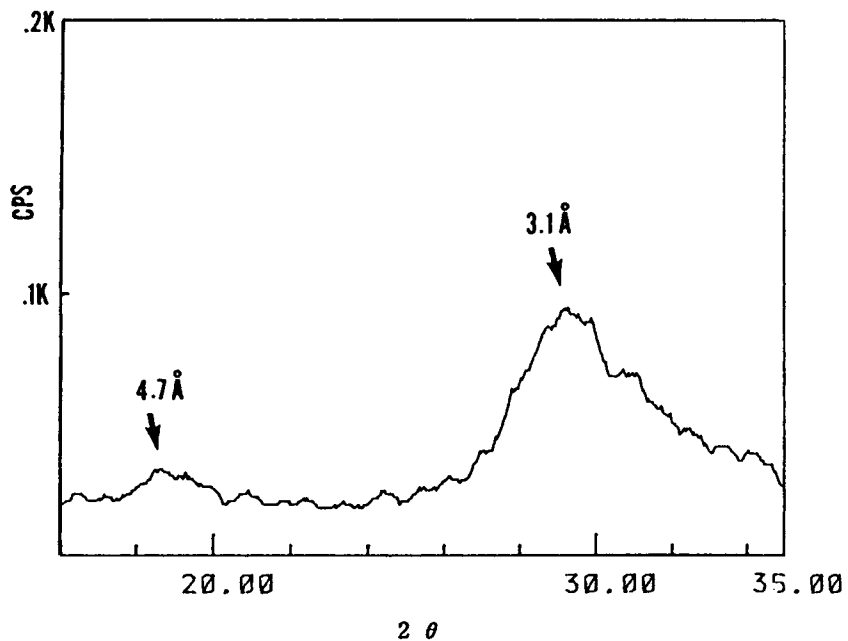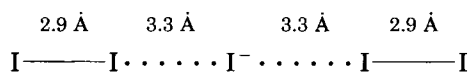

Figure 5   Meridional X-ray diffraction profile (transmission mode) of PAN–iodine complex film ($I/M = 0.62$).

mainly of I_5^- are expected to orient parallel to the orientation axis of PAN film.

The meridional hyperbolic curves of the 3.1 Å reflection cone on flat film indicate that the iodines form linear arrays perpendicular to the incident radiation and parallel to the c-axis of the film. The asymmetric shape of the 3.1 Å reflection, rising sharply on the low-angle side and falling off slowly toward higher angles, suggests that the positions of the iodine atoms in the neighboring polyiodine columns are not correlated. The weak 4.7 Å reflection is attributed to the second order of the 9.5 Å repeat of I_3^- columns.[2] Though this reflection indicates the presence of ordered arrays of triiodide ions, it alone does not provide any evidence for I_3^- in the polyiodine columns. This is because the iodine atoms in the polyiodine column are considered to form linear I_5^- consisting of I^- symmetrically bound to two I_2 units as shown the following structural motif:

$$
\begin{array}{ccccc}
2.9\ \text{Å} & 3.3\ \text{Å} & & 3.3\ \text{Å} & 2.9\ \text{Å} \\
\text{I}\!\!-\!\!\!-\!\!\!-\!\!\text{I} & \cdots\cdots & \text{I}^- & \cdots\cdots\text{I} & -\!\!\!-\!\!\!-\!\!\text{I}
\end{array}
$$

Symmetrical, linear structural motif for I_5^- parallel to PAN molecular cylinders in crystalline region of PAN–iodine complex.

Structures of Crystalline Phase

Figure 6 shows the equatorial X-ray diffraction profile of the PAN–iodine complex film. The equatorial diffraction peaks appear at $2\theta = 7.2°$, $11.3°$, $15.4°$, $21.6°$, and $22.8°$, corresponding to the spacings of 12.3, 7.8, 5.8, 4.1, and 3.9 Å. These peaks are not related to any diffractions of the original PAN crystal regardless of the starting PAN being in the hexagonal form. All reflections of the original PAN crystal, including the (100) reflection characteristic of PAN hexagonal lattice, are absent. This is proof of the disruption of PAN crystals and implies that a new crystalline structure of the PAN chain with iodine is formed due to ability of the iodine to complex with the nitrile groups as a driving force.

