Structure of iodine–nylon 6 complex: 1. The investigation of the lattice constants and hydrostatic compression of the complex crystal

Akio Kawaguchi
Department of Physics, Faculty of Science, Kyoto University, Kyoto 606-01, Japan

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Nylon 6 is doped with iodine to form a complex. The doubly oriented specimen of the complex crystal is investigated by X-ray diffraction. The lattice constants of the complex crystal are determined; it has a monoclinic unit cell of the space group $P2_1/a$ or $P2_1$: $a = 0.913$ nm, $b = 1.62$ nm (chain axis), $c = 1.79$ nm and $\beta = 59.7°$. The hydrostatic compression of the crystal shows that the compressibility has become isotropic around the chain axis; doped iodines weaken the hydrogen bonds formed in the α-form of nylon 6. The structure of the complex crystal is discussed on the basis of the packing and orientation of polyiodine ions, I_3^- and I_5^-, in nylon 6.

(Keywords: iodine; nylon 6; lattice constants; hydrostatic compression)

INTRODUCTION

Nylon 6 has been reported[1–6] to have at least three crystal forms: α, β and γ. In the α-form, which is crystallized from the melt, hydrogen bonds are formed between amide groups of the antiparallel chains of nylon 6. On the other hand, hydrogen bonds are formed between those of the parallel chains in the γ-form. The transformation from the α- to the γ-form occurs through iodine treatment: immersing the α-form of nylon 6 into an iodine/potassium iodide (I_2–KI) aqueous solution followed by the desorption of doped iodine in a sodium thiosulphate aqueous solution[7,8]. Hence iodine atoms or molecules have been argued to play an important role in the transformation intermediate between the α- and the γ-form through the iodine-doped nylon 6 intermediate. It is believed that iodine atoms or polyiodine ions are arranged between the hydrogen-bonded planes of the α-form and weaken the hydrogen bonds between antiparallel chains; they contribute to the rearrangement of hydrogen bonds between the antiparallel chains into those between the parallel chains on doping and desorption to give rise to the transformation.

Iodine-doped nylon 6 has attracted much attention[9–12] due to its electrical properties since the 1970s. However, the structure of this intermediate state has not been clarified yet. Recently, Murthy *et al.* reported on the structure of the intermediate state studied by X-ray, Raman spectroscopy and n.m.r.[13–16]. They proposed several models for the structure of the intermediate state; I_3^- and I_5^- ions lie between the hydrogen-bonded planes. However, the crystal structure of this iodine–nylon 6 complex, even the unit cell, was not determined. The difficulty of determining the unit cell lies in the situation that the doping of iodine usually destroys the double orientation of specimens that is useful for the investigation of the structure of polymeric materials.

In the present paper, results are reported for X-ray diffraction of a doubly oriented iodine–nylon 6 complex obtained successfully in a rather dilute I_2–KI aqueous solution at a low temperature. The hydrostatic compression of the complex is also studied by X-ray diffraction to clarify the anisotropy of the compressibility around the chain axis of the complex crystal.

EXPERIMENTAL

The nylon 6 used was a commercial polymer ($M_w = 42\,000, M_w/M_n = 1.4$). A film (0.5 mm thick) was melt-pressed on a hot stage, quenched in ice water and drawn three times its original length to be a doubly oriented thin film (0.14 mm thick). The film was annealed at 210°C for 1 day in argon atmosphere. The crystallinity of the samples was measured to be ~25% by d.s.c. measurements[17].

The film was immersed in a 0.1 N I_2–KI aqueous solution at 5°C for a certain time from several minutes to several days or months. The immersed film was rinsed, dried for several hours at room temperature and weighed to estimate the amount of doped iodide. The doping was uniform along the film thickness as confirmed by observation of the cross-section of the doped film by optical microscopy. The iodine doping depends sensitively on the film preparation; in one case, a film immersed for 1 month could not be doped appreciably.

For Raman spectroscopy the complex film was set in a cryostat at liquid nitrogen temperature to avoid iodine volatilization. The incident beam was the 514.5 nm line from an argon laser (200 mW). The incident beam was normal to the surface of the film plane; the Raman spectra were obtained from the 180° scattered light with a double monochromator (Spex model 1402).

