Crystallization of Syndiotactic Polystyrene Monitored by Angular Distributions of Polarized Fluorescence

CRYSTALLIZATION OF SYNDIOTACTIC POLYSTYRENE MONITORED BY ANGULAR DISTRIBUTIONS OF POLARIZED FLUORESCENCE

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The method to measure *polarized fluorescence by rotating a sample around the excitation light* (PFR) was applied to observe the initial stage of crystallization of syndiotactic polystyrene (SPS) induced by the exposure of naphthalene (NP) vapors. At room temperature, no crystallization of SPS appeared when the stretched films were exposed by NP vapors. PFR well clarified that the NP molecules were distributed not uniformly but rather with a sort of orientation in the oriented amorphous SPS. NP molecules were clathrated in SPS films in the case of the exposure at 80°C. However, the exposure of NP vapors at 60°C was found to produce SPS/NP clathrate cocrystalline structure with only a small amount but rather mainly produce a trans planar mesomorphic phase. In this initial stage, the wide angle X-ray diffraction revealed diffuse and unclear, whereas PFR was effective to determine orientation and distribution of the NP molecules. The NP molecules staying in the amorphous region were shown to be oriented due to the formation of a trans planar mesomorphic phase, and their main arrangements were first determined by PFR.

INTRODUCTION

The measurements of polarized fluorescence of a chromophore in a film by rotating it around the excitation light beam are quite efficient for the determination of the arrangement of chromophores in the film. This method to measure polarized fluorescence by rotation of a sample (PFR) was first claimed by Nishijima (1,2), but unfortunately has not been used at all for 30 years because (i) there have appeared no sample films where most chromophores are oriented in regular order and (ii) the arrangement of chromophores is difficult to be calculated even if there is a sort of order among chromophores. However, Guerra et al. succeeded to prepare syndiotactic polystyrene (SPS) films where δ-empty crystalline and cocrystalline regions containing guest molecules clathrated were oriented with quite high regularity all over the film (3-6). Then, we successfully applied the PFR method using polarized excitation light to determine the three-dimensional position of a guest naphthalene (NP) molecule in a crystalline unit (7). In the same way, we could determine the arrangement of 1,4-dimethylnaphthalene (14DMN) in SPS/14DMN cocrystals where the crystals are of intercalate form (8). In the present paper, we have applied the same method to monitor the crystallization of SPS due to the exposure of NP vapors to the drawn SPS films.

SPS is known to have a complex polymorphic behavior (9). It has two stable conformations of polymer chain, all trans zigzag conformation and 2_1 helical confomation. Nonsolvated crystalline forms α and β consist of all trans conformation, while the other crystalline forms γ, δ and ε consist of 2_1 helical conformation. In particular, the δ and ε forms are quite interesting because they have cavities inside the crystalline phase, which is quite rare. Since small molecules can enter and settle down in these cavities, they can form cocrystals with guest molecules such as in clathrate form or intercalate form. The δ-empty form of SPS is monoclinic (space group $P2_1/a$; $a = 1.74$ nm; $b = 1.18$ nm; $c = 0.78$ nm; $\gamma = 117°$) and exhibits per unit cell two identical cavities centered on the center of symmetry and bounded by ten phenyl rings (14,15). Usually SPS cocrystals with guest molecules such as NP are prepared by way of δ semicrystalline films that are obtained by exposing SPS amorphous films to vapors of small molecules such as CS_2 and by subsequent drying under vacuum. Then, the clathrate films can be obtained from these δ-empty form films by exposure of another vapor such as NP or by immersion in bulk or solutions of guest molecules. As for the nanoporous δ phase, Guerra et al. have demonstrated that it is possible to prepare films with $a_{//} c_{//}$ (3,16) or $a_{//} c_{\perp}$ (4) or $a_{\perp} c_{//}$ (5) uniplanar orientations.

