An Optical Study on Shear-Induced Crystallization of Polymers

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The process of shear-induced crystallization of some polymers was examined by means of an X-ray TV system and the polarized light scattering method. The process of shear-induced crystallization under low stress was proved to be essentially the same as that of spherulitic growth. Under high shear stress, light scattering was observed as a premonitory sign of crystallization before X-ray crystalline reflections start to appear. The strong scattering on the equator in the Vv light scattering pattern before the crystallization point indicates that many elongated bodies, which are precursors of the row structure, have occupied a large portion of the specimen at the crystallization point. It is inferred from the results that, in the course of shear-induced crystallization under high stress, there may exist a mesomorphic state during transformation from the amorphous to the crystalline state.

INTRODUCTION

Most polymer processing operations involve crystallization from stressed melts. The application of a stress to polymer melts results in molecular orientation due to the long–chain nature of the molecules, and has a substantial effect on the crystallization kinetics and morphology of the end product.

Amano, Kajita, and Katayama[1] reported that the structure formed during crystallization from low-elongated melts is quite similar to the central portion of a spherulite, which is called a sheaflike structure.[2] Under higher stress the resulting morphology is a stacked lamellar structure, that is, the row structure.[3] Some exellent works[4~6] have been published on shear-induced crystallization. However most morphological studies, so far, have dealt with specimens obtained after the completion of crystallization.

In our previous paper,[7] we have discussed some requirements which an apparatus has to fulfill for measuring shear-induced crystallization, and described our apparatus for continuous observation of the changes in the polarized light scattering pattern and in the diffracted X-ray intensity during crystallization. In the present paper, an X-ray TV system and a newly devised light scattering apparatus for simultaneous observation of both Hv and Vv patterns will be described, and some results obtained with these setups are presented and discussed.

APPARATUS

An apparatus for observing the X-ray diffraction pattern during shear-induced

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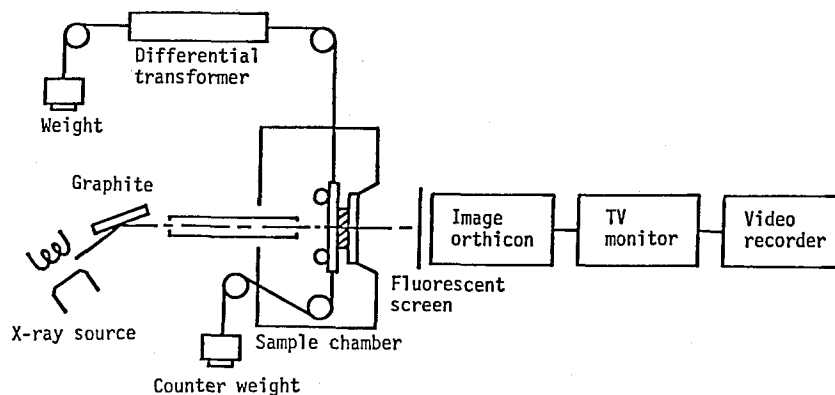K. NOGAMI, S. MURAKAMI, K. KATAYAMA, and K. KOBAYASHI

Fig. 1. Schematic diagram of the setup with an X-ray TV system.

crystallization is schematically shown in Fig. 1. The change in X-ray diffraction pattern can be observed and recorded with the aid of an X-ray TV system, which consists of a fluorescent screen, an image orthicon, a monitor TV and a video recorder (Rigaku X-ray TV system). A thin polymer specimen is sandwiched between two beryllium plates. First the specimen was heated and melted above its melting point and quenched quickly to a crystallization temperature. Then a load was applied to one of the beryllium plates to deform the supercooled specimen in shear, while the other beryllium plate was firmly fixed to the frame of the apparatus. The changes in shear strain and temperature of the specimen were recorded on a chart at the same time.

The setup for observing the change in light scattering pattern was described in our previous paper.[7] In the case of light scattering the X-ray sourse, beryllium plates and the X-ray TV system in Fig. 1 were replaced with a He-Ne gas laser, glass slides and a photographic film, respectively, and two polarizing plates, *i.e.* a polarizer and an analyzer, were added. For simultaneous observation of the Vv and the Hv patterns, a special analyzer was introduced. This analyzer is made up of two semicircles. The vibration direction of one semicircle is parallel and that of the other is perpendicular to the direction of the seam between two semicircles. This analyzer is placed so that the direction of the seam is parallel to the flow direction. The polarizer is placed so that its vibration direction is also parallel to the flow direction. This analyzer, therefore, enables us to obtain a half of the Vv pattern and that of the Hv pattern at the same time.