Figure 7(a) shows a two-dimensional intercalation model that is the projection onto the a–b plane perpendicular to the chain cylinder axis. This model was constructed on the basis of Lindenmeyer's PAN crystal cell[16] in which PAN molecular cylinders were packed parallel with each other, forming a hexagonal lattice with a nearest chain-to-chain distance of approximately 6 Å.

The PAN crystal can easily transform from a hexagonal to an orthorhombic structure by treatment with various solvents,[17] as the spacing of lattice
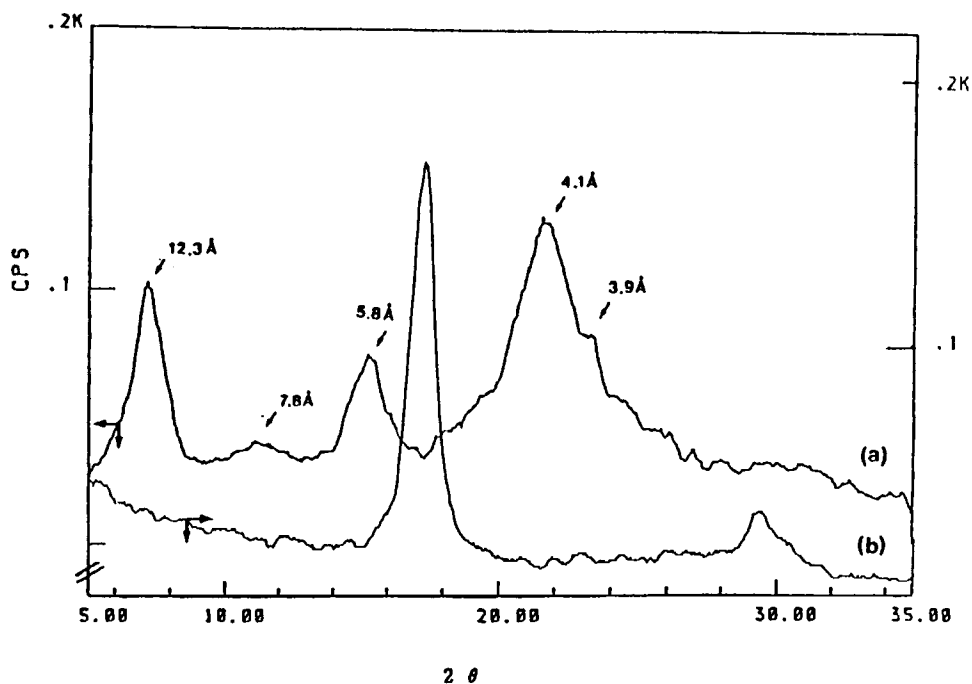

Figure 6   Equatorial X-ray diffraction profile (transmission mode) of (a) PAN–iodine complex film ($I/M = 0.77$) and (b) original PAN film.
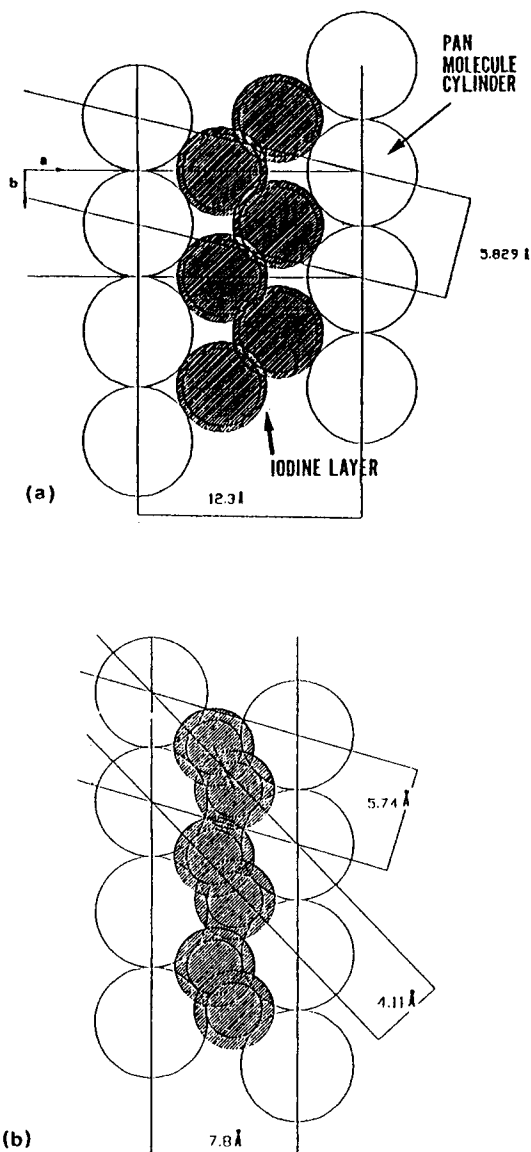
Figure 7   Two proposed structures of PAN–iodine crystal: (a) two-dimensional intercalation model; (b) space-filling model. The drawings are a projection onto the a–b plane perpendicular to the PAN cylinder axis.