The present paper deals with the crystallization of SPS films due to the exposure of NP molecules. The structural changes caused by the direct exposure of NP to amorphous SPS have not been reported except the paper of Venditto et al. where we collaborated together (6). Our purpose of the present work is not only because we are interested in the structural change induced by a larger molecule such as NP but also because we have started with the studies on orientation of amorphous region when it is stretched. We stretched atactic polystyrene (APS) films and exposed NP vapors to

them (17). The patterns of angular distributions of polarized fluorescence intensities of NP were found to be different between the case where NP molecules were introduced into a drawn film by exposure of NP vapors and the case where NP molecules were doped into APS films and then stretched uniaxially. We did the same experiments using SPS films in order to ascertain whether the stereoregularity of polymers influences the orientation of guest molecules that would be absorbed by their vapor exposure to the films.

In the present work, we discuss the structural change of SPS induced by a larger molecule such as NP. We also consider the effects of orientation of amorphous region in the stretched SPS. We observe the effect of stretched SPS using PFR and wide angle X-ray diffraction (WAXD), and discuss the accuracy of PFR by comparison of WAXD.

METHODS

PFR method: Polarized Fluorescence Measurements by Rotating a Sample Around the Excitation Light

First we show our method to measure polarized fluorescence of a chromophore and its angle distribution, and explain how the orientation of a chromophore is related to its polarized fluorescence.

(Figure 1)

Fig. 1 demonstrates the general measurement of polarized fluorescence of a sample. Two sets of polarizers are used for the measurements: polarizer 1 is always set as Iv shown in the figure and selects the polarized light whose vector of electric field is vertical to the direction of progress as the excitation light of a sample. The polarizer 2 is set in front of the detector as is shown to be either parallel (Iv) or vertical (Ih) to polarizer 1. The fluorescence intensity of a sample is defined to be I0 and I90 when polarizer 2 (fluorescence) is set as Iv and Ih, respectively. I0 and I90 are dependent on how much a sample absorbs the polarized excitation light and how much its polarized fluorescence can go through the polarizer 2. We can estimate I0 and I90 of a chromophore in a film. Here the transition moments for absorption and fluorescence of a chromophore are described to be μ_A and μ_F, respectively. Let us imagine that all the chromophores, being isolated from each other, have the same arrangement in a film and their molecular motions are restricted perfectly. We define the angle between μ_A of the chromophore and the Iv of excitation light to be α (degree), and the angle between μ_F and the Iv (of polarizer 2 (fluorescence)) to be β(degree). If a chromophore is excited at a wavelength of the first absorption band according to the transition to the lowest excited state, namely, from S_0 to S_1, β is identical with a. However, we can change μ_A, namely α, by changing excitation light wavelength to be shorter. Here the intensity for a chromophore in the film to absorb the excitation light shown as Iv is proportional to $\cos^2\alpha$, while the possibility for the

polarized fluorescence of the chromophore able to pass through polarizer 2 is proportional to $\cos^2\beta$. Thus, the intensity of I0 monitored by the detector at the back of polarizer 2 is given by Eq. (1).

$$I0 = K\Phi \cos^2\alpha \cos^2\beta \tag{1}$$

where K is the maximum probability of excitation attainable when the molecular axis of the chromophore coincides with the direction of Iv of excitation light, and Φ is the energy yield of fluorescence. I90 is obtained for the polarized fluorescence able to go through polarized 2 when it is set as Ih, namely, perpendicular to the case to monitor I0. Because the angle between μ_F and Ih (of polarizer 2 (fluorescence)) is to be 90-β degree) in this case, I90 is given by Eq. (2).

$$I90 = K\Phi \cos^2\alpha \sin^2\beta \tag{2}$$

We can know the transition moments for absorption and fluorescence of a chromophore, μ_A and μ_F, however, α and β are dependent on three-dimensional position of the chromophore against Iv and Ih. Thus, it is obvious that the measurement of I0 and I90 for one position of the film is not enough for determining the arrangement of the chromophore even if the arrangement of all the chromophores is unique and the same in a film.

Then, Nishijima et al. (1,2) introduced the smart method to determine the arrangement of chromophores in a film. It is the method to measure each I0 and I90 of the chromophore by rotating the sample film around the excitation light beam by every 10 or some degrees. This rotation increases the information about the arrangement of the chromophores in a film. At each position of the rotation, because the angles between the transition moments (μ_A and μ_F) and the three vectors of electric field (Iv of the excitation and Iv and Ih of the fluorescence) must change, we can have the information of precise arrangement of chromophores three dimensionally. Accordingly these three vectors of electric field can be used as the standard coordinates.

