Structure of iodine–nylon 6 complex: 3. Modification of double orientation of the complex with doping

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On preparation of the doubly oriented iodine–nylon 6 complex through iodine doping, modified double orientation is observed by X-ray diffraction. In iodine doping, double orientation of the complex is occasionally modified in the central part of a long strip of the doubly oriented specimen. Hydrogen-bonded planes of nylon 6 chains are oriented perpendicular to both film surfaces of the specimen with modified orientation, while in normal doubly oriented specimens the planes are oriented parallel to the surfaces, as in the nylon 6 α-form. Even in the modified specimens, the orientation of the chain axis is maintained parallel to the draw direction. Iodine doping gives rise to rotation of double orientation at an angle of 90° about the draw direction. The modification is thought to be due to diffusion of polyiodide ions through the film surfaces of the specimen.

(Keywords: nylon 6; iodine; intercalation)

Introduction

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

The complex is also a hybrid material with interesting properties. Various processes are possible[5–13], for example oxidation and reduction, charge transfer, reorientation or coordination with polyiodide ions, I_n^-. However, the structure of the complex had not been clarified sufficiently. In the latter half of the 1980s, Murthy and co-workers reported uni-oriented and non-oriented complex specimens[8–11]. We also succeeded in preparing a doubly oriented iodine–nylon 6 complex and investigated it by X-ray diffraction and Raman spectroscopy; we determined lattice constants of the unit cell of a complex crystal and, furthermore, discussed arrangements of I_3^- or I_5^- ions along the chain axis[7,12–14]. There are various kinds of ordered structures in the complex: an unstable 'one-dimensional' structure, a stable structure and the complex crystal. In these structures, the polyiodide ions are intercalated between each plane composed of the nylon 6 chains. The planes correspond to hydrogen-bonded planes in the α-form.

The iodine–nylon 6 complex shows interesting structures in addition to those reported previously. In this paper, we report the modification of double orientation observed by X-ray diffraction of the complex.

Experimental

The doubly oriented complexes were prepared from doubly oriented films (0.14 mm thick) of nylon 6 α-form. The film specimens of the α-form were doped with a 0.1 N I_2–KI ($0.05\,\mathrm{mol\,l^{-1}}\,I_2$) aqueous solution at 5°C. The preparation procedure for the doubly oriented complex specimen has been reported before[12].

X-ray diffraction photographs were taken with a flat-film camera with MoKα radiation monochromatized by a graphite monochromator.

Results and discussion

In the α-form, hydrogen bonds are formed between the anti-parallel nylon 6 chains. In the undoped starting specimens, the hydrogen-bonded planes are oriented parallel to the surfaces of film specimens. The chain axis is oriented parallel to the draw direction and the hydrogen-bonded planes are parallel to the film surfaces (double orientation)[12,15].

This double orientation is destroyed by rapid iodine doping with a concentrated I_2–KI aqueous solution; orientation of the hydrogen-bonded planes is disturbed, while orientation of the chain axis is maintained. Successive doping with dilute I_2–KI aqueous solution (0.1 N) at a low temperature (5°C) can induce the doubly oriented complex. The hydrogen-bonded planes in ordinary doubly oriented complex specimens are arranged parallel to the surfaces of the film specimen as in the starting α-form. It should be noted, however, that the hydrogen bonds in the complex are weakened by intercalation with the polyiodide ions between the nylon 6 planes; the hydrogen-bonded planes in the complex are composed of the anti-parallel nylon 6 chains *without* regular hydrogen bonding.

Some doubly oriented complex specimens, however, show modification of double orientation. *Figure 1* shows an X-ray photograph of a complex specimen with such modified double orientation; the incident X-ray is parallel to the draw direction and the surfaces of the film specimen are arranged parallel to the meridian. In the modified specimens, the hydrogen-bonded planes are oriented *perpendicular* to the surfaces, even though double orientation is maintained. Spacings derived from Bragg reflections for the modified specimens are exactly the same as those for the ordinary specimens; modification of double orientation does not change the lattice constants. Hence the photograph means that doping induces 90° rotation

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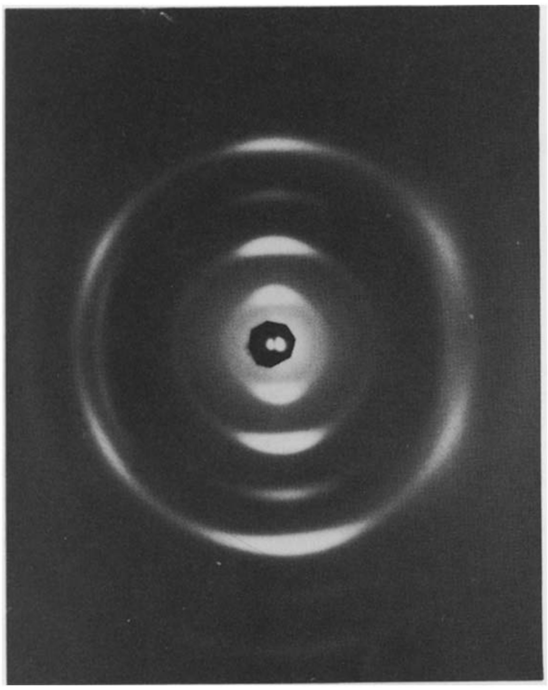

