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Structure of iodine–nylon 6 complex: 4. Irregular stacking of intercalated iodine in the complex

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Oriented iodine-doped nylon 6 specimen which was prepared in an I_2–KI aqueous solution was immersed into a KI aqueous solution. The 're-immersed' specimen indicated an irregular intercalation of iodine stacked between hydrogen-bonded planes of nylon 6 in the complex. In the irregular stacking, iodine atoms or polyiodides are not intercalated between all of the interlayer region, while they are between each hydrogen-bonded plane of nylon 6 chains in ordinary complex; spacing of the planes is 1.95 nm in the irregular intercalation while it is 1.56 nm in the ordinary specimens. In the complex with the irregular stacking, however, the ordering along the chain axis is similar to the ordinary one. This irregular structure is induced by applying an inhibitive effect of the I^- ion to prevent doping in the I_2–KI aqueous solution. It suggests that the iodine–nylon 6 complex can introduce various intercalated structures such as graphite intercalation compounds. Copyright © 1996 Elsevier Science Ltd.

(Keywords: nylon 6; iodine; intercalation)

Introduction

Iodine-doped nylon 6 (iodine–nylon 6 complex) was regarded as an intermediate state on a transition from α-form to γ-form of nylon 6; iodine-doping with an I_2–KI aqueous solution and desorption with a sodium thiosulfate aqueous solution cause conversion of hydrogen bonds[1–4]. Hydrogen bonds are formed between anti-parallel chains in the α-form of nylon 6 and are formed between parallel chains in the γ-form. Hence iodine-doping had been argued to be regarded with the conversion of hydrogen bonds between nylon 6 chains.

On the other hand, the complex can be a hybrid material with characteristic properties. There can occur various processes; for example, oxidation and reduction, charge transfer, re-orientation of drawn specimen or alteration of polyiodides, I_n^- [5–8]. In the latter half of the 1980s, Murthy *et al.* reported significant works with uni-oriented and non-oriented specimens[8–11]. We also investigated doubly oriented specimens of the complex with X-ray diffraction, determined the lattice constants of the unit cell of the complex crystal and, furthermore, discussed transition of the arrangements of polyiodides along the chain axis[7,12,13]. Considering ordering along the chain axis, there are various kinds of ordered structures and transitions in the complex: for example, unstable one-dimensional structure, stable one and the complex crystal. In these structures, at least two polyiodide ions, I_n^- ($n = 3$ or 5), are intercalated between each plane of nylon 6 which corresponds to the hydrogen-bonded planes in the α-form. It should be noted that the hydrogen-bonded planes in the α-form are constructed by hydrogen bonds between the anti-parallel nylon chains. On the other hand, the planes in the complex are done by coordination with polyiodides and nylon chains; they may be called 'coordinated planes'.

However, the iodine–nylon 6 complex can show another intercalation of iodine different from the ordinary scheme reported previously[12], where the doped polyiodides are intercalated between each plane of nylon 6. Such irregular stacking observed in X-ray diffraction is reported additionally in this paper.

Experimental

Two kinds of a 0.3 N I_2–KI (0.15 mol l^{-1} for I_2) aqueous solutions, A and B, were prepared for investigation of the effect of I^- ions on doping for non-oriented nylon 6 specimens. I_2 can hardly be dissolved in water without the I^- ion; the I^- ion is necessary to prepare the aqueous solution[14]. First, an aqueous solution was prepared with the least possible quantity of KI which can dissolve 0.15 mol l^{-1} I_2 into the solution (solution A). Then excessive KI was added to the solution A (solution B). Added substances of the 0.3 N solutions are listed in *Table 1*. Finally a KI aqueous solution (1 mol l^{-1}) was prepared.

Nylon 6 samples were melted on a hot plate and quenched to the non-oriented specimens (ca. 0.4 mm in thickness). Pieces of the non-oriented specimens were immersed in the aqueous solutions A and B for a respective time at room temperature and increases in mass (Δm) were measured as a parameter for doping.

A doubly oriented specimen of the complex was prepared with a 0.1 N I_2–KI aqueous solution in 5°C. A procedure of preparation for the doubly oriented complex has been reported previously[12]. The doubly oriented complex specimen was immersed into the 1 mol l^{-1} KI aqueous solution after iodine-doping. This 're-immersion' process for the oriented complex to the KI aqueous solution was achieved for 10 days at room temperature.