planes expands in one direction. When this complex film is washed with acetone at ambient conditions, the reflection pattern of the PAN–iodine cocrystal recovers the original reflection pattern of PAN as shown in our previous report.[1] On the other hand, as a conformational transition of the PAN chain[18,19] occurred with the iodine content over $I/M = 0.77$, the iodine can penetrate into the crystalline phase without a conformational transition at a lower iodine content. Moreover, as contrasted with the dimensional change of the higher iodinated film that con-

tracted to about 24% of its original dimension in the stretched direction, the dimension of the lower iodinated film changes very little.[20] These several phenomena imply that the iodine intercalates between PAN molecular cylinders of the crystalline phase without a significant change of molecular conformation. This model, therefore, is suggested on the assumption that iodine intercalates into the expanded interplanar spacing of PAN molecules.

Taking the radius of close-packed PAN molecular cylinder as 3.0 Å, the bond length of nitrile groups protruded from the cylinder as 0.5 Å, the van der Waals radius[21] of iodine as 2.15 Å, and average I— I distance[9] of iodine ions as 3.08 Å, the packing of staggered iodine layers between the layers of PAN molecular cylinders gives a dimension of 12.3 Å, as shown in Figure 7(a). The appearance of the 12.3 Å spacing is especially significant because it provides information about the intermolecular chain without going into the more detailed radial distribution function. An alternating arrangement of iodine layers, separated by close-packed planes of PAN, can be surmised. The intercalation of iodine between chains would be most likely to have occurred in the position in which the PAN molecular cylinder was located, because of the direction of the nitrile groups. The (200) plane of the orthorhombic lattice of the original PAN would have expanded to ca. 12.3 Å. The spacing of the (010) plane in this two-dimensional monoclinic lattice model is calculated to be about 5.83 Å, close to the observed d-spacing.

However, the plane causing broad 4.1 Å and weak 7.8 Å reflections could not be explained in this model. Furthermore, it was impossible to construct the model to satisfy all terms of the reflection results simultaneously.

PAN molecular cylinders are nearly perpendicular to the a–b plane, and its hexagonal packing is caused mainly by the attraction forces of dipole-dipole bound nitrile groups. Therefore, if the isotactic and syndiotactic portion of the mixed stereoregularity of PAN has some regularly helical conformation, of which the dihedral angles of projections of adjacent nitrile groups in the a–b plane are 60° or 120°, i.e., TG-(3/1), T$\bar{\text{G}}$-(3/1), TS-(6/ 1), T$\bar{\text{S}}$-(6/1), etc., the identity period of each tacticity portion is at least over 6 Å. This spacing may be sufficient for iodine to be inserted about 1 Å into the PAN molecular cylinder.