If we can specify the three-dimensional arrangement of a guest chromophore in a film, we can calculate I0 and I90 of the chromophore no matter how the film is set around the exitation light. Or if the arrangement of a guest molecule is unique, we can estimate the arrangement by reproducing all the I0 and I90 values obtained by rotating the sample.

(Figure 2)

Just as an example, we show a case where all the NP molecules are oriented such as in Fig. 2. When an NP molecule is excited at 280 nm, which corresponds to the transition from S_0 to S_2, the μ_A of NP is parallel to the short axis of NP. The fluorescence peaks of NP appear at 325- and 337-nm corresponding to the transition from S_1 to S_0. This fluorescence transition moment, μ_F, is parallel to the long axis of NP. Thus, in the case where an NP molecule is oriented with high regularity such as in Fig. 2A, this molecule absorbs with the highest probability the polarized excitation light whose vector of electric field is Iv. However, the I0 value must be 0 because the vector of its polarized fluorescence is perpendicular to Iv of polarizer 2: namely, the angle β in this case becomes 90°, giving cos β to be 0. On the contrary, the I90 value is expected to be the highest,

because the angle β in this case becomes 0°, giving cos β to be 1, the maximum value. Note that what we have to pay attention to is only the direction of the long and short axes of NP, that is to say, the direction of μ_A and μ_F against Iv and Ih. When irradiated at 280 nm, any NP rings at any angles shown in Fig. 2B can be excited identically, namely with the highest probability, because μ_A of all the NP molecules shown in Fig. 2B is parallel to the vector of electric field of the excitation light, i.e., α=0 and cos α=1. Moreover, polarized fluorescence emits towards any directions keeping the parallel vibration to the μ_F of NP. Thus, any fluorescence from the NP in Fig. 2A proceed towards all the directions around the long axis. After the measurements of I0 and I90 of NP at the position shown in Fig. 2, the film is rotated around the excitation light beam by every 10 degree, inducing the changes of any angles between the transition moments, namely the direction of the short and long axes of NP, and the vectors of electric field, Iv and Ih, resulting that I0 and I90 come to show different values from those obtained at the position shown in Fig. 2A.

(Figure 3)

Definition of rectangular coordinates system of SPS film and NP molecule

The present paper mainly deals with the case where SPS films are stretched uniaxially. In such drawn films, many SPS polymer chains are assumed to be parallel to the stretching direction of the films. In order to explain a distribution of fluorescent molecules in a film, we define here the two kinds of rectangular coordinate systems for the SPS film and the NP molecule. In Fig. 3A, the coordinate of the film is defined as X-axis being perpendicular to the film surface and Z-axis parallel to the stretched direction. On the other hand Fig. 3B indicates the molecular coordinate system where z-axis is parallel to the long axis of NP and y-axis parallel to the short axis.

(Figure 4)

Simulated Angular Distributions of I0 and I90 Obtained by PFR Method

It is not easy to illustrate an image of a distribution of fluorescent molecules in a film corresponding to the angular distributions of their I0 and I90. In particular, we set a film such as in Fig. 4, then the rotation of the film should be in the same plane inclined at 30° against the excitation beam. In order to give a clear image, we demonstrate some examples of the angular distributions of polarized fluorescence, I0 and I90, with a sketch of orientation of NP molecules in a film. It is needless to say that I0 and I90 at any setting angle should be constant if all the NP molecules are uniformly distributed at random. Each value of I0 and I90 at an angle is the sum of the values of both molecules having regular and random orientation.

(Figure 5)

Let us imagine that all the NP molecules in a film are situated as in Fig. 5A where all the NP molecules have a single arrangement that their short axes are perpendicular to the surface of the film and their long axes are parallel to the stretching direction (y//X and z//Z). Fig. 5B shows the angular distributions of polarized fluorescence, I0 and I90, when many NP molecules in a film are

situated as in Fig. 5A. Thus, if both I0 and I90 happen to show the angular change as Fig. 5B, the arrangement of NP molecules can be considered to be as in Fig. 5A. Note that both I0 and I90 must fit to the simulation at the same time.

