

용액성장 Nylon 4, 6의 결정구조 및 형태학에 관한 연구

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Structure and Morphology of Solution Grown Nylon 4, 6 Crystals

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요 약 : 여러 온도의 용액상태하에서 Nylon 4, 6을 결정화시킨 다음 그들의 형태학적 거동과 결정구조를 해석하였다. 결정산물은 판상형(lath-shaped)의 결정들이 나뭇단(sheaves) 모양의 형태로 뭉쳐서(aggregated) 나타나고 있었으며, 결정내부는 사슬이 규칙적으로 굴곡된 라멜라(chain folded lamellae) 형태를 취하고 있음이 광각(wide angle) 및 소각 X-선 회절(small angle X-ray diffraction) 그리고 투과 전자현미경(transmission electron microscopy)에 의해 확인되었다. 라멜라의 두께는 진공하에서 용매를 완전히 제거시킨 후 소각 X-선 회절에 의해 측정되었으며 결정온도에 따라 변화하는 양상을 보였다. 결정온도에 따른 라멜라의 두께는 약 130°C 이하의 결정온도에서는 일정한 값을 유지하였으나 그 이상의 온도에서는 단조증가(monotonous increase)하는 현상을 나타내었다. 또한, Nylon 4, 6의 결정내부에 사슬들은 라멜라 표면(fold surface)에 수직하게 배열(perpendicular chain packing)되어 있었으며 이것은 Nylon 6,6과 같은 여타 폴리아미드의 경우 사슬이 라멜라 표면에 기울어져(inclined chain packing) 배열되어 있는 현상과 가장 두드러진 결정구조상의 차이점을 나타내고 있다.

Abstract : Structural and morphological behavior of solution grown nylon 4,6 crystals has been determined and compared with other polyamides, especially nylon 6,6. The lath shaped crystallization products, aggregated in the form of sheaves, possessed the characteristics of chain folded single crystals. The measured layer thickness by small angle X-ray diffraction varied with crystallization temperatures. The dependence of the layer thicknesses on the crystallization temperatures showed a horizontal plateau followed by a monotonous increase with the high crystallization temperature(T_c) of about 130 °C. The comparison of wide and small angle X-ray reflections combined with the examination of electron diffraction patterns of sedimented mat of crystals shows that the chains in the nylon 4,6 are perpendicular to the lamellar surface and the {001} planes are inclined to the fold surface, which are quite contrast to other polyamides where the chains are inclined to the lamellar surface and the {001} planes are parallel to the fold surface.

INTRODUCTION

Nylon 4,6 is a polyamide which has a high amide content and a symmetrical molecular structure. Its synthesis and melting points have been reported by several authors,^{1~4} as early as 1938 by carothers.⁵ But still its morphological and structural properties have been little known despite its comparable and excellent mechanical properties compared to nylon 6,6.⁴ One of the reason for the little attention is thought to be due to its difficulty of making high molecular weight products and of melt processibility because of its rather high melting points.

The morphology and chain folded structure of single crystals in other polyamides,^{6~11} especially nylon 6,6, have been studied widely not only because of its technological importance as a useful commercial polymer, but also because of the complexity of morphological changes associated with its crystallization behavior. The basic crystal morphology is typically lath shaped chain folded lamellae and of limited lamellar thickness (50~70Å) when crystallized from solution. It has been shown that these crystals are formed of few crystallographic repeat units^{7~9} and the hydrogen bonding of CO-NH dipolar arrays in polyamides¹² strongly influence the internal stability of crystals formed.

A combined analysis of both wide and small angle X-ray diffraction data on single crystal mats have shown that the 001 planes within a lamella are parallel to the lamellar surfaces and the chains in the lamella are inclined to the fold surfaces.^{6~8} Furthermore, due to small number of repeat units within the crystal stem, (n-2) weak, where n is the number of repeat units in the structure, subsidiary X-ray diffraction maxima between the first order of small angle and the 001, and between the 001 and 002 reflections have been observed.^{6,14} These features provide a direct measure of the number of crystallographic repeats along the straight chain segments traversing the lamellae provided where such submaxima are discernible.

As a further refinement, the related intensities

of the subsidiary maxima themselves provide potential information on the nature of the chain portion constituting the fold. In an attempt to determine which portion of the nylon 6,6 monomer unit is involved in the fold, Atkins et. al.⁶ showed that it is the acid unit portion which is more likely to form the fold. The above conclusion is somewhat surprising as there are fewer methylene groups in the acid portion than in amine to complete the fold.

The principal scattering planes giving rise to meridional diffraction are those associated with oxygen atoms attached to the chains. Thus the chemical structure of polyamides is directly related to the fold structure of crystals, and their characteristic layer thickness which is represented as horizontal plateau in crystal thickness vs. crystallization temperature. The objective of the present paper is to report results of the morphological behavior and the fold structure of solution grown nylon 4,6 single crystal, which are being of availability as potential engineering plastics.