X-ray diffraction photographs and intensities were taken with a flat-film camera of an imaging plate (IP)

Table 1 Composition of 0.3 N I_2–KI aqueous solutions

Solution	I_2 (mol l^{-1})	KI (mol l^{-1})
A	0.15	3.3
B	0.15	6.6

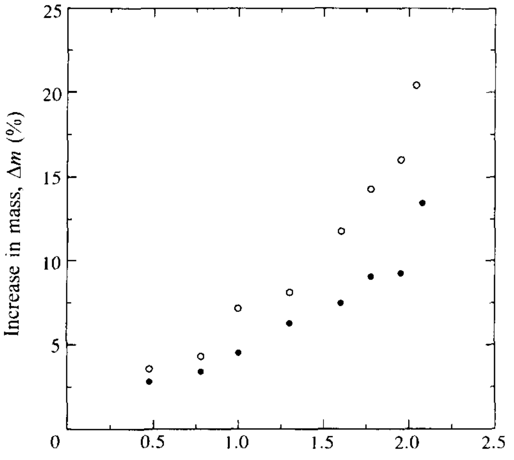

Figure 1 Increase in mass of doping, Δm, vs immersing time in two I_2–KI aqueous solutions. A (○) and B (●) in *Table 1*

with Mo Kα radiation monochromatized by a graphite monochromator. Intensities observed on the imaging plate were corrected with a Lorentz polarization factor, $P(\theta)$, and a layout factor, $D(2\theta)$. The factor $D(2\theta)$ is a geometric correction since the intensities are observed on the flat-film camera of the imaging plate; the observed intensities on the flat-film camera, $I_{\mathrm{obs}}(q)$, should be estimated as $I'(q)$, which are intensities on a sphere of a radius L equal to the camera length of the flat-film camera. A normal of a pixel on the IP forms an angle of 2θ with the scattered beam and the intensities $I_{\mathrm{obs}}(q)$ are proportional to $1/(L^2 + L^2 \cdot \tan^2(2\theta))$. Then $I_{\mathrm{obs}}(q) = I'(q) \cdot \cos(2q) \cdot L^2/(L^2 + L^2 \cdot \tan^2(2\theta)) = I'(q) \cdot \cos^3(2\theta) \equiv I'(q) \cdot D(2\theta)$. Absorption with the light path and volume of the sample is neglected.

Results and discussion

Successive iodine-doping introduces a doubly oriented complex with the hydrogen-bonded planes which are parallel to the surface of the specimen similar to the original doubly oriented specimen of the α-form. In exceptional cases or through rapid doping, such double orientation is modified or destroyed[12,15]. However, even in modified or destroyed orientation, spacing of the planes are unchanged in X-ray diffraction. After all, disordering of double orientation observed in X-ray diffraction is attributed to disordering of orientation of crystallites following doping, not to the rearrangement of the planes in each crystallite. Then, the hydrogen-bonded planes in the complex are imaged to be rigid planes though they have lost regular hydrogen bonding. If substances are intercalated in the interlayer region between the rigid planes, there is expected variation of intercalation such as graphite intercalation compounds (GIC)[16,17]. However, ordinarily doping for the complex with the I_2–KI aqueous solution introduces only a spacing of 1.56 nm for intercalation; it means intercalation of polyiodides into all of the interlayer region between the planes of nylon 6 [7]. Here, an inhibitive effect of the I^- ion against doping is applied.

I_2 is hardly soluble in water without the I^- ion. Then, on preparation of the I_2–KI aqueous solution, the I_2 molecule has to coordinate with (mono)iodide ion, I^-, into the tri-iodide ion, I_3^-, which is soluble in water[14]. On the other hand, iodine doping into nylon 6 cannot be achieved with the KI solution; the I^- ion cannot be doped nor forms the complex by itself.

Figure 1 shows an effect of excessive KI on increase in mass with iodine doping (Δm) of non-oriented specimens. Even though concentration of prepared I_2 ($\approx [I_3^-]$ in the solution) of solution B is equal to that of solution A, the former is less efficient than the latter. In a case of more excessive KI addition, iodine doping did not progress even if concentration of prepared I_2 was 0.3 N. It means that excessive KI inhibits iodine doping or permeation of polyiodides into nylon 6; the I^- ion prevents iodine doping in nylon 6.