RESULTS AND DISCUSSION

The materials used are high density polyethylene (Sholex 6050), polybutene-1 ($M_\eta=$ 4.7×10^5) and polyethylene oxide ($M_\eta=5\times10^5$). A typical strain curve of polyethylene oxide is shown in Fig. 2. Figure 3 shows a time series of the X-ray diffraction patterns which were observed and recorded with the X-ray TV system, on the same run. The crystallization point is at 13 seconds after loading, when crystalline reflections begin to appear. In this and other figures, the time below each pattern means that which elapsed after loading, and the flow direction is vertical. It can be seen from Figs. 2 and 3 that, as soon as crystallization starts, the specimen undergoes changes in rheological properties and the rate of shear strain begins to decrease rapidly to zero. This phenomenon took
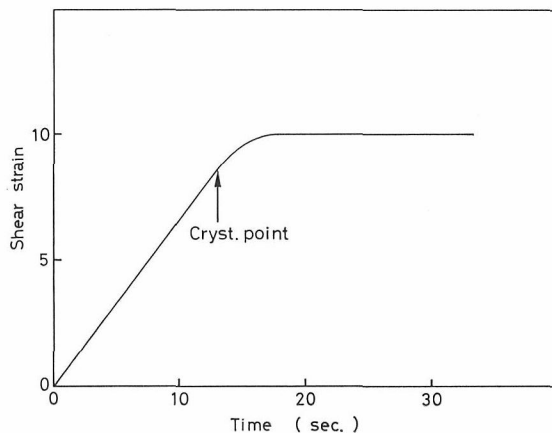
Fig. 2. Strain curve of polyethylene oxide.
Stress: 1.4×10^6 dyne/cm², Cryst. temp.: 47°C
Cryst. point: 13 sec.
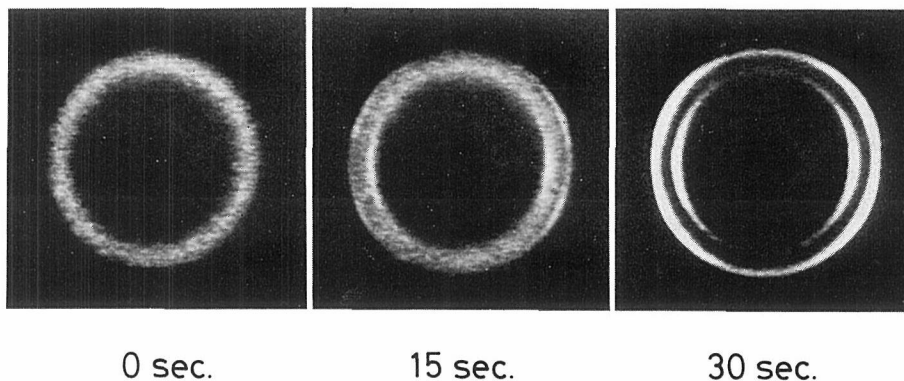

0 sec.   15 sec.   30 sec.

Fig. 3. Time series of X-ray diffraction patterns of polyethylene oxide. Obtained on the same run as shown in Fig. 2.

place in other polymers and at any amount of stress, except for the application of such a high stress as to deform the specimen until it was fractured. This means that we can find the crystallization point in the strain curve without observing the change in the X-ray diffraction pattern. Since the strain curves can be obtained in common with the apparatus for X-ray diffraction and light scattering, the results obtainable with different apparatus can be compared through the intermediation of the strain curve.

