

Crystallization and Orientation of Isotactic Polypropylene Film by Stretching

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INTRODUCTION

Several studies of the orientation in polymer film samples by x-ray diffraction have been reported in the past few years. Recently quantitative studies of the orientation in the polyethylene film have been studied by Stein¹ and other workers.^{2,3}

In previous papers^{4,5} the authors reported on the orientation and the quasi-crystalline structure of

linearly with stretching. This means that the crystallinity increases by stretching, as it does with ordinary polymers.

X-Ray Diffraction

The x-ray diffraction intensity curves of the samples (the surface plane of the film was set parallel to that of the sample holder) with various

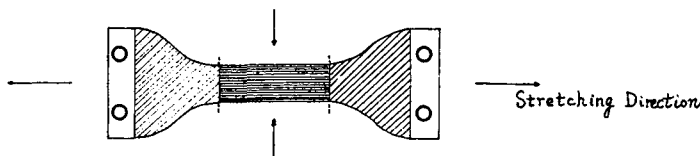


Fig. 1. A schematic presentation of stretching process of the specimen.

isotactic polypropylene. In this paper, crystallization, orientation, and formation of quasi-crystalline structure of isotactic polypropylene film by stretching are reported. The crystallinity of the specimens in each stretching ratio was estimated by measurement of x-ray diffraction and the density.

EXPERIMENTAL

The specimen used in this investigation was a thin film of 0.03 mm. thickness with an intrinsic viscosity $[\eta]$ of 1.0 in tetraline solution at 135°C. The specimen had ca. 30% crystallinity in the initial state. The film was elongated at 20°C. in air, at 80–100°C. in water, and at 120°C. in silicone oil by the method shown in Figure 1. The x-ray diffraction was measured by a Geiger counter spectrometer, using nickel filtered $\text{CuK}\alpha$. The density was measured in mixtures of methanol and water at 20°C.

RESULTS AND DISCUSSION

Density

The relation between density and stretching ratio is shown in Figure 2. The density increases

degree of stretching are shown in Figure 3. The measurement of x-ray diffraction was carried out by a reflective method in the *para*-focusing system. Figure 3 shows that the peak intensity at $2\theta = 21^\circ$

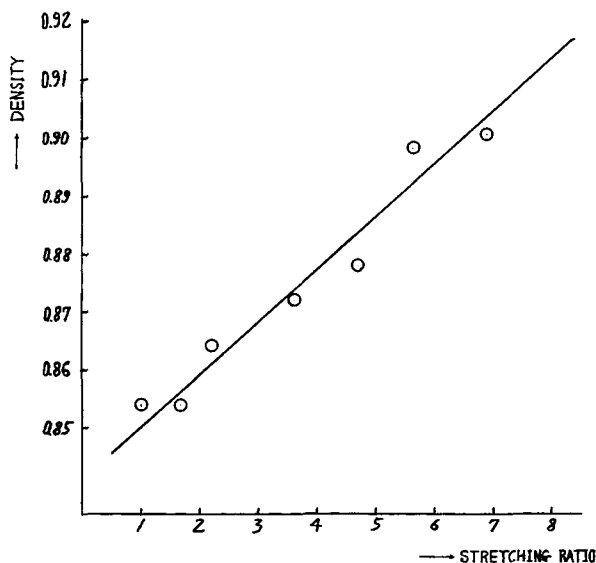


Fig. 2. The relation between the stretching ratio and the density.