<div align="center">(Figure 6)</div>

In contrast with Fig. 5A, Fig. 6 exhibits the case where all the NP molecules have a single arrangement that their short axes are parallel to the stretching direction and their long axes are perpendicular to the surface of the film (y//Z and z//X). Fig. 6B shows the perfectly different angular distributions of I0 and I90 from Fig. 5B.

<div align="center">(Figure 7)</div>

In Fig. 7A, NP molecules have a uniaxial orientation with z//Z, where x and y axes are uniformly rotated around the z-axis. The angular distributions of I0 and I90 change as shown in Fig. 7B, although this includes the arrangement of Fig. 5A. In order to obtain the averaged value, we have to integrate all the values of I0 and I90 because the angle between the short axis of an NP molecule and the stretching direction can take any degree. Like these examples, we always calculate all the values of I0 and I90 when the NP molecules has a uniaxial orientation.

<div align="center">(Figure 8)</div>

In the case of a uniaxial orientation of NP molecules, whose x-axis is parallel to Z-axis (x//Z), the angular distribution indicates monotonic oscillation as shown in Fig. 8B. This orientation is possible to occur when the NP molecules would collide with SPS and enter the free space between side-chain phenyl groups from the perpendicular direction of c axis of the SPS polymer chain, as mentioned in the introduction.

<div align="center">(Figure 9)</div>

When an NP molecule is also uniaxially oriented by x//Y as shown in Fig. 9A, the angular distributions of I0 and I90 of NP are shown as in Fig. 9B. If there are some voids parallel to the stretching direction of the film and these cracks are wide enough for NP molecules to enter, the angular distributions of I0 and I90 of the NP molecules in these cracks would be those shown in Fig. 9B.

In any rate, note that the angular distributions of I0 and I90 are quite different if the arrangement of NP molecules is different, as is shown in Figs. 5 to 9.

EXPERIMENTAL

Materials

SPS was supplied by Idemitsu Kosan Co. Ltd. [13]C nuclear magnetic resonance characterization showed that the content of syndiotactic polystyrene triads was over 98%. The weight-average molar mass obtained by gel permeation chromatography (GPC) in trichlorobenzene at 145°C was found to be $M_w = 2.33 \times 10^5$ with the polydispersity index, $M_w/M_n = 2.0$.

All the SPS films were first prepared by melting polymer beads at 300°C under the pressure of 15MPa for 5 min, and by quenching films quickly into iced water. These amorphous SPS films were drying for more than 24 hrs under vacuum at 40°C. All of them were stretched uniaxially at some drawing ratios by manual stretching machine, at a constant deformation rate of 0.06 fold/sec, in the temperature range of 105-110°C. After the stretching, all the films were drying under vacuum for 3 days at 40°C. The SPS films named Sn (n=3 to 120) were obtained at a draw ratio of $\lambda \approx 3$, and exposed to naphthalene (NP) vapors for n hrs at 60°C, while SL and SH were obtained at $\lambda \approx 3$, and exposed to NP vapors for 120 hrs at room temperature and at 80°C, respectively. SXm's were obtained at a draw ratio of $\lambda \approx m$, and exposed to NP vapors for 3 hrs at 60°C. All the films exposed to NP vapors were dried under vacuum for 3 days at 40°C in order to get rid of NP molecules that were not fixed so much. The content of NP in films was determined by using a Rigaku Thermo Plus2 TG8120 thermogravimeter under nitrogen gas flow. The characterization of the films was summarized in Table 1.

(Table 1)

Methods

Fluorescence and Polarized Fluorescence Measurements, and Infrared Absorption Measurements

Fluorescence depolarization was measured at 25°C on a Hitachi F-4500 spectrofluorometer. All the films containing NP were stuck on a holder with a circle hole whose diameter is 2.0 mm in order to irradiate the exact same part no matter how the film was rotated. Fluorescence measurements of films were carried out by placing the films on aluminum disks set in a holder shown in Fig. 3. Films were rotated by every 10° in the same plane whose center was at 60° to the exciting beam. In particular, in the case of the films stretched, the stretching direction was defined to be 0°. To measure NP polarized fluorescence, a Hitachi automatic polarizer was attached to a Hitachi F-4500 spectrofluorometer. Excitation wavelength was 280 nm. The I0 and I90 values were determined by averaging the polarized fluorescence intensities around 337 nm peak (16 points) measured repeatedly: two or three times each for one angle from 0 to 360° and again from 360 to 0°. Thus, the I0 and I90 values are the average of at least 64 data.