In the I_2–KI aqueous solution, I_5^- or I_2 are minor solutes while I^- or I_3^- are majorities[14,18]. However, in the iodine–nylon 6 complex, polyiodide ions are intercalated as I_2, I_3^- or I_5^- [7–13]. The complex crystal which is formed with aging after iodine doping contains I_3^-. On the other hand, I_5^- or I_2 coordinated with I_3^- are contained in the stable one-dimensional structure or the unstable one, which are formed immediately after doping[7].

Increase in concentration of I^- should decrease the concentration for I_5^- or I_2, since the following equilibrium is expected:

$$2I_3^- \leftrightarrow I_5^- + I^- \ (\text{or } I_3^- \leftrightarrow I_2 + I^-) \qquad (1)$$

The prevention by I^- of iodine doping in nylon 6 suggests that I_5^- or I_2 play a chemically essential role on an earlier stage of iodine doping.

Synonymously, the one-dimensional structures which contain I_5^- or I_2 should be essential for the doping process. These one-dimensional structures are formed through earlier doping in the I_2–KI aqueous solution[7]. In other words, the iodine-doping process in nylon 6 with the solution should be studied taking account of these minor solutes other than the major I_3^- ion.

Then, it is expected that addition of I^- ions not only prevents iodine doping but also decreases concentration of polyiodides doped in the complex and that it leads to a structure with a lower concentration of iodine.

$$\begin{aligned} &I_3^- \text{ (bound in complex)} + I^- \text{ (solute)} \\ &\leftrightarrow I^- \text{ (in complex)} + I_3^- \text{ (solute)} \qquad (2) \end{aligned}$$

This equilibrium should move to right side since the I^- ion can hardly be doped in the complex.

X-ray photographs in *Figures 2a* and *2b* are taken for a doubly oriented complex immersed in the 1 mol l^{-1} KI solution for 10 days at room temperature after iodine doping. Increases in mass, Δm, were 200 and 155% for the specimen just after doping and the one 're-immersed' in the KI solution, respectively. An irregular ordering of 1.95 nm period around the chain axis is observed, while usual ordering of 1.56 nm period has disappeared[7,12]. While the 're-immersed' specimen had lost double orientation, it maintained orientation of the chains along the drawn direction (uni-axial orientation). Taking account of spacing, the sample showing the

