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Measurement of X-Ray Diffraction of Biaxially Oriented Specimens of Isotactic Polypropylene

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INTRODUCTION

It is well known that stereospecific polymers have ordered structures, that is, both chemical and geometrical regularity. Isotactic polypropylene is one of the representative stereospecific polymers. The unit cell dimensions were given by Natta[1] as $a' = 6.56$ A., $b' = 5.46$ A., $c = 6.50$ A., and $\gamma' = 106°30'$, where a' and b' are the projections of a and b on the plane perpendicular to the fiber axis c, and γ' is the angle between a' and b' axes.

A highly biaxially oriented specimen was obtained from isotactic polypropylene by rolling and stretching.

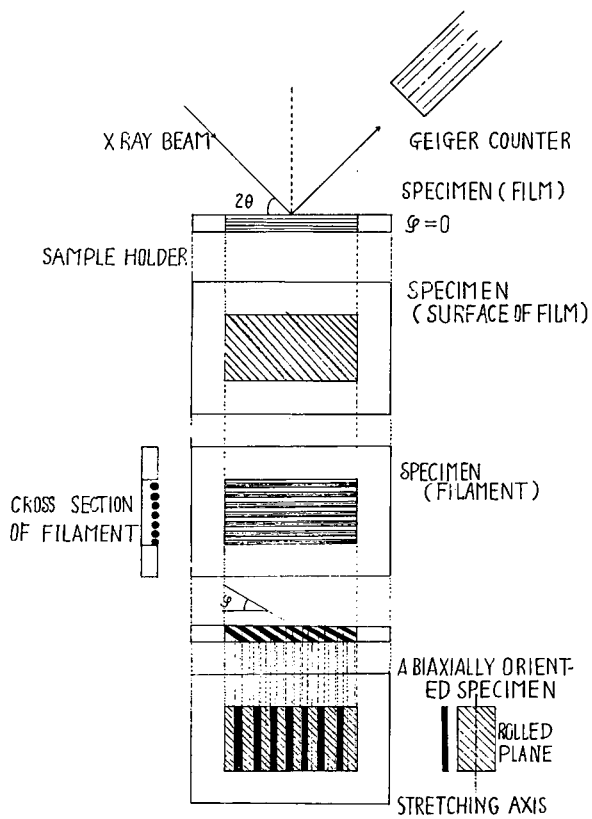

Fig. 1. The apparatus for measurement of x-ray diffraction.

The object of this paper is to elucidate the process of orientation by rolling and stretching and the structure of the highly oriented specimen.

EXPERIMENTAL

Preparation of Oriented Specimens

Several kinds of isotactic polymers which are insoluble in n-heptane were used. Some samples were kindly offered by Nissan Chemical Co., and others were prepared in our laboratory with the use of Ziegler catalysts, $Al(C_2H_5)_3$ and $TiCl_4$. The filament used in experiment (B) was obtained by melt spinning at 200°C. in a nitrogen atmosphere. The mean value of the cross-sectional area of the filament was about 0.12 mm.^{2}.

Specimens of various orders of orientation were prepared by the following treatments.

(A) An isotropic specimen was obtained from a Tetralin solution of the polymer by cooling and by precipitating with acetone.

(B) A specimen highly oriented along the fiber axis was obtained by stretching the filament mentioned above, about 10 times the initial length.

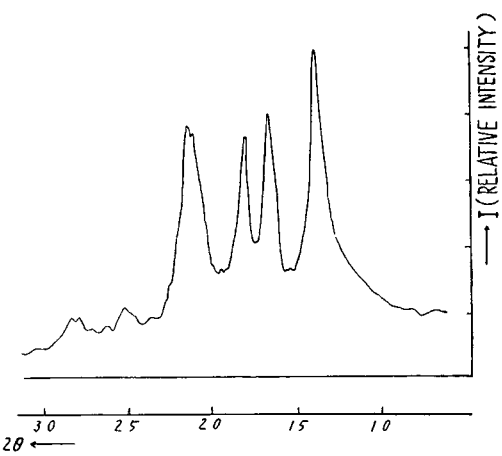

Fig. 2. Scattering curve for an unoriented specimen (A).

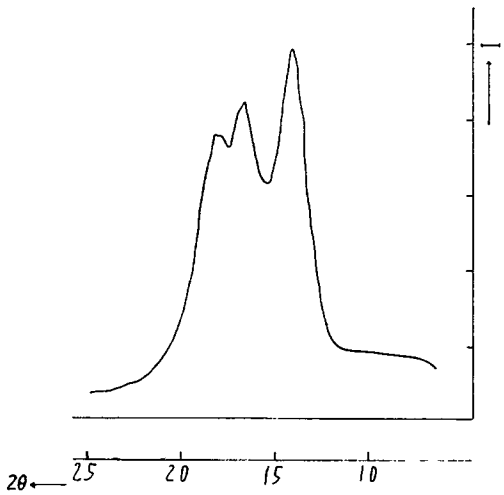

Fig. 3. Scattering curve for specimen oriented by stretching (B).

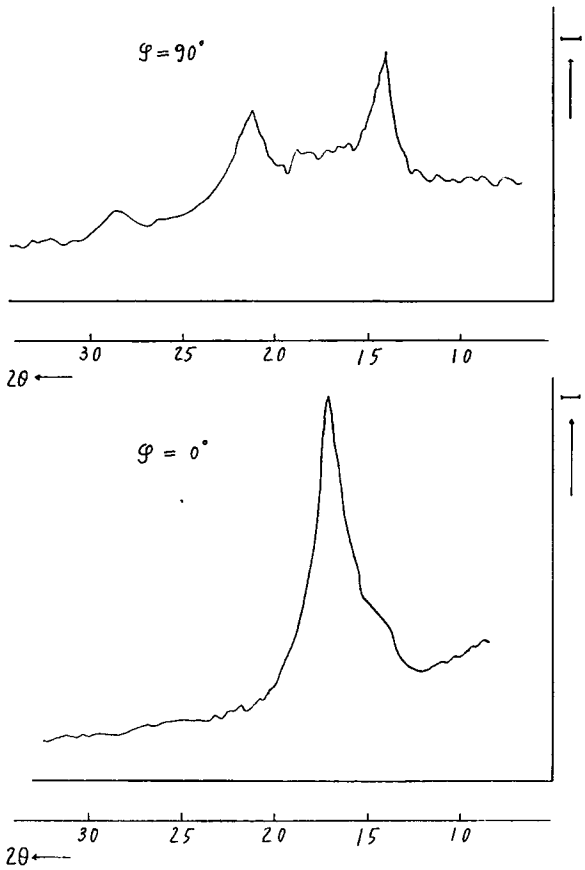

Fig. 4. Scattering curves for uniplaner oriented specimen (C) obtained by rolling $\varphi = 0°$, $\varphi = 90°$.

(C) One of the specimens was obtained by rolling the isotropic specimen (*A*) in various directions at room temperature without stretching.

(D) A highly biaxially oriented specimen was prepared by stretching and rolling repeatedly in one direction.

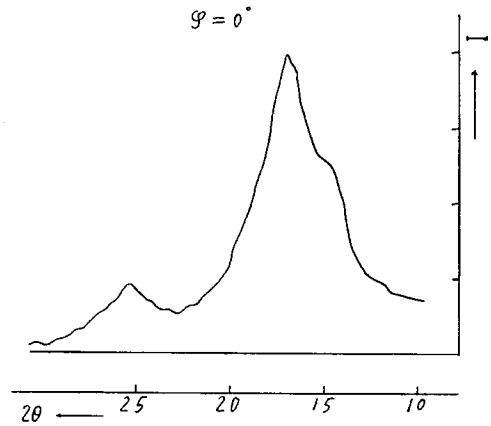

Fig. 5*a*. Scattering curve for highly biaxially oriented specimen (D) with $\varphi = 0°$.

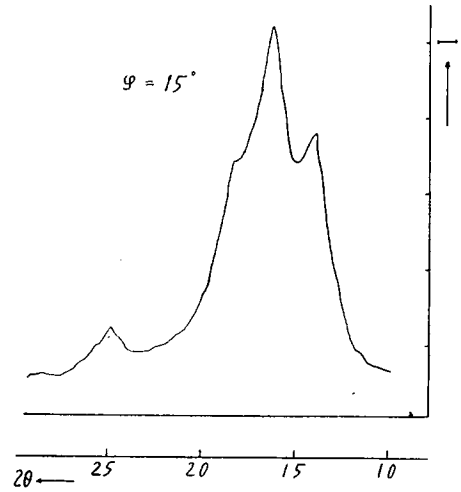

Fig. 5*b*. Scattering curve for highly biaxially oriented specimen (D) with $\varphi = 15°$.

X-Ray Diffraction Measurement

A Geiger counter spectrometer was used in the measurement of X-ray diffraction. Nickel-filtered copper radiation was used in this work. The Geiger counter for the measurement of the diffracted beam intensity was so mounted that it could be moved in a horizontal plane around a graduated circle about the axis of rotation. The measurement apparatus is shown in Fig. 1. In this measurement, only the diffraction from the lattice plane parallel to the surface of the sample holder is predominant.

RESULTS

The intensity diffraction curve shown in Figure 2 for the powdery sample obtained by precipitation

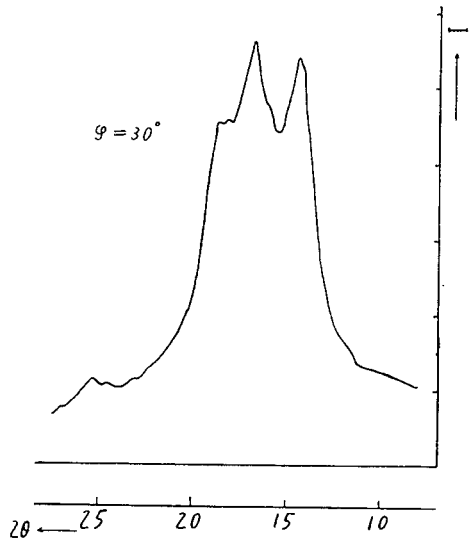

Fig. 5c. Scattering curve for highly biaxially oriented specimen (D) with $\varphi = 30°$.

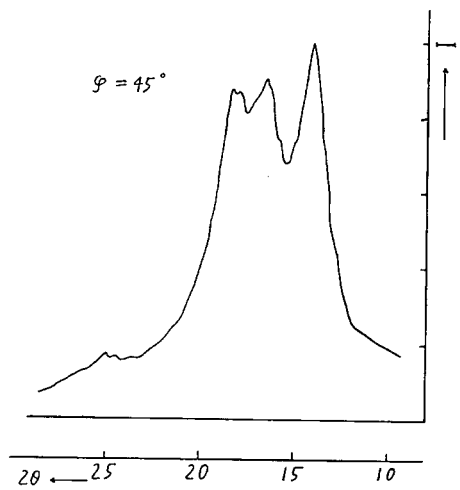

Fig. 5d. Scattering curve for highly biaxially oriented specimen (D) with $\varphi = 45°$.

corresponds to the Debye-Scherrer ring in an ordinary x-ray diffraction pattern. Figure 2 shows that the specimen is isotropic in this form.

Three principal peaks are observed in the intensity curve for the stretched filament (B) as shown in Figure 3. Three of the peaks correspond to those observed in the equatorial scan of the isotropic specimen (A), but the fourth in the latter completely disappeared in the stretched filament. The relative intensities of the three peaks at θ = 14.2, 16.4, and 18.2° are changed only slightly by stretching the filament and are almost the same as in the case of isotropic specimen. From these facts, it is obvious that the filament is highly oriented in

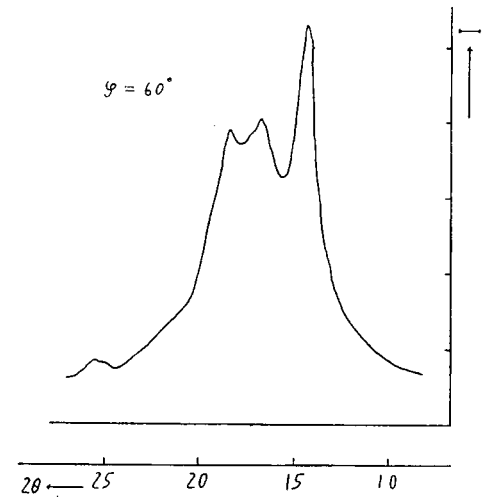

Fig. 5e. Scattering curve for highly biaxially oriented specimen (D) with $\varphi = 60°$.

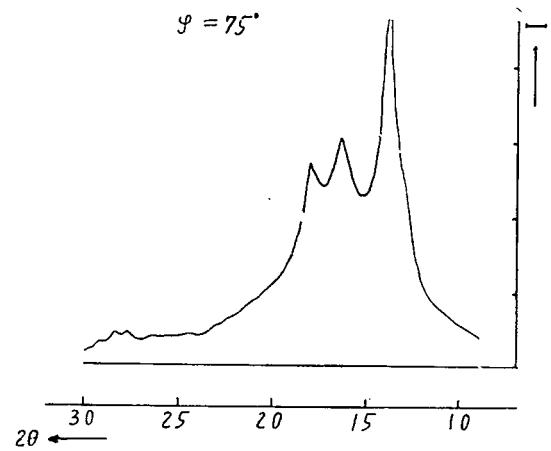

Fig. 5f. Scattering curve for highly biaxially oriented specimen (D) with $\varphi = 75°$.

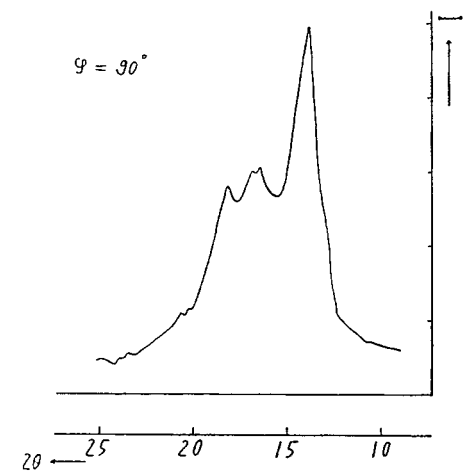

Fig. 5g. Scattering curve for highly biaxially oriented specimen (D) with $\varphi = 90°$.

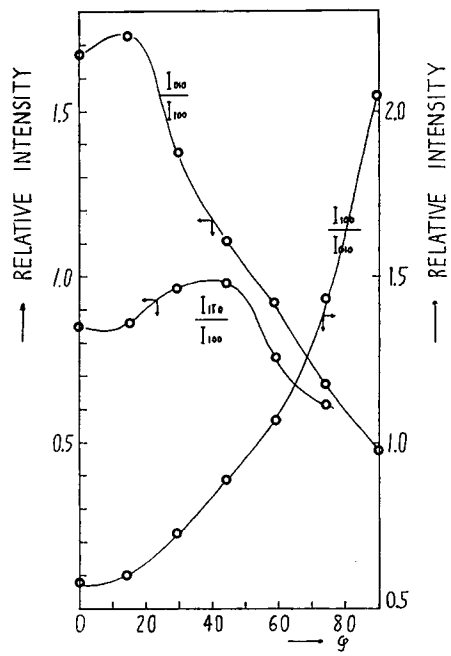

Fig. 6. The relation between relative peak intensity and the tilt angle.

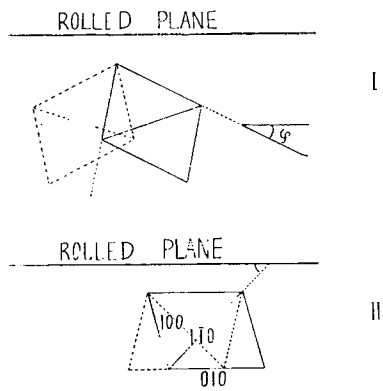

Fig. 7. Section of the specimen showing the relation of the unit cell to the plane of rolling; (I) considerably oriented specimen; (II) completely oriented specimen.

the direction of stretching but is isotropic in the radial direction.

The diffraction intensity curves for specimen (C) at tilt angles $\varphi = 0$ and 90° are shown in Figure 4. At $\varphi = 0$, the diffraction for the 010 plane is predominant and all other diffraction peaks almost disappear. At $\varphi = 90°$, however, the diffraction for the 010 plane completely disappears in contrast with the case of $\varphi = 0°$. This indicates that the 010 plane is oriented completely parallel to the rolled plane.

The dependence of the diffraction intensity curves on the tilt angle was measured at $\varphi = 0$, 15, 30, 45, 60, 75, and 90°, as shown in Figures 5*a–g*.

The relation between the relative peak intensity and the tilt angle φ is shown in Figure 6. From these results, it is obvious that the orientation in the direction of stretching occurs as in the case of the stretched filament. The relative diffraction intensity for the 010 spacing increases gradually with the tilt angle, reaching a maximum value at the angle $\varphi = 90°$; and the relative diffraction intensity for the $1\bar{1}0$ spacing reaches a maximum value near $\varphi = 45°$. It is also obvious that the 010 spacing is oriented parallel to the plane of rolling and that the $1\bar{1}0$ spacing is oriented at an angle of 45° to the plane of rolling. The orientation in the plane perpendicular to the stretching axis in such a treatment is shown in Figure 7. Thus, a highly biaxially oriented specimen can be obtained by stretching and rolling.

References

1. G. Natta, *J. Polymer Sci.*, **16**, 143 (1955).

Synopsis

A highly biaxially oriented isotactic polypropylene was obtained by stretching and rolling repeatedly. In such treatment, it was confirmed by x-ray examination that the 010 spacing was oriented parallel to the plane of rolling.

Résumé

Un polypropylène isotactique hautement orienté dans deux directions a été obtenu par étirements et calendrages répétés. Dans de tels traitements, la configuration 010 est orientée parallèlement au plan de calendrage ainsi qu'il est démontré par les rayons X.

Zusammenfassung

Ein in hohem Grade doppelt orientiertes, isotaktisches Polypropylen wurde durch wiederholtes Strecken und Walzen erhalten. Durch diese Behandlung wurde, wie die Prüfung mit Röntgenstrahlen bestätigte, die 010-Ebene parallel zur Walzebene orientiert.

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