Infrared absorption spectra were measured on a Perkin Elmer SPECTRUM1000 FT-IR spectrophotometer with resolution of 1 cm^{-1}.

X-ray Diffraction Measurements

Wide-angle X-ray diffraction patterns were measured at room temperature using a Rigaku MicroMax7HFM, which was installed at Center for Instrumental Analysis of Shizuoka University, with a beam of CuKα radiation (λ = 0.15418 nm) that was finely focused by a confocal mirror and a collimator. The diffraction patterns were detected by a Rigaku R-axisIV++ and recorded on an

imaging plate. The data were analyzed by using FIT2D program, Diffraction intensities at constant 2θ shown in a diffraction pattern were obtained by the integration of all the diffraction intensities around the beam.

(Figure 10)

RESULTS AND DISCUSSION

Exposure of NP at Room Temperature to Stretched SPS Films

Fig. 10A shows the WAXD patterns of SL, which was obtained by stretching SPS films at $\lambda \approx 3$ and exposed to NP at room temperature. As expected, crystallization did not take place at all. However, we succeeded to demonstrate that the space for NP molecules able (or ready) to go into was distributed not uniformly but rather with a sort of orientation in these amorphous films by the stretching procedure. Fig. 10B shows the angular distributions of I0 and I90 of NP in SL. If all the NP molecules in the films were distributed isotropically, each value of I0 and I90 should be constant at any setting angles of the film. However, Fig. 10B demonstrates the angular distributions of I0 and I90 of NP are not isotropic but biased to some directions: the higher intensities of I0 appeared at 0, 90, 180, and 270º of the setting angle, while those of I90 appeared at 45, 135, 225, and 315º. The angle 0º indicates the direction of stretching the films. The patterns of angular distributions of I0 and I90 (Fig. 10B) were found to be identical with those of NP in APS that was stretched uniaxially (17). Thus, the orientation of NP molecules staying in polystyrene films that are stretched uniaxially beforehand is the same both in atactic and syndiotactic.

It is needless to say that all the NP molecules are in the amorphous area because no crystals were formed in SL. Since the stretching procedure of any SPS films was carried out at temperatures higher than Tg of SPS, the existence of cracks or voids is not probable. Even if there should be cracks or voids in SL and many NP molecules happen to settle there, their positions must be those shown in Fig. 9A (or Figs. 5A or 6A), so the experimental distributions of I0 and I90 can be a proof that most NP molecules do not enter and stay at the cracks produced during stretching films or a proof that the voids parallel to the stretching direction were not produced.

The orientation degrees of the molecules absorbed into a polymer film that was stretched uniaxially beforehand have been obtained using infrared and uv-visible absorption method (18). The long axis of an NP molecule in a stretched polyethylene film was shown to be preferably oriented along with the stretching direction by infrared linear dichroism measurement (19). The present PFR results (Fig. 10B) cannot be reproduced only by the assumption that the long axis of NP is parallel to the stretching direction (z // Z) (see some examples such as Figs. 5, 7, and 9). These angular distributions of I0 and I90 are considered to be the sum of some arrangements of NP molecules in drawn SPS films and to reflect the fact that NP molecules are located in an *amorphous* region with the selective orientation in SL.

The fluorescence intensities of NP are assumed to be proportional to concentration of NP. Thus,

the fraction of NP molecules that are distributed at random, f_{rdm}, and that are highly oriented towards some directions, f_{or}, can be discriminated from the angular distributions of I0 and I90, because the minimum values of I0 and I90 with regular orientation are considered to be 0. In the case of NP in SL shown in Fig. 10B, the isotropic intensities, namely the valley values of periodical changes, of I0 and I90 are ~0.715 and ~0.576, respectively, and the angular changes of I0 and I90 of the NP molecules that are distributed in an orientated area of the film are assumed to be between 1 and 0.715 for I0 and between 0.708 and 0.576 for I90. Thus, f_{or} can be estimated to be about 0.28 ($\approx$ (1-0.715)/1)) or 0.19 ($\approx$ (0.708-0.576)/ 0.708)) to first approximation.