X-ray diffraction photographs were taken with a flat-film camera with Mo Kα radiation monochromatized by a graphite monochromator. For hydrostatic compression up to 1 GPa, a diamond anvil cell was used as the high pressure cell. A stainless steel gasket was used

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for applying hydrostatic pressure. The specimen was pressed together with a small piece of graphite (reference material for pressure calibration) in silicone oil (pressure transmitting fluid) between the diamond anvils at room temperature. The method of pressure calibration has been described elsewhere[18].

RESULTS AND DISCUSSION

Iodine doping depends on the temperature and the concentration of iodine in the aqueous solution; nylon 6 cannot be doped with iodine at temperatures above 50°C. Doped at room temperature in a 1 N I_2–KI aqueous solution, doubly oriented nylon 6 forms a complex losing its double orientation. At 5°C in a 0.1 N solution the doubly oriented complex can be obtained.

The Raman spectra of the complex agreed well with that reported by Murthy *et al.*[14]; the band assigned to I_5^- ($170\,\mathrm{cm}^{-1}$) was observed only with the incident polarization parallel to the chain axis (*b*-axis) while the band for I_3^- ($115\,\mathrm{cm}^{-1}$) was observed with both parallel and perpendicular polarization. Anisotropic Raman polarizability (α') of the iodine ions is larger in the direction of their long axes. Hence I_5^- ions exist in the crystal with the long axis parallel to the chain axis in the crystal, while I_3^- ions lie with the long axis both parallel and perpendicular to the chain axis and/or may exist in the amorphous part.

Determination of unit cell

In the original sample of the α-form of nylon 6, the hydrogen-bonded plane, (002), is oriented parallel to the film surface.

Figure 1a is an X-ray photograph of the doubly oriented complex with the incident X-ray parallel to the chain axis (*b*-axis). There appears a strong reflection of 1.55 nm spacing with its higher order reflections perpendicular to the film surface (on the equator). The 00*l* reflections for odd *l* decrease in intensity after iodine treatment. Besides the equatorial reflections, three reflections are observed which are not perpendicular to the film surface: 0.439 (medium), 0.394 (strong) and 0.345 nm (weak). They show that the unit cell is monoclinic. Indexing the 1.55 nm reflection as 001, we index the three reflections as not (10*l*) but (20*l*) because at least two nylon 6 chains (parallel and antiparallel) should exist in the direction of the *a*-axis in the unit cell. With the samples which have lost double orientation, the 0.345 nm reflection cannot be observed and the 0.394 nm reflection cannot be separated from the 004 reflection.

With the incident X-ray perpendicular to both the chain axis and the film surface, Bragg reflections are observed on a layer line $0.6\,\mathrm{nm}^{-1}$ apart from the equator (*Figure 1b*); they are observed only for the doubly oriented specimen and their indices are (21*l*). No reflection is observed on the meridian in the layer line.