Figure 7(b) shows a space-filling model in which iodine layers composed of a bent column are arrayed separately. The 4.1, 5.8, and 7.8 Å spacings observed in the PAN–iodine complex can be identified as
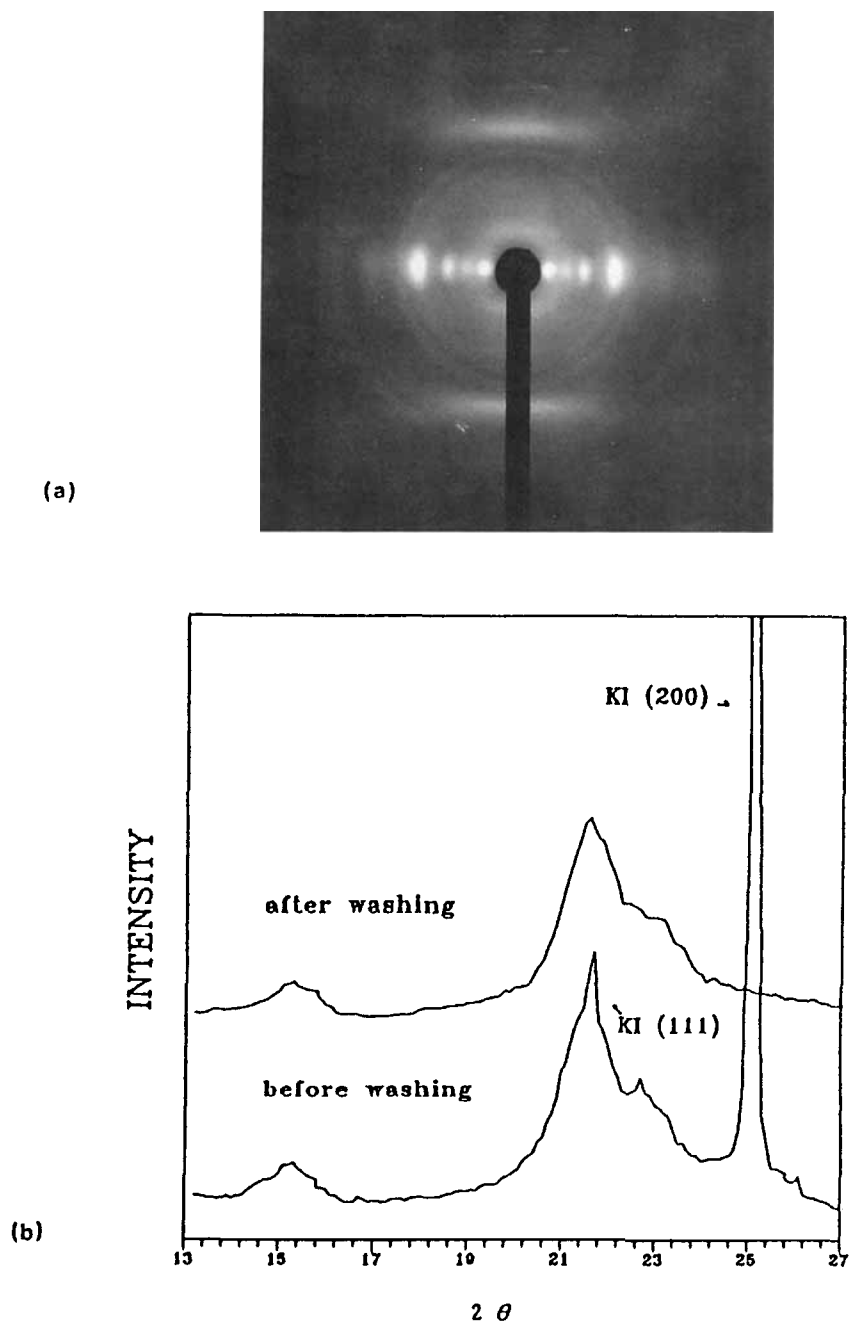
(a)

(b)

Figure 8   X-ray diffraction of PAN–iodine complex films ($I/M = 0.77$) with and without inorganic crystal: (a) photograph before washing; (b) equatorial profiles before and after washing.

(110), (100), and (010) planes of this two-dimensional monoclinic lattice, respectively. However, the 12.3 Å spacing is absent from this model. The crystal structure of the PAN–iodine complex therefore is expected to be a mixed structure of the above two assumed models.