The f_{or} obtained from I0 and I90 is 0.28 and 0.19, respectively, so, almost 24% (the average of 0.28 and 0.19) of all the NP molecules are considered to be in oriented positions.

The f_{or} obtained from I0 and I90 is found to be almost identical both in the cases of SL and APS (17): 0.28 and 0.19 for SL and 0.29 and 0.22 for an APS that was stretched at a draw ratio of $\lambda \approx 3$ and exposed by NP vapors at room temperature. Thus, almost 25% (the average of 0.28, 0.19, 0.29, and 0.22) of all the NP molecules are considered to be in oriented positions. Accordingly, the free space for vapor NP molecules to enter in a polystyrene film is concluded to be orientated in the same manner by stretching it uniaxially both in SPS and APS.

(Figure 11)

Exposure of NP at high temperatures to Stretched SPS Films: Monitored by the WAXD

We tried to study on the crystallization process of SPS when stretched SPS films were exposed to vapors of NP at high temperatures. Since the molecular size of NP is not too small, the crystallization process could be different from the case where SPS films are exposed to small molecules such as CS_2. Fig. 11 shows the WAXD pattern of SH: it was prepared by stretching SPS films at $\lambda \approx 3$ and exposed to NP at 80°C. Fig. 11 clearly shows that the oriented crystallization of SPS is highly developed under this condition. The diffraction intensity, which is integrated from the meridian to the equator, is shown in Fig.13.

The X ray diffraction pattern of SH was found to be identical with that of SPS/NP clathrate cocrystal that have been already reported (6). The peaks shown in Fig. 13 were observed at $2\theta \approx 7.9$ (P1), 10.5 (P2), 17.1 (P3), 19.8, 23.0, and 28.8° for Cu Kα radiation. They are typical of SPS clathrate crystalline form (6, 20-22), which is monoclinic, and correspond to 010, $\bar{2}$10, 111, $\bar{3}$21/301, $\bar{4}$11/$\bar{4}$21, and 302/322, respectively. Accordingly, SPS/NP clathrate cocrystals were formed definitely by the exposure of NP vapors to stretched SPS films at 80°C.

Next, we examined the crystallization process of drawn SPS films under the mild conditions at 60°C. Fig. 12 shows the change of the WAXD pattern with the exposure time of NP vapors to stretched SPS films at 60°C. It is quite clear that the oriented crystallizaion of SPS took place by the exposure of NP vapors at 60ºC for 120 hrs. However, up to 12 hrs, the crystallization was difficult to be monitored by WAXD measurements.

(Figure 12)

(Figure 13)

Under the mild condition, the efficiency of crystallization appears to be quite low, but the X-ray diffraction pattern observed for S120 shown in Fig. 13 present peaks at $2\theta \approx 7.9$ (P1), 10.5 (P2), and 17.1º (P3) for Cu Kα radiation. As described above, these three peaks correspond to the typical ones of SPS/NP clathrate cocrystal. Thus, it is obvious that the small amount of δ clathrate form was produced by exposure of NP vapor at 60ºC. However, Fig. 13 indicates that no trace of P1, P2, and P3 was observed for S3 to S48, although the peak around 20º was sharpened and shifted to wider angles gradually with exposure time.

According to Petraccone et al. (23), two peaks at $2\theta \approx 12.2$ and 20.9º observed in Fig. 13 (S3 to S48) can be assigned to a trans planar mesomorphic form (23-25). The WAXD peaks of SPS unoriented amorphous samples were reported to change with an increase in annealing temperatures: the peaks corresponding to a trans planar mesomorphic form appeared at 130ºC, then this mesomorphic phase changed to SPS α crystalline form consisting of trans zigzag conformation by annealing at higher temperatures than 140ºC (23). Although Manfredi et al. (26) showed that SPS δ empty form can be transformed into another mesomorphic form retaining the chains in the helical conformation, the WAXD peaks of this "helical" mesomorphic form appeared at $2\theta \approx 10$ and 19.5º, which are different from ours.