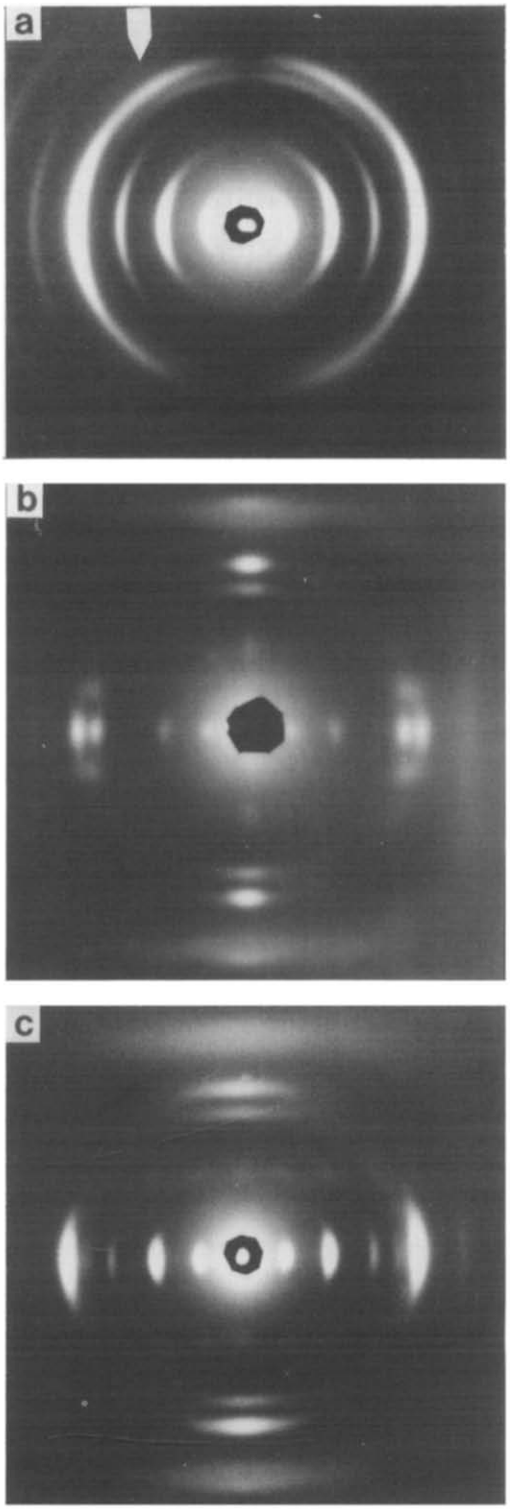

Figure 1 X-ray diffraction of the iodine–nylon 6 complex with incident X-ray (a) parallel to the chain axis (the arrow indicates the $20\bar{1}$ reflection), (b) perpendicular to the sample surface (parallel to c^*-axis) and (c) perpendicular to the chain axis and parallel to the sample surface

Figure 1c shows an X-ray photograph with the incident X-ray perpendicular to the chain axis and parallel to the film surface. Besides the 1.55 nm and its higher order reflections on the equator, several Bragg reflections can be observed on layer lines 1.24 and $2.48\,\mathrm{nm}^{-1}$ apart from the equator. We also observed diffuse streaks other than Bragg reflections on the layer lines in the X-ray photograph of the complex. Diffuse layer scatterings are also observed at 2.12, 3.13 and $3.37\,\mathrm{nm}^{-1}$. The diffuse streaks change their intensities after doping; after 2 days in the atmosphere the diffuse scatterings at 2.12 and $3.13\,\mathrm{nm}^{-1}$ vanish and Bragg reflections appear more clearly while that at $3.37\,\mathrm{nm}^{-1}$ remains unchanged. These reflections, 0*kl* and diffuse streaks on *Figure 1c*, have been reported by Murthy *et al.* for uniaxially oriented samples and they proposed several models for the structure of the complex[16].

Table 1 Observed and calculated spacing of iodine–nylon 6 complex crystal

hkl	*d* (obs.) (nm)	*d* (calc.) (nm)
001	1.550 ± 0.023	1.540
002	0.769 ± 0.009	0.771
003	0.513 ± 0.003	0.514
004	0.386 ± 0.002	0.386[a]
200	0.394 ± 0.004	0.394[a]
201	0.439 ± 0.003	0.439[a]
$20\bar{1}$	0.345 ± 0.005	0.343
020	0.801 ± 0.018	0.810
040	0.405 ± 0.003	0.405[a]

[a] Spacings used for determination of lattice constants

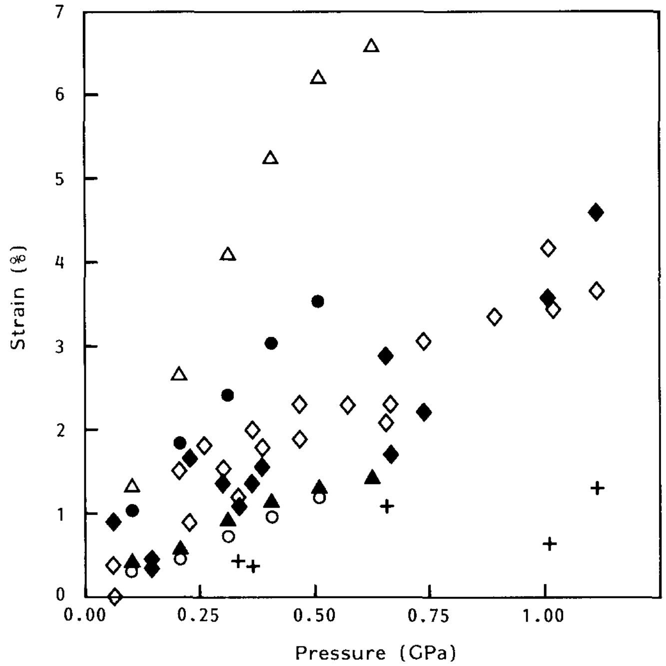

Figure 2 Compression strain *versus* pressure of iodine–nylon 6 complex: (◇) (002); (◆) (201); (+) (040) (complex); (●) (002) of α-form; (○) (002) of α-form; (△)(200) of γ-form; (▲) ($20\bar{2}$) of γ-form (nylon 6)[6]

It is to be noted that the Bragg angles remain unchanged while the intensities of the Bragg reflections of the complex vary with time; the lattice constants do not change.