The 4.1 Å reflection is a doublet superimposed on the 3.9 Å reflection that seems to be the second order of the 7.8 Å and broader than the (100) reflection of the pure PAN. This apparent broadening may be due to superimposed reflections. As iodine intercalates between PAN molecular chains, forming

a pseudohexagonal lattice, an anisotropic expansion in the lateral dimension of the crystal and a deviation of the expansion may cause the asymmetric peak. Likewise, the intensities of reflections for different reflection planes of the lattice may also cause a more asymmetric peak in the doublet profile as shown in the suggested models. It is not presently possible to compare the observed intensity with the calculated intensity because of the uncertain positions of atoms in the PAN crystal and limited X-ray diffraction data now available.

Figure 8 shows the X-ray diffraction of PAN–iodine complex films with and without inorganic crystal. The 4.08, 3.53, and 2.48 Å reflections are associated with (111), (200), and (220) plane reflections of KI, respectively. These peaks appear before washing the complex film with water, but disappear after washing. These inorganic lattice planes are ascertained by circular reflections in the diffraction photograph. The inorganic crystal therefore seems to form on the surface of the PAN–iodine complex film during the drying process of the iodinated film.

Some reflection angles from the inorganic lattice, especially the 4.08 and 3.97 Å reflections, were nearly coincident with the maximum intensity angles of some reflections, 4.1 and 3.9 Å, from the PAN–iodine complex. Nevertheless, the most intense 3.53 Å reflection of KI was not superimposed over any reflections of the complex. This fact seems to explain that the structural order of the complex tends to form the similar interplanar spacing with some planes of inorganic KI/KI₃ crystal that crystallizes on the surface of PAN–iodine complex film. However, further research is needed on the details.

Thermal Transition of the Crystalline Phase

Figure 9 shows DSC thermograms of the PAN–iodine complex. There are several characteristic exothermal peaks at temperatures of 107.8, 178.5, and 260.0°C (denoted as peaks 1, 2, and 3, respectively). In the second scanning for the sample heated up to 150°C in the first scanning, peak 1 disappears. In the third scanning for the sample heated up to 210°C in the second scanning, peak 2 also disappears. Or-
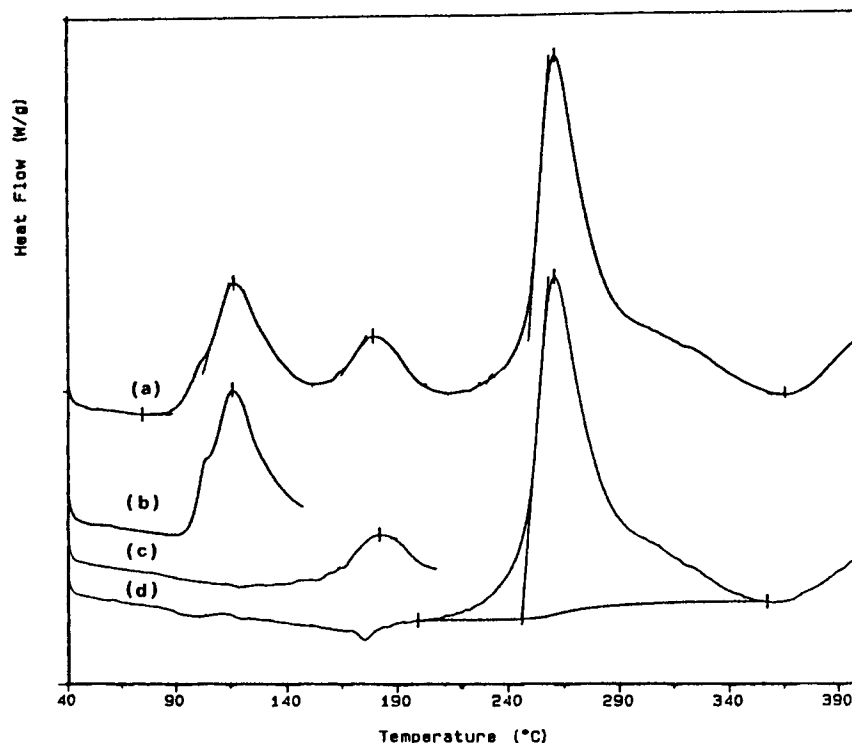