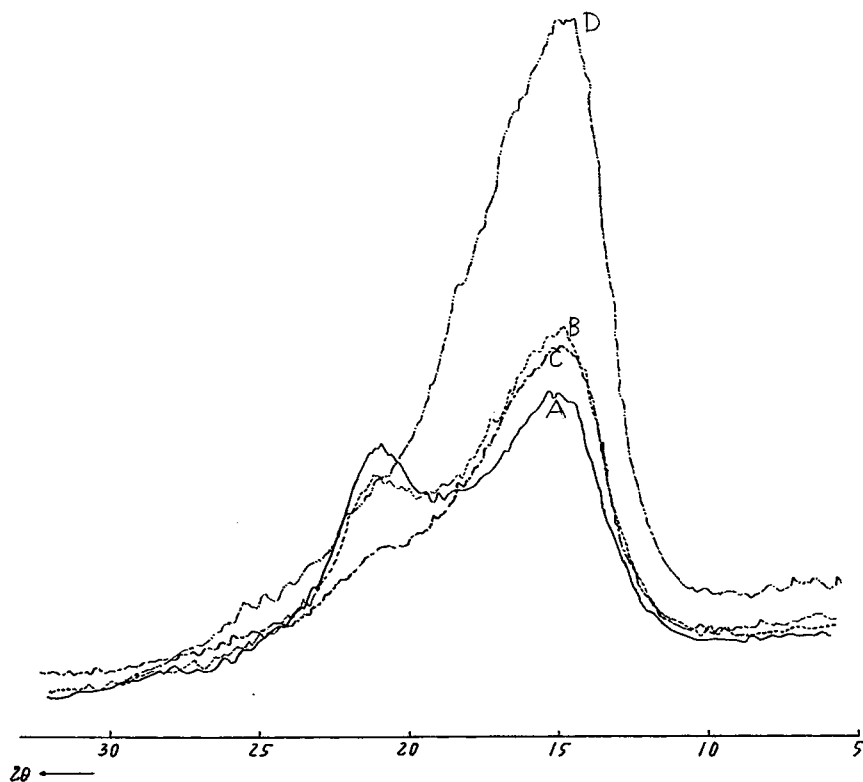


Fig. 3. The x-ray diffraction intensity curves of the specimens with various degree of stretching ratio. (A), unstretched; (B), 60% stretched; (C), 150% stretched; (D), 270% stretched.

(a diffraction spot in "layer line") decreases with stretching, and therefore the crystallites are oriented along the stretching direction. The diffraction intensity curve of the specimen obtained by

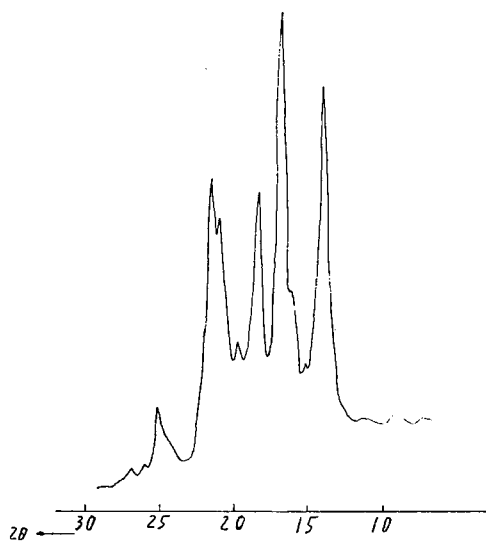


Fig. 4. The x-ray diffraction intensity curve of the specimen annealed from the melted state.

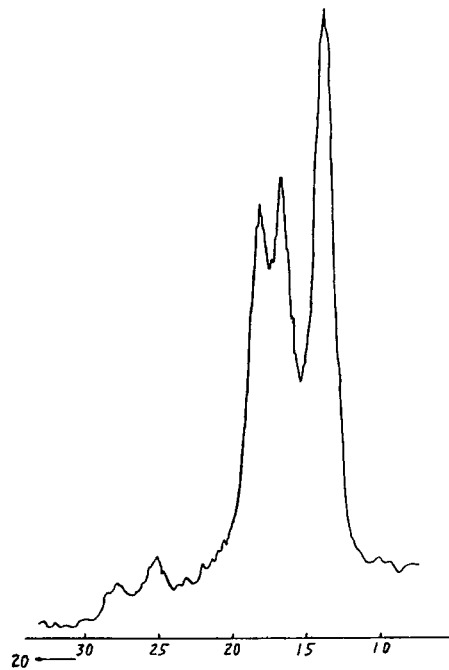


Fig. 5. The diffraction intensity curve of the specimen 90% stretched at 90°C. in water.

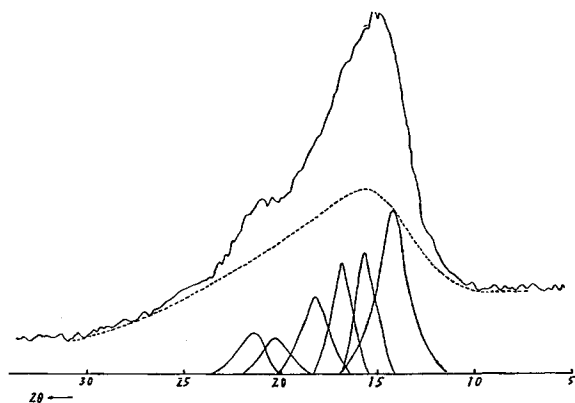


Fig. 6. The construction of the diffractive intensity curve of 150% stretched film as superposition of several peaks. The background was obtained by the measurement in various radial scans.