Torres et al. have clarified that two infrared absorption peaks at 1223 and 571 cm^{-1} of SPS solids correspond to the trans planar (27) and 2_1 helical (28) phases, respectively, because the detection of these absorption bands does not require a long range order of polymer chains like WAXD technique. We measured infrared absorption spectra of Sn films and observed sharp absorption peaks not only at 1223 cm^{-1} but also at 571 cm^{-1} for S120. Thus, S120 turned out to consist of a trans planar mesomorphic form and SPS/NP δ clathrate cocrystalline form as was already shown by the WAXD data. Finally the exposure of NP molecules at 60ºC was found to be almost equal to the annealing at higher than Tg as for the procedure of producing trans planar phases.

In summary, the X-ray diffraction measurements clearly showed that (i) the exposure of NP vapor to stretched SPS films at 60ºC induced the oriented crystallization in the end but the crystallization is quite vague even after the exposure of NP vapors for 48 hrs (no trace before 12 hours at all) and (ii) the main WAXD diffracrion peaks observed for S3 to S120 are due to SPS trans planar mesomorphic form although there is a small quantity of SPS/NP clathrate form in S120. In any rate, information could not be obtained much at the initial stage of this crystallization process up to 48 hrs by the X-ray diffraction because no significant change was observed. Thus, we tried to measure the change of PFR under the mild condition where drawn SPS films were exposed to NP vapors at 60°C.

(Figure 14)

Exposure of NP at high temperatures to Stretched SPS Films: Monitored by the PFR

We monitored the exposure time dependence of the SPS stretched films by measuring the angular distributions of I0 and I90 of NP in each film (Fig. 14). After the procedure of NP exposure to the SPS films, all the films were dried under vacuum at 40ºC for 3 days in order to get rid of the NP molecules staying on the film surfaces or the voids of the films if they happened to have. The angular patterns of I0 and I90 were found to change with the exposure time. The important change of I0 is from a pattern with 4 peaks at 0, 90, 180, and 270º, which is typical of the pattern in the stretched amorphous area, to another pattern with 2 peaks at 90 and 270º, while the change of I90 is from a pattern with 4 peaks at 45, 135, 225, and 315º to another pattern with 2 peaks at 0 and 180º. The gradual changes of I0 and I90 are easy to be recognized to monitor the values at 0 and 180º. Up to S48, the contents of NP in the films were low, though they are uneven. The NP content of S120 is found to be 8.0%.

Fig. 14 suggests the followings: (i) our polarized fluorescence method (PFR) is more sensitive than the WAXD method, so we can get the information on the change of structure at the initial stage when no changes were observed in the X-ray diffraction patterns, (ii) the change of I0 and I90 is concluded to take place by one simple process (it is not a complicated process at least): that is to say, a component of I0 whose peak is at 0 and 180º decreases monotonously with the exposure time, while a component of I90 whose peak is at 0 and 180º increases monotonously.

(Figure 15)

The experimental results obtained by using SPS films stretched at different drawing ratios supports the above summary. Fig. 15 shows the WAXD patterns and the angular distributions of I0 and I90 of NP in SX4 and SX5, which were obtained by stretching amorphous SPS films at $\lambda \approx 4$ and 5, respectively, and by the exposure of NP vapors at 60ºC for 3 hrs. As compared with S3 (SPS films drawn at $\lambda \approx 3$ and exposed by NP vapors at 60ºC for 3 hrs), the change turns out to be so rapid in spite of the exposure of NP vapors only for 3 hrs. The angular distributions of I0 and I90 for SX4 and SX5 observed in Fig. 15 are as same as that of S6, exposure for 6 hrs, and S12, exposure for 12 hrs, in Fig. 14. This reduction in exposure time to induce changes would be due to SPS chains being oriented much more when the films were stretched at higher λ.

The fraction of NP molecules that are distributed at random, f_{rdm}, and that are highly oriented towards some directions, f_{or}, can be discriminated from the angular distributions of I0 and I90, because the minimum values of I0 and I90 with regular orientation are considered to be 0. In the case of NP in S120 shown in Fig. 14E, the isotropic fractions, namely the valley values of periodical changes, of I0 and I90 are ~0.754 and ~0.654, respectively. Finally, f_{or} can