EXPERIMENTAL

Materials. Commercial grade nylon 4,6 (M_w : 25,000) used in this work was kindly supplied by DSM Co. in Netherland, as polymer chips, free of additives.

Single Crystal Preparations. The solution was made up by dissolving nylon 4,6 chips in 1,4-butanediol with polymer concentration of 0.04% (w/v). Crystals were grown isothermally by the self-seeding techniques¹⁵ and filtered in situ in the crystallization bath at the crystallization temperatures of 110°C to 160°C. For the preparation of single crystal mat the samples were dried by keeping them overnight between mica plates in a vacuum oven at 70°C. Heat treatments were carried out in an atmosphere of nitrogen within an Abderhalden drying apparatus.

Electron Diffraction and Microscopy. TEM specimens were prepared by putting a drop of crystal suspensions onto a carbon-coated microscope grid

and allowing the solvent to be evaporated in a vacuum oven. In most cases the crystals were shadowed with Pt/Pd to improve contrast. A philips 301 transmission electron microscope operating at an accelerating voltage of 100 KV was used for observation.

X-ray Diffraction. Single crystal mats were examined using both wide and small angle X-ray diffraction techniques. Fine collimation and an evacuated camera were found advantageous for investigating reflections in both the wide angle and subsidiary maxima regions. For present purpose philips PW1729 camera set has been used. Small angle X-ray patterns were recorded with a Rigaku Denki small angle camera. Ni-filtered $\text{CuK}\alpha$ X-ray source was employed throughout the X-ray work.

RESULTS AND DISCUSSION

Morphology and Electron Diffraction. The electron micrograph of nylon 4,6 single crystals is shown in Fig. 1, which are crystallized in the form of sheaves similar to that of nylon 6,6. Fig. 2a shows electron diffraction pattern of nylon 4,6 at the sheaf extremities in which crystals lie in twinning modes. Reflections were assigned as (010) or (110) spacings for outer ones corresponding to 3.7 Å and (100) spacings for inner ones measured as 4.4 Å, which conform to Bunn and Garner structure¹⁶ and are similar to the tilted electron diffraction pattern of nylon 6,6 by Holland.¹⁷

Holland showed that the chains in nylon 6,6 are

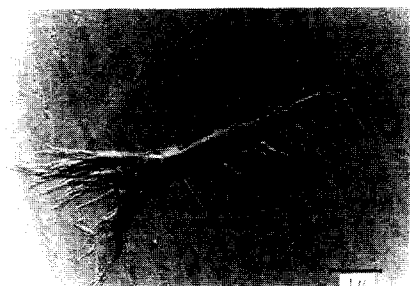
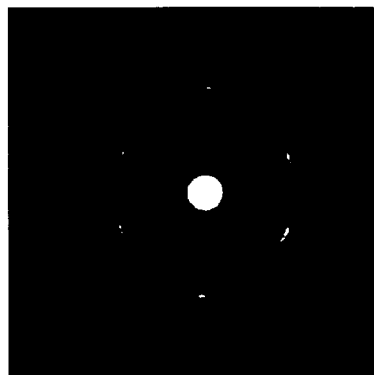
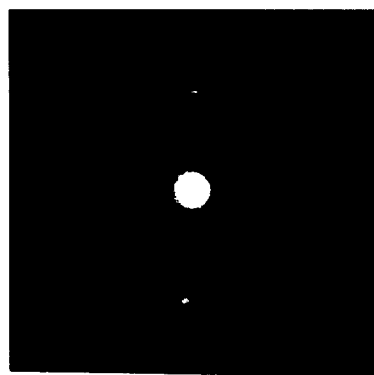


Fig. 1. Transmission electron micrograph of a sheaf of nylon 4,6 prepared from 1,4-butanediol.



(a)



(b)

Fig. 2. Electron diffraction patterns from a sheaf extremity of a) nylon 4,6, and b) nylon 6,6 with Pt/Pd.

tilted in the (100) planes approximately 46° from the vertical (fold surface) within the crystal platelets. Fig. 2b shows corresponding electron diffraction pattern of nylon 6,6 with the beam normal to the tip of the sheaf in which only one reflections at 4.4 Å corresponding to (100) spacings are shown.

The electron diffraction pattern of nylon 4,6 single crystals suggests that the chains of nylon 4,6 are perpendicular to the lamellar surface.