Figure 9   DSC thermograms of PAN–iodine complex film: (a) first scanning up to 400°C; (b) first scanning up to 150°C; (c) second scanning up to 210°C; (d) third scanning up to 400°C.
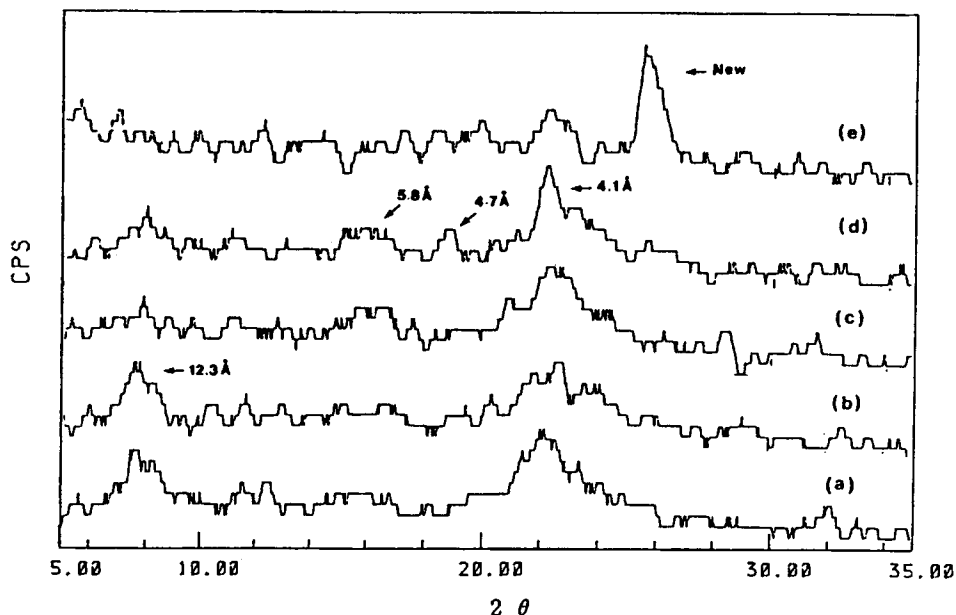
Figure 10 High-temperature X-ray diffraction profiles of PAN–iodine complex film at
(a) 0°C, (b) 80°C, (c) 110°C, (d) 140°C, and (e) 180°C.

dinary PAN polymer exhibits an exothermal cyclization peak only, i.e., T_g is not easily detected and T_c and T_m are missing. The exothermal behaviors of peaks 1 and 2 seem to be attributed to certain crystallization and/or a crystalline phase transition in the PAN–iodine complex.

The detailed investigation was carried out by high-temperature X-ray diffraction analysis as shown in Figure 10. The temperatures for the scattering analysis were chosen by the characteristics given in the DSC curves. The reflection at 0°C is similar to that at room temperature. The reflections at 80°C are slightly lower except for the 12.3 Å reflection. At 110°C, the temperature at which peak 1 appeared in the DSC thermogram, the 12.3 Å reflection weakens notably, whereas the other reflections, especially the 5.8 Å reflection, broadly increases. At 140°C, the temperature that corresponds to the valley on the low-temperature side in the DSC thermogram, the 4.7 Å reflection (may be attributed to triiodide anions) appears and the 4.1 Å reflection strengthens. At 180°C, the temperature at which peak 2 appeared in the DSC thermogram, the 4.1 Å reflection weakens and a new reflection adds to the intensity notably, which are signs of the appearance of another structural order in the complex. The spacing of the newly appeared reflection at 2θ = 25.5° is about 3.49 Å, which is close to the stron-

gest (200) reflections of KI: 3.53 Å. This is similar to crystallizing on the surface of the complex film, as discussed above.

Consequently, the exothermal heat flow at 110°C is caused by a phase transition of PAN–iodine cocrystals, which may indicate a transform from the less packed structure as proposed in Figure 7(a) to the more packed structure as proposed in Figure 7(b). The close-packed structure develops considerably with increasing temperature. As thermal energy strengthens molecular motions in the crystalline phase at 180°C, most of the crystals will rupture or transform so that most reflections weaken.

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