annealing the initial specimen from melt state is shown in Figure 4. It shows that an annealed specimen takes the stable ordinary crystal structure. The diffraction intensity curve of a highly stretched specimen at 90°C. in water is shown in Figure 5. In this case, the specimen also takes the ordinary crystalline structure, and its crystallites are very regularly oriented along the fiber axis. In the first case (stretching of the film at room temperature), the crystal structure is different from that in the latter two cases, that is, a peak of diffraction intensity at near $2\theta = 15^\circ$ is always observed. The diffraction intensity curves of the specimen 150% stretched could be constructed as the superposition of several principal peaks as shown in Figure 6. The peak at $2\theta = 15^\circ$ completely disappears by heating the specimen at high temperature. From these experimental results it is obvious that the peak which appeared at $2\theta = 15^\circ$ is due to the formation of a quasi-crystal structure. Therefore, the film stretched at room temperature contains both the ordinary stable crystalline and the quasi-crystalline structures. In a film with a low degree of crystallinity, the quasi-crystalline structure appears at low stretching, which is not the case with the filament.

Estimation of Degree of Crystallinity

The degree of crystallinity was estimated by a conventional method⁶ from measurements of x-ray diffraction, taking the structural anisotropy into consideration. The relation between the degree of crystallinity obtained by this method and the stretching ratio is shown in Figure 7. On the other hand, the degree of crystallinity x can be obtained

from the density d by the following formula:

$$1/d = (x/d_{cr}) + [(1-x)/d_{am}]$$

where d_{cr} is the density of crystalline part and d_{am} is that of amorphous part. The results obtained by

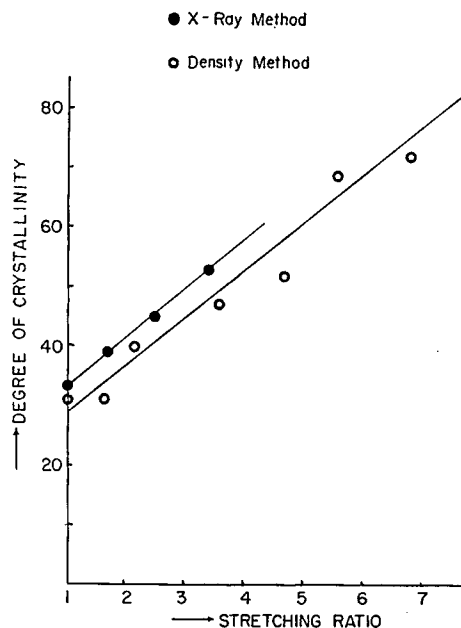


Fig. 7. The relation between the degree of crystallinity and the stretching ratio.

the x-ray method coincide to a large degree with those by the density method. It is evident from the results obtained above that the apparent degree of crystallinity increases with stretching under the conditions in this experiment.

Transformation of Crystalline Structure

It has been shown above that the ordinary crystal structure with high orientation along the fiber axis was formed by stretching the film at higher temperature (80–150°C.). But it is obvious, as described above, that a mixture of ordinary and quasi-crystal structures is developed by stretching a thin film with low crystallinity at relatively low temperature. The facts described above are also evident from the following experimental results. In this case, the x-ray experiment was carried out using radiation from a point source in the transmission method. The x-ray diffraction pattern of ca. 450% stretched film (stretched at room temperature) is shown in Figure 8A. The stretched specimen was then treated under various conditions, maintaining the constant length of the

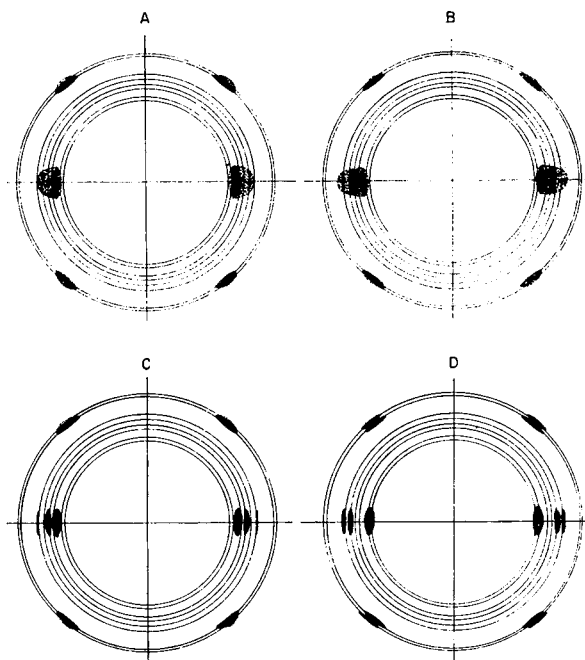


Fig. 8. (A) The x-ray pattern of ca. 450% stretched film at room temperature. (B) The x-ray pattern of specimen (A) treated at 100°C. for 20 min., keeping the constant length of the specimen. (C) The x-ray pattern of specimen (B) treated at 100°C. for 2 hr., keeping the constant length of the specimen. (D) The x-ray pattern of specimen (B) treated at 120°C. for 5 min., keeping the constant length of the specimen.