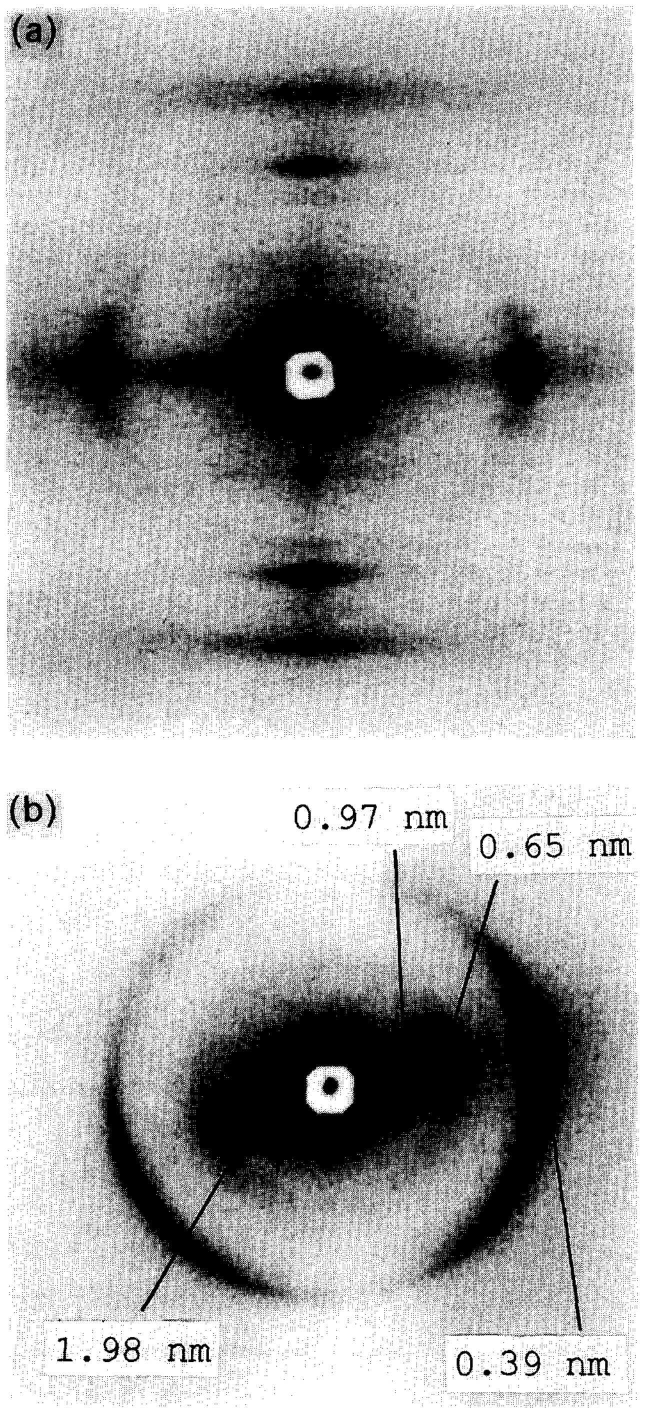

Figure 2 X-ray photographs of irregular stacking showing 1.95 nm spacing; (a) with X-ray incident perpendicular to chain axis; (b) parallel to it

irregular ordering also indicates similar diffractions along the chain axis (*Figure 2a*); with incident perpendicular to the chain axis, there are observed Bragg reflections with the 1.95 nm period and streaks similar to the ordinary specimen[12]. This irregular spacing of the 1.95 nm period means that there can be another scheme of intercalation of polyiodides stacked between the hydrogen-bonded planes of nylon 6.

Intensities along the horizon of *Figure 2a* were observed with an imaging plate and corrected by the following equation after background intensities were subtracted (*Figure 3*)

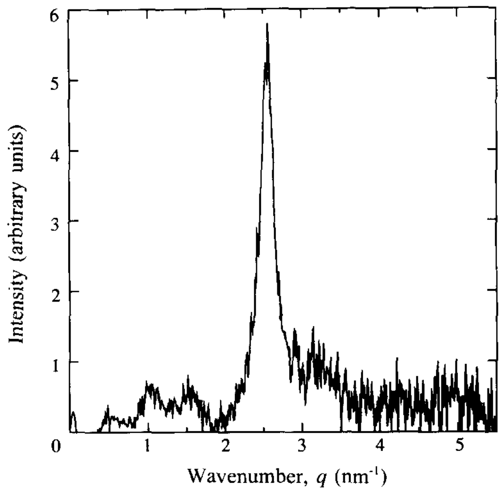

Figure 3 $I_0(q)$, corrected intensities along horizon of *Figure 2a* vs q (nm^{-1})

$$I_{\mathrm{obs}}(q) \propto I_0(q) \cdot D(2\theta) \cdot P(\theta), \qquad (q = 2\sin\theta/\lambda)$$

$$D(2\theta) = \cos^3(2\theta), \quad P(\theta) = \frac{1+\cos^2(2\theta)}{\sin(2\theta)} \qquad (3)$$

Corrected intensities in *Figure 3*, $I_0(q)$, show that the intensity of the 5th order of the 1.95 nm is strongest and those of the 2nd and 3rd orders follow, while those of the 1st and 4th orders are weak.

Here, a 'three-layer' model can be suggested with the 1.95 nm spacing: two layers occupied by polyiodides and one vacant layer (*Figure 4a*). The occupied layer corresponds to one hydrogen-bonded plane of nylon 6 coordinated with polyiodides in the ordinary complex and the vacant one corresponds to a plane of non-doped nylon 6. The parameters used are estimated with spacing of the hydrogen-bonded planes in the complex crystal and that of hydrogen-bonded planes in the non-doped nylon 6: spacing for the occupied layer, 0.78 nm[12] and that for the vacant one, 0.39 nm. This value for the vacant layer, 0.39 nm, is suggested to fit the observed value, 1.95 nm, and can be appropriate for the spacing between the hydrogen-bonded planes in the α-form, 0.37 nm[1]. *Figure 4b* shows Fourier transformation of a one-dimensional Patterson function for a linear arrangement of polyiodides and nylon 6 in the 'three-layer' model shown in *Figure 4a*.