Time series of light scattering patterns of polyethylene, polybutene-1 and polyethylene oxide are shown in Figs. 4, 5, and 6, respectively. Since we could obtain only a half of the whole Hv or Vv light scattering pattern, we duplicated the original half and combined these two halves to construct the whole pattern. According to the strain curves, the Hv patterns begin to come out in the neighborhood of the crystallization point, where X-ray crystalline reflections start to appear. The Hv light scattering pattern of elongated four-leaf type, shown in these figures, is easily observed on polymers which are melt crystallized under low stress. It was reported in a previous publication[1] that the structure which appears
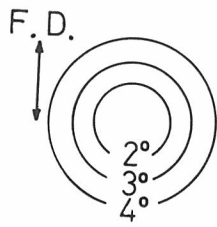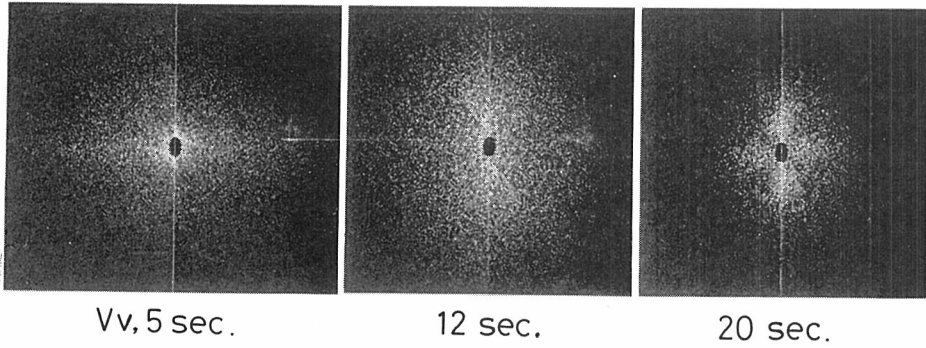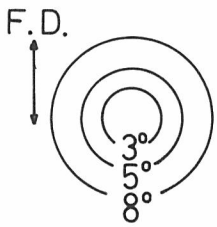
Vv, 5 sec.　　　　　12 sec.　　　　　20 sec.

F.D.

2°
3°
4°

Fig. 4.

Hv, 12 sec.　　　　20 sec.

Vv, 25 sec.　　　　40 sec.　　　　60 sec.

F.D.

3°
5°
8°

Fig. 5.

Hv, 40 sec.　　　　60 sec.

Vv, 5 sec.   10 sec.   30 sec.

F.D.

5°
10°

Fig. 6.

Hv, 10 sec.   30 sec.