specimen along the stretching axis. These results are shown in Figures 8B, C, and D. From the figures it is observed that the transformation of the crystal structure occurs gradually at temperatures below about 100°C., but rapidly at higher temperatures. The peak of the quasi-crystal structure completely disappears by treating the specimen, Figure 8C, at 120°C. for several minutes.

Orientation of Crystallites in the Plane Perpendicular to the Stretching Axis

The relative peak intensity $I_{(010)}/I_{(100)}$ of the diffraction from (100) and (010) planes was measured. The relative intensity in completely oriented filaments of ordinary stable crystal form was 0.667 when the filament was placed perpendicular to the incident x-ray beam. The diffraction intensity curves of the specimens with isotropic crystalline structure were also measured at room temperature and at higher temperatures. The values $I_{(010)}/I_{(100)}$ are 0.718 at room temperature (84% crystallinity), 0.675 at 145°C. (32% crystallinity), and 0.625 at 153°C. (18% crystallinity).

The mean value of these data is 0.67. It means that the crystallites are distributed isotropically in the plane perpendicular to the stretching axis when the relative intensity is ca. 0.67.

The relative intensities of the stretched films were measured. The relation between the relative intensity and the stretching ratio is shown in Figure 9. The relative intensity decreases with the stretching ratio. It is obvious from these phenomena that the ordinary stable crystalline part in the mixed crystallites takes a definite orientation in the plane perpendicular to the stretching axis in

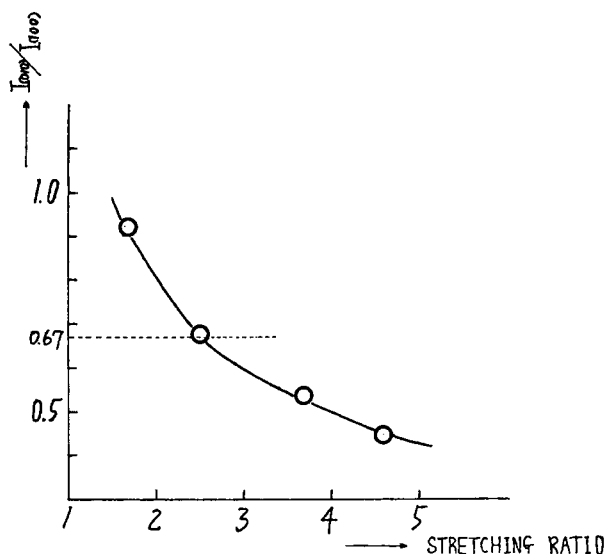


Fig. 9. The relation between the relative peak intensity $I_{(010)}/I_{(100)}$ and the stretching ratio.

highly stretched state. Orientation with high regularity was not obtained, due to the coexistence of the quasi-crystalline structure. A schematic orientation is shown in Figure 10. From the foregoing, a thin film could be biaxially oriented by stretching at room temperature, though the extent is not very large. It is most remarkable that this is quite different from the biaxial orientation by both roll and stretching as reported in a previous paper.³ In this case, the thickness of film does not change remarkably in the stretching process, though the width of the film decreases considerably as shown in Figure 1. It is easily understood from this fact that almost all compressive stress would act in the direction of the arrowhead shown in Figures 1 and 10. On the other hand, it is evident from the measurements of the coefficients of thermal expansion in the lattice planes by x-ray analysis

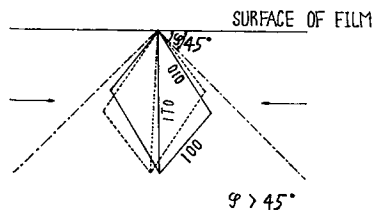


Fig. 10. A schematic presentation of biaxial orientation of the ordinary crystalline part in a cross section perpendicular to the stretching direction.

that the interaction between (100) planes is considerably larger than that between (010) planes.