With the values for the spacings, $d_{004} = 0.386$, $d_{200} = 0.394$, $d_{201} = 0.439$ and $d_{040} = 0.405$ nm, the lattice parameters are determined: $a = 0.913$ nm, $b =$ 1.62 nm (the chain axis), $c = 1.79$ nm and $\beta = 59.7°$. The observed and calculated spacings are listed in *Table 1*.

It is to be noted that the spacing of the (001) plane of the complex is 1.55 nm and is four times larger than that of the hydrogen-bonded plane (002) of the α-form of nylon 6. An iodine atom has a radius of 0.133 nm and the ion, I^-, has a radius of 0.216 nm. A linear I_5^- ion is from 1.3 to 1.5 nm in length[19]. Assuming that there are two layers of nylon 6 chains in the unit cell of the complex crystal, the increase in spacing between each nylon 6 layer should be 0.41 nm. This value is reasonable to accommodate rod-like iodine molecules between the hydrogen-bonded planes of nylon 6: two layers of nylon 6 and two layers of iodine in the unit cell.

Since the reflection condition for the $0k0$ reflections is $k = 2n$, the space group should be one of the following: $P2_1$, $P2_1/m$ and $P2_1/a$. $P2_1/m$ can be discarded because the nylon 6 chain does not have mirror symmetry perpendicular to the chain axis. The space group $P2_1/a$ generally requires at least four I_5^- ions in the unit cell, while $P2_1$ requires two ions.

The increase in weight with doping varies from specimen to specimen. The maximum observed increase was ~230%. However, the space group of the complex crystal could not be determined to be either $P2_1$ or $P2_1/a$, even taking into account the volume of the unit cell, the molar weight of iodine and the increase in weight. The determination of the space group of the complex crystal requires diffraction intensities. This situation is analogous to that encountered in the determination of the space group of the α-form of nylon 6 crystals[1]. As described above, the diffraction intensities of the complex, in particular, for the $0kl$ reflections ($k = 2n$) change with time after doping. Hence we could not determine definite intensities.

Pressure dependence

In the X-ray diffraction under high pressure we observed the following reflections: 001, 002, 003, 004, 040 and 201. The curves for a series of $00l$ ($l = 1, 2, 3, 4$) reflections can be superposed on a curve within experimental error. Strain *versus* pressure curves are shown in *Figure 2* together with those of d_{200} and d_{002} of the α-form and d_{200} and $d_{20\bar{2}}$ of the γ-form[6]. The linear compressibilities of the ($00l$) plane of the complex crystal were obtained by the least squares method with a second order polynomial up to 600 MPa to be 7.6×10^{-11} Pa^{-1}. Though the experimental error for the (201) plane is large, the value is almost the same as that of the ($00l$) plane on the strain *versus* pressure curves. The linear compressibilities of the complex crystal have values between those for the (200) spacing and the (002) spacing of the α-form of nylon 6: 2.6 and 10.5 ($\times 10^{-11}$ Pa^{-1}) for (200) and (002), respectively; also between those for the (200) spacing and the ($20\bar{2}$) spacing of the γ-form of nylon 6: 16.3 and 3.8 ($\times 10^{-11}$ Pa^{-1}) for (200) and ($20\bar{2}$), respectively[6]. Hence, the anisotropy observed in the α-form or γ-form crystals has been significantly lost in the complex.

The lattice constant b (along the chain axis) is little compressed as in the α-form or the γ-form[6].

The hydrogen bonds in the α-form of nylon 6 are expected to be weakened by iodine doping. The co-ordination of the polyiodine ions therefore makes the hydrogen bonds of the original nylon 6 weaker in the complex and gives rise to stronger binding between the hydrogen-bonded planes than the van der Waals force in the α-form of nylon 6.

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