Fig. 4.   Time series of light scattering patterns of polyethylene.
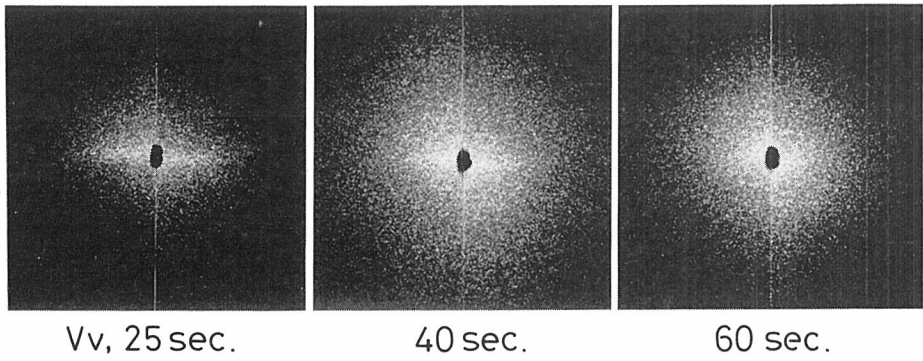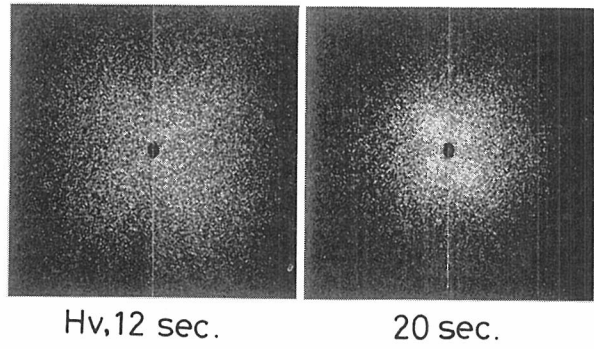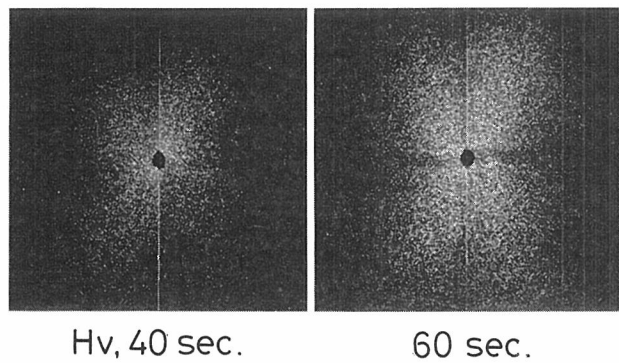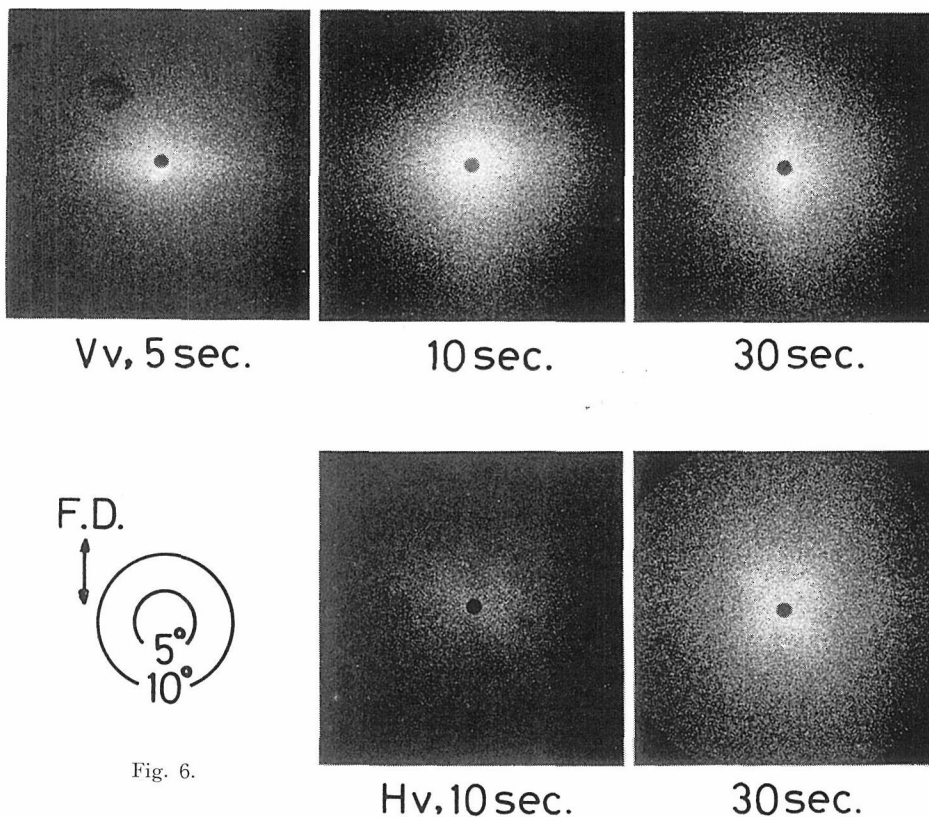Stress: 3.5×10^5 dyne/cm², Cryst. temp.: 125°C
Cryst. point: 10 sec.

Fig. 5.   Time series of light scattering patterns of polybutene-1.
Stress: 6.3×10^5 dyne/cm², Cryst. temp.: 96°C,
Cryst. point: 38 sec.

Fig. 6.   Time series of light scattering patterns of polyethylene oxide.
Stress: 2.0×10^6 dyne/cm², Cryst. temp.: 53°C,
Cryst. point: 9 sec.

during crystallization from low-elongated melts is quite similar to the central portion of a spherulite, which is called a sheaflike structure, and it was suggested that the Hv pattern of elongated four-leaf type is attributed to this structure. In order to confirm this, the light scattering intensities were calculated based on a simplified model of a sheaflike structure (See Appendix). Figure 7 shows a comparison of calculated patterns with observed ones of polyethylene obtained after the completion of crystallization. Good agreement between the observed and calculated patterns is obvious, and it is confirmed that the entity which appears in the process of shear-induced crystallization under low shear stress has a sheaflike structure. Hashimoto *et al.*[8] made similar calculations based on a more simplified model, and obtained almost the same results.