$$F(q) = A \cdot \sum_{j,k} f_j \cdot f_k \cdot \exp(-2\pi i q r_{jk}/R) \qquad (i^2 = -1) \qquad (4)$$

A is a factor of normalization. R is 1.95 nm of the period and r_{jk} are distances between each one-dimensional elements (see *Figure 4a*). $F(q)$ for two cases are indicated: a result neglecting attribution of nylon 6 chains (scattering amplitude $f_j = 320$ for polyiodides, $f_j = 0$ for nylon chains) and one considering them ($f_j = 320$ for polyiodides, $f_j = 248$ for nylon chains). Actual specimen should introduce an intermediate line between these two lines in *Figure 4b*. The approximated values

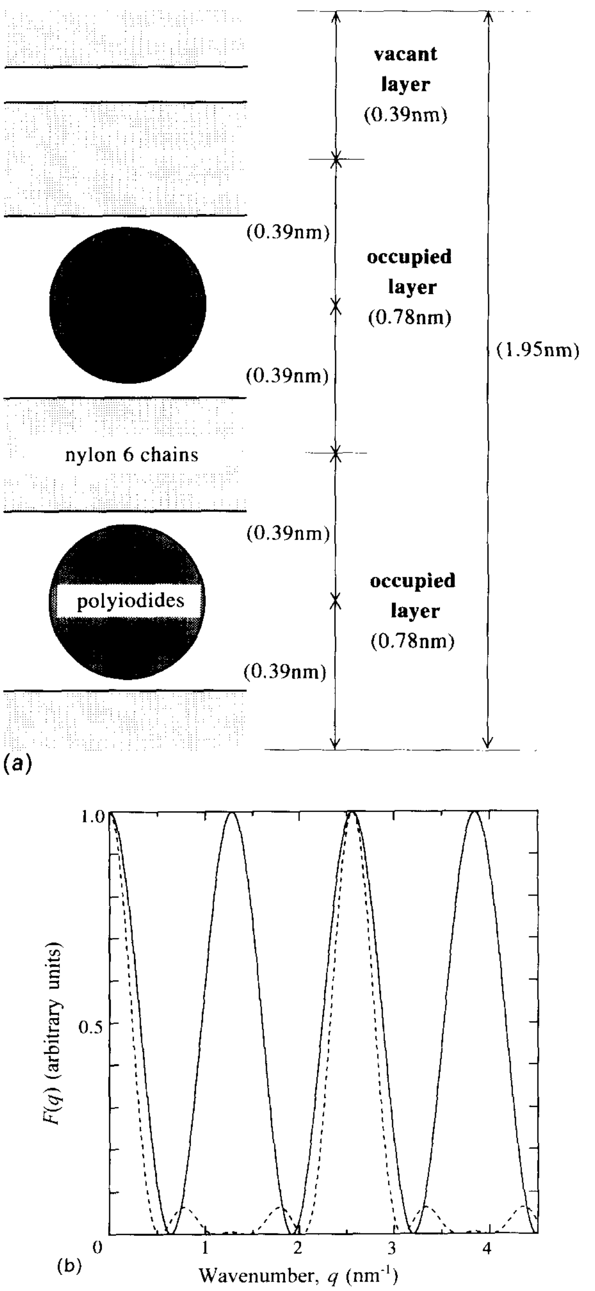

Figure 4 (a) Model for linear lattice with 1.95 nm period; (b) relative intensities of $F(q)$; Fourier transformation of Patterson function for two cases: one by neglecting nylon chains (——) and another by considering them (– – –)

of f_j correspond to two molecules of I_3^- intercalated between nylon 6 chains per unit of chain axis; four I_3^- are coordinated per unit cell of the α-form. And expected intensities should be observed by product with a Laue function followed by the 1.95 nm period.

Even in either case, calculated results predict that intensity for the 5th order followed by the 2nd and 3rd orders of the 1.95 nm period is strong. It quantitatively seems to reproduce the experimental result and, therefore, the 'three-layer' model indicated in *Figure 4a* can be efficient. Then, there can be variations of stacking with polyiodides between the hydrogen-bonded planes in the complex. It is intercalation with the polyiodides through coordination; the iodine–nylon 6 complex should be suggested as an intercalated material similar to GIC. Concentration of I^- in the aqueous solutions can be one of the parameters for preparation of this intercalation.

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