Wide Angle X-ray Diffraction(WAXD). Wide angle X-ray diffraction pattern of sedimented crystal mats of nylon 4,6 taken with the beam parallel to the mat plane is shown in Fig. 3a, and corresponding pattern of nylon 6,6 is shown in Fig. 3b. Seve-

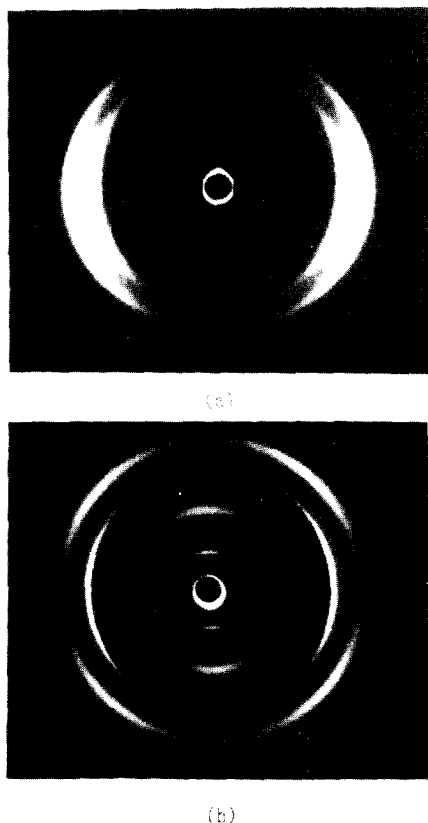


Fig. 3. Wide angle X-ray diffraction patterns of a sedimented mat of a) nylon 4,6, and b) nylon 6,6 crystals. Mat normal, vertical.

ral common features stand out. First there are arcs parallel to the mat normal (on the equator), which are reflections related to the lateral separation of chains and indexed as (100) for inner ones and (010) or (110) planes for outer ones. Second there are arcs on the meridian, these are reflections associated with the periodicity along the chain and indexed as (001).

But several significant differences are also observed. Firstly, in contrast to the nylon 6,6, (010) reflection is not split about the equator which means lateral separation of chains are perpendicular to the lamellar plane. Secondly, (001) reflection is missing in nylon 4,6 which is due to the approximate equal distance of the oxygen planes along the chains as is shown in Fig. 4, and only

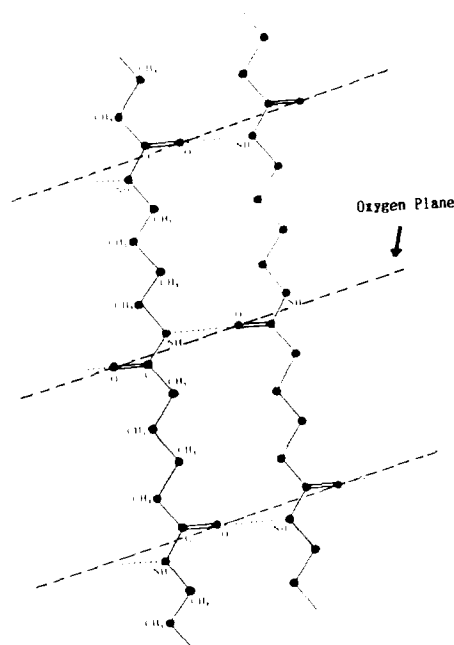


Fig. 4. Structure of nylon 4,6 crystal with oxygen scattering planes.

(002) reflection which is split around meridian is observed, which is due to the inclination of (001) planes. Thirdly, subsidiary maxima which are distinct features in nylon 6,6 are not shown in nylon 4,6.

In general, for a given number of units within a lattice, there are $(n-2)$ subsidiary maxima between the principal maxima at angles predicted by Bragg's law. For most observable lattices, n is sufficiently large for these peaks not to be observed, but a lamellar unit of nylon 6,6 is composed of four subunits, so that the subsidiary maxima are not to be negligible and 2 subsidiary maxima are observed. In case of nylon 4,6, it has been found that a lamellar unit is also comprised of four repeat units, but due to the approximately equal distances of oxygen planes along the chains, it brings the effect of 8 pseudo subunits where subsidiary maxima are too weak to be observed due to their cancellation effects and splitting around meridian.

Small Angle X-ray Diffraction (SAXD). Small angle X-ray diffraction photographs in Fig. 5, taken

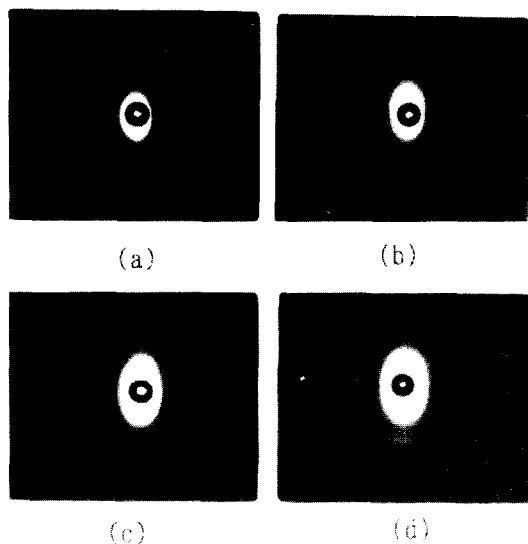


Fig. 5. Small angle X-ray diffraction patterns of a sedimented mat of nylon 4,6 crystals at (a) 110°C, (b) 130°C, (c) 150°C and (d) 160°C.