Since the deformation stops at a very early stage of crystallization process, the application of low shear stress may not have a substantial effect on the subsequent crystallization
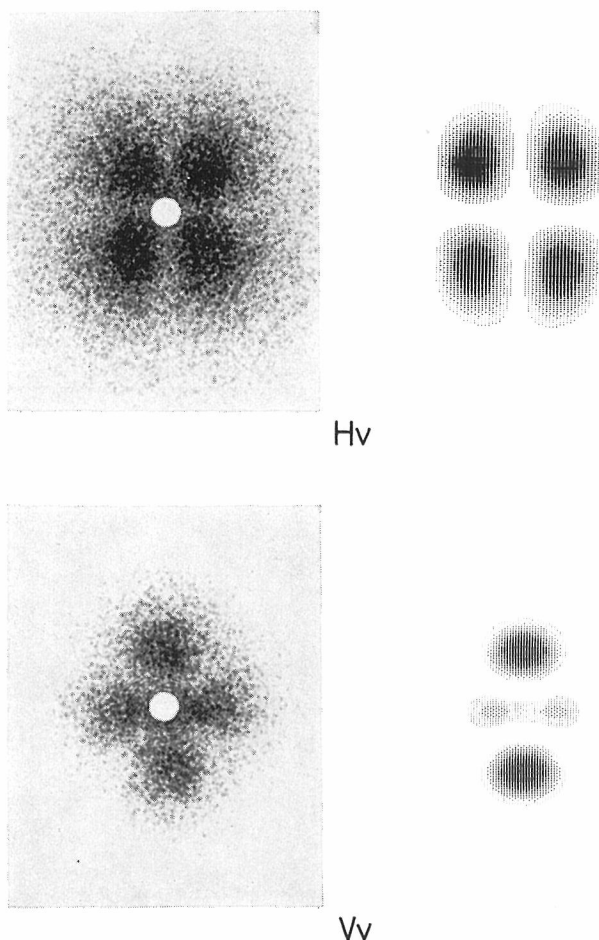
Polyethylene

Hv

Vv

Fig. 7. Observed and calculated light scattering patterns of polyethylene.
$a=3.00\,\mu$, $L=\infty$, $\beta=45°$. (See Appendix)

process. The growth mechanism of shear-induced crystallization under low stress, therefore, essentially the same as that of spherulitic growth. The major difference between these two cases is that the molecules in the nuclei are oriented parallel to the flow direction in case of shear-induced crystallization. A sheaflike structure continues to grow up to be a flattened spherulite,[1] and the growth finally stops by impingement with neighboring flattened spherulites.

In case the applied shear stress is medium, a streak appears on the equator in the Vv light scattering pattern before the Hv pattern appears (Figs 4, 5, and 6). The observations with the X-ray TV system indicate that crystalline reflections begin to arise at 10 sec., 38 sec., and 9 sec. after loading for polyethylene, polybutene-1 and polyethylene oxide, respectively. The streak on the equator in the Vv pattern, therefore, turns out to have appeared prior to crystallization. This fact suggests that there are optically anisotropic bodies which are elongated and aligned parallel to the flow direction while the

specimen is still amorphous in the X-ray crystallographic sense. This elongated body is a precursor of the row structure.

In this range of shear stress, first the precursor of the row structure comes out prior to the crystallization point and then the sheaflike structure begins to appear. Therefore, row structures and flattened spherulites coexist. In the cases shown in Figs. 4, 5, and 6, numerous flattened spherulites come out and occupy a remarkably larger portion of the specimen when crystallization is completed. The light scattering patterns in these figures, except for the streak on the equator in the Vv pattern, are mainly attributed to these flattened spherulites.