It could be easily assumed that the interaction between molecular chains with the same configurations (interaction between *ddd...* and *ddd...* chains) and that between the chains with opposite configurations (interaction between *ddd...* and *lll...* chains) are different. From experimental results and the foregoing considerations, it is evident that (010) planes would more easily slide by each other than (100) planes. The macroscopic phenomenon whereby planes with a large tendency to slide past each other are apt to orient to the direction normal to the compressive stress may well correspond to this microscopic phenomenon. When the biaxially oriented crystallites are treated at temperatures above 100°C., the crystal orientation becomes completely isotropic in the plane perpendicular to the stretching axis.

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References

1. R. S. Stein, *J. Polymer Sci.*, **31**, 327 (1958); *ibid.*, **31**, 335 (1958).
2. D. R. Holmes and R. P. Palmer, *J. Polymer Sci.*, **31**, 345 (1958).
3. W. J. Dulmage and A. L. Geddes, *J. Polymer Sci.*, **31**, 499 (1958).
4. H. Sobue and Y. Tabata, *J. Appl. Polymer Sci.*, **1**, (1959).
5. H. Sobue and Y. Tabata, *J. Appl. Polymer Sci.*, **2**, 62 (1959).
6. H. Sobue and Y. Tabata, unpublished.

Synopsis

Crystallization and orientation of isotactic polypropylene film by stretching were investigated. The specimen used was a film of thickness 0.03 mm. and had ca. 30% crystallinity in the initial state. It was observed both by x-ray examination and measurement of density that the crystallization of the stretched film increased proportionally to the stretching ratio. And it was confirmed that a quasi-crystalline structure was already developed in the low stretching ratio coexisting with the ordinary stable crystal-

line structures. This quasi-crystal structure can be easily transformed into the ordinary stable state at above 100°C., as well as the quasi-crystal structure in melt spinning filament, as described in a previous paper. It was also confirmed that the ordinary stable crystalline part was biaxially oriented by high stretching at room temperature, that is, (110) plane of the crystallite was preferentially oriented perpendicular to the surface plane of the film in the cross section perpendicular to the stretching axis. This phenomenon was elucidated from both the cohesive interactions between lattice planes and the compressive stress in the stretching process.

Résumé

La cristallisation et l'orientation par étirement de film de polypropylène isotactique ont été étudiées. Le spécimen utilisé était un film de 0.03 mm d'épaisseur et on avait environ 30% de cristallinité à l'état initial. On a observé au moyen des rayons X et par des mesures de densité que la cristallisation du film étiré augmentait proportionnellement à l'étirement. On a également confirmé qu'une structure quasi-cristalline était déjà développée lors d'un faible étirement et cela en coexistence avec les structures cristallines ordinairement stables. Cette structure quasi-cristalline peut être facilement transformée en un état ordinaire stable au delà de 100°C de même que la structure quasi-cristalline obtenue lors de la fonte de filament de filature comme cela est décrit dans un article antérieur. On a aussi confirmé que la partie cristalline ordinaire stable était orientée d'une façon biaxiale lors d'un étirement élevé, à température de chambre; c'est le plan (110) du cristallite qui est préférentiellement orienté perpendiculairement à la surface plane du film dans la section transversale perpendiculaire à l'axe d'étirement. Ce phénomène a été élucidé à partir des interactions de cohésion entre les plans de la maille et à partir de la force de compression dans le processus d'étirement.

Zusammenfassung

Kristallisation und Orientierung von Filmen aus isotaktischem Polypropylen durch Reckung wurden untersucht. Zur Untersuchung wurde ein Film von 0,03 mm Dicke und 30% kristallinem Anteil im Ausgangszustand benützt. Durch röntgenographische Messung und Dichtebestimmung wurde festgestellt, dass die Kristallisation des gereckten Films proportional dem Dehnungsverhältnis zunahm. Schon bei niedrigem Dehnungsverhältnis konnte das Auftreten einer quasikristallinen Struktur neben den normalen, stabilen kristallinen Strukturen gezeigt werden. Diese quasi-kristalline Struktur kann ebenso wie die schon früher bei Fäden, die nach dem Schmelzspinnverfahren hergestellt wurden, beschriebene quasi-kristalline Struktur bei Temperaturen über 100°C. in den normalen, stabilen Zustand umgewandelt werden. Ebenso wurde gezeigt, dass ein Teil der normalen, stabilen Kristallstruktur durch starke Reckung bei Raumtemperatur eine biaxiale Orientierung erhielt, in dem Sinne, dass im Querschnitt senkrecht zur Reckungsachse die (110)-Ebene der Kristallite bevorzugt senkrecht zur Filmoberfläche orientiert war. Dieses Phänomen wurde einerseits durch die Kohäsionswechselwirkung zwischen den Gitterebenen und andererseits durch die Kompressionsspannung beim Reckungsvorgang erklärt.

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