with the beam parallel to the mat plane revealed arced reflections with a maximum intensity on the mat normal and a spread broadly parallel to the (001) arcs. This is consistent with the conclusion that the small angle reflection is due to the stacks of layers deposited horizontally. The unit cell dimension of nylon 4,6 in chain direction was calculated as 14.7Å based on the Bunn and Garner structure.¹⁶ The long spacing in the original mat was 65~67Å which was then reduced to about 58Å by annealing at 230°C. We interpret this reduction as due to improved lamellar packing, and accordingly relate the corresponding spacing to the true thickness of an individual lamella.

Since the chains in nylon 4,6 are perpendicular to the fold surface, about four chemical repeat units exist in the each folded chains. The small angle X-ray spacings of the crystal mats vary with crystallization temperatures at high crystallization temperature region.

The dependence of small angle diffraction spacings of the nylon 4,6 single crystals shows a horizontal plateau at low crystallization temperature region followed by a monotonous increase with the

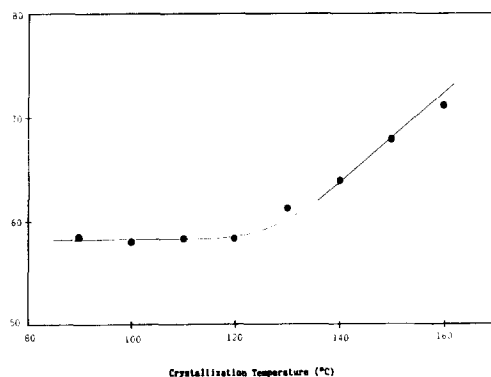


Fig. 6. Dependence of the lamellar thickness of nylon 4,6 crystals on the isothermal crystallization temperatures (T_c).

high crystallization temperature of about 130°C as shown in Fig. 6.

The Structure of the Chain Folds. From the small angle and wide angle X-ray diffraction patterns combined with electron diffraction the chain folded lamellae of nylon 4,6 are different from those of other polyamides. In case of nylon 4,6 the polymer chains are perpendicular to the lamellar surface, and the (001) scattering planes, i. e. oxygen planes, are inclined to the fold surface as is schematically shown in Fig. 7, whereas in case of nylon 6,6 the polymer chains are inclined to the lamellar surface, and the (001) planes are parallel to the fold surface.

The fold structure of nylon 4,6 is similar to that of solution grown single crystals of linear aliphatic polyesters¹⁸ in the sense that the chains are perpendicular to the fold surface and the (001) scattering planes are not parallel to the lamellar surface.

However, the lamellar thickness of solution crystallized polyesters increases continuously with crystallization temperatures, which is different from the behavior of nylon 4,6 where a horizontal plateau followed by a monotonous increase with the high crystallization temperature has been observed.

One of the most striking feature of nylon 4,6 single crystals is the observation of the weak

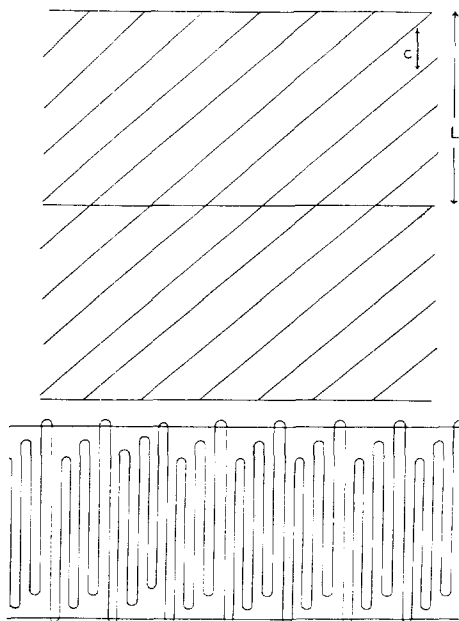


Fig. 7. A hypothetical model for chain folded molecular structure within an individual layer of nylon 4,6 lamellar with the mean lamellar thickness of 58Å. The oblique lines are traces of the (001) planes as seen long crystallographic a^* direction.

equatorial reflections around 12.5Å. These reflections are assigned as the spacing corresponding to approximately three repeat distance in (100) plane direction. This suggest that the long range order of fold formation occurs on approximately every three repeat units in (100) plane direction.

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