In case the shear stress exceeds a certain value which depends on the crystallization temperature, polyethylene gives a streak on the equator both in the Vv and the Hv light scattering patterns before crystallization, as shown in Fig. 8. The streak on the equator in the Hv pattern indicates not only that there are elongated bodies along the flow direction, but also that the optic axis of the body is inclined with respect to the flow direction. As
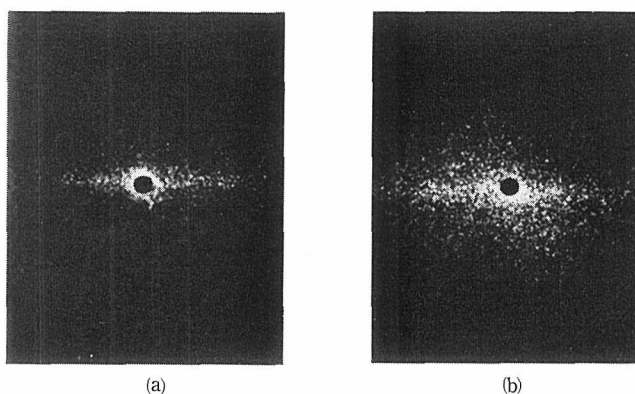

(a)   (b)

Fig. 8.   Time series of Hv light scattering patterns of polyethylene.
(a) 18 sec., (b) 21 sec.
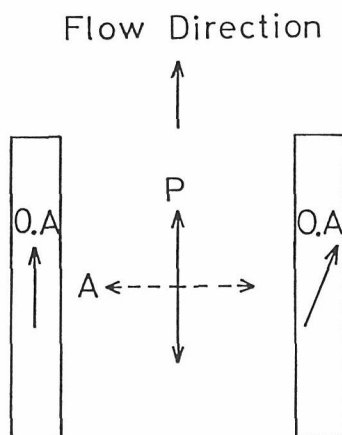Stress: 2.5×10^5 dyne/cm^2, Cryst. temp.: 126°C,
Cryst. point: 20 sec.

Fig. 9.   Direction of the optic axis in the elongated body of polyethylene.

Fig. 9 shows, we can expect no Hv light scattering if the optic axis of the body is parallel to the polarization direction of the incident light, because the scattered light from the specimen is polarized along the flow direction and cannot pass through the analyzer.

The streak appears earlier and its intensity becomes higher with increasing shear stress. This may be attributed to that the crystallization rate and the number of elongated bodies increase with stress. Under high shear stress, only a streak is observed on the equator in the Vv light scattering pattern even after the completion of crystallization. It is deduced from this result that the resulting morphology is exclusively the row structure. Polyethylene gives a streak also on the equator in the Hv pattern. Other polymers show no Hv pattern in the range of high stress, indicating that the molecules are oriented along the flow direction on the average. We observed the process of shear-induced crystallization of polyethylene oxide with a polarizing microscope, and found that numerous elongated bodies have appeared before crystallizataion and occupied a large portion of the specimen. These elongated bodies would give clear X-ray crystalline reflections if they were crystalline (See Fig. 10).

What sort of fine structure, then, does this body have? The streak in the light scattering pattern which comes out before crystallization reminds us an earlier experimental fact that a small angle X-ray scattering was observed on the meridian just before the appearance of wide angle X-ray crystalline reflection in the process of melt spinning.[4] This suggests that there are already platelike density fluctuations in the filament before the onset of crystallization, and that the part with higher density has not yet established enough regularity to show wide angle X-ray crystalline reflections. Small angle X-ray scattering provides structural information in the range of $50\sim1000$ Å, while light scattering provides that in the range of $1\sim100$ μ. The elongated body along the flow direction, therefore, has a fine structure which gives rise to a small angle X-ray scattering on the meridian.

These results lead to a conclusion that the process of shear-induced crystallization involves the development of a mesomorphic state during transformation from the amorphous to the crystalline state, and that the precursor of the row structure, which is in the
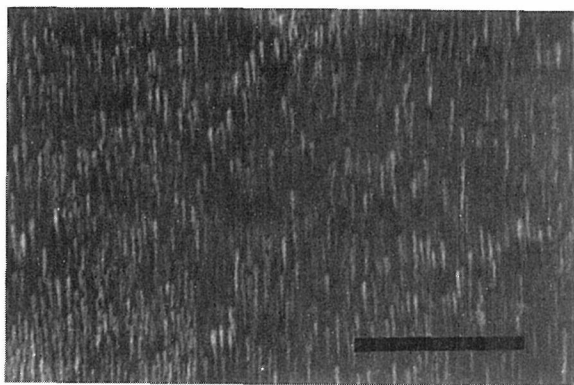