Figure 1 X-ray photograph of iodine–nylon 6 complex specimen with modified double orientation. The incident X-ray is parallel to the chain axis and the surface of the film specimen is arranged in the meridional direction

of orientation of the hydrogen-bonded planes about the draw direction (*Figure 2*).

Such modified orientation was occasionally observed in the central part cut from a long strip of the doubly oriented specimen. An edge part or a short strip of the specimen displayed ordinary double orientation, where the hydrogen-bonded planes are oriented parallel to the surfaces.

Raman spectra and X-ray diffraction for the ordinary doubly oriented iodine–nylon 6 complex suggest that linear I_5^- and I_3^- ions exist in various ordered structures of the complex[7,12]. I_5^- ions which exist in the stable 'one-dimensional' structure are arranged parallel to the chain axis. On the other hand, I_3^- ions are contained in the complex crystal and in the unstable 'one-dimensional' structure, where I_3^- ions are not arranged parallel to the chain axis but perpendicular or inclined to it.

Thus it is expected that diffusion of the polyiodide ions intercalated perpendicular to the chain axis in the complex should modify orientation of the hydrogen-bonded planes. Unidirectional diffusion of iodine (maybe I_3^-) through both surfaces of the thin specimen should induce modification; diffusion has to proceed only through the film surfaces at the central part of the long strip. On the other hand, in the edge part of the long strip or in a sufficiently short strip, diffusion of iodine cannot always proceed through the film surfaces, in which case the specimens can be doped with iodine without modification of double orientation.

Murthy *et al.* reported reorientation of the chain axis induced by doping; iodine doping to a non-oriented nylon 6 film induced reorientation of the chain axis perpendicular to a surface of the specimen[8]. However, in our experiments modification of double orientation is not followed by such reorientation of the chain axis.

Rapid doping with the concentrated I_2–KI solution is so radical that modified and/or ordinary double orientation is destroyed. Nevertheless, fixing of the chain axis by drawing is so strong in the oriented specimens that, even with rapid doping, the chain axis is maintained parallel to the draw direction. On the other hand, gentle diffusion of iodine does not destroy double orientation. Unidirectional and gentle diffusion into the thin film specimens induces modification of double orientation without reorientation of the chain axis because of fixing by drawing.

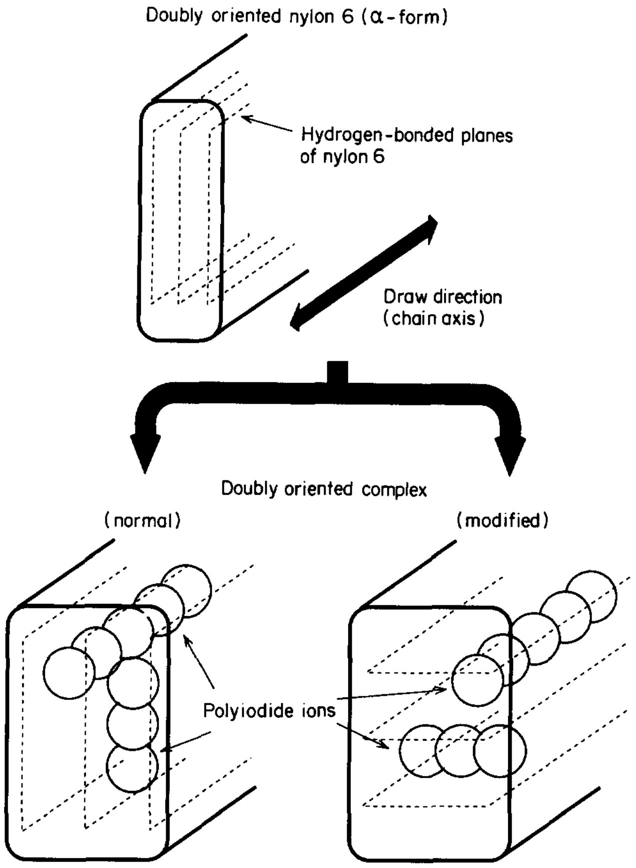

Figure 2 Sketch of modified and ordinary double orientation of the complex

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