Fig. 10.   Polarized light micrograph of polyethylene oxide.
Taken at 1.8 sec. after loading.
Stress: 2.5×10^6 dyne/cm^2, Cryst. temp.: 55°C,
Cryst. point: 4.5 sec.

mesomorphic state, consists of stacked-lamellae-like structure with molecular chains loosely packed. In case of polyethylene, in addition, it is suggested that the average direction of molecular chains is tilted with respect to the normal of lamellae, while lamellae are stacked along the flow direction. The streak on the equator in the Hv light scattering pattern, however, is characteristic of polyethylene, and other polymers such as polybutene-1 and polyethylene oxide show no streak in the Hv pattern at any amount of stress. The evidence in support of the existence of a mesomorphic state during shear-induced crystallization is not sufficient at present, but this idea will serve as a clue to understand the mechanism of the crystallization of polymers under molecular orientation.

APPENDIX

A simplified model of the sheaflike structure is shown in Fig. 11. In the cylindrical coordinates (r, ϕ, z), the z-axis is parallel to the flow direction and perpendicular to the propagation direction of the incident light. Sphere O' has a radius a which depends on the growth rate and the branching frequency of lamellae. The path of minimum length along which lamellae grow from O to P is OQP, where OQ is an arc along and QP is a tangent to sphere O'. The length of OR and the angle between QP and OR are denoted by ρ and ψ, respectively.

Some assumptions were introduced in order to simplify the calculations: (a) the lamella at P will grow along QP twisting with a period L; (b) molecular chains are perpendicular to QP and inclined by β (radian) away from the normal of lamellae; (c) the structure has the polarizabilities α_1 and α_2 parallel and perpendicular to the molecular direction, respectively; (d) the structure is in a medium having the polarizability α_s along the flow direction.

Under these assumptions, following equations were obtained for Hv and Vv light scattering amplitudes, where the integration with respect to ϕ has already been executed.

$$A_{Hv} \propto (\alpha_2 - \alpha_1) \int\int (\rho - a\psi) \ \{v \cos^2\left(\frac{2\pi\rho}{L} + \beta\right)\sin 2\psi + q \ \sin\left(\frac{4\pi\rho}{L} + 2\beta\right)$$

$$\times \cos\psi\} \sin\omega \cdot J_1(u)/u \cdot r \ d\psi d\rho,$$

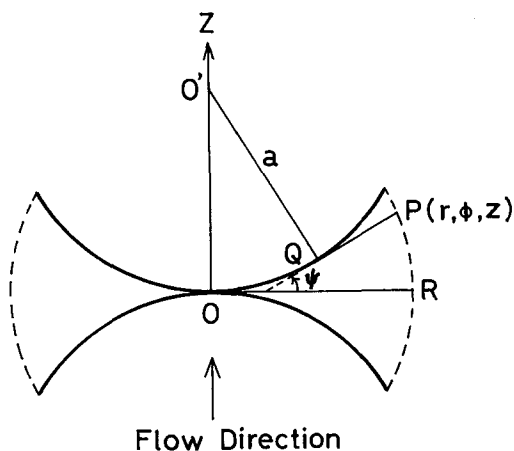Fig. 11. Simplified model of a sheaflike structure.

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$$A_{Vv} \propto \iint (\rho - a\psi) \left\{ (a_1 - a_2)\cos^2\left(\frac{2\pi\rho}{L} + \beta\right)\cos^2\psi + (a_2 - a_s) \right\} \cos \omega \cdot J_0(u) \, r \, d\psi d\rho,$$

where, $J_0(u)$ and $J_1(u)$ are the Bessel functions,

$$q = \frac{4\pi}{\lambda} r \sin^2 \frac{\theta}{2},$$

$$u = \frac{4\pi}{\lambda} r \sin \frac{\theta}{2} \left(1 - \cos^2 \frac{\theta}{2} \cos^2\mu\right)^{1/2},$$

$$v = \frac{2\pi}{\lambda} r \sin\theta \sin\mu,$$

$$\omega = \frac{2\pi}{\lambda} z \sin\theta \cos\mu,$$

and θ, μ and λ are the scattering angle, the azimuthal angle and the wave length of the incident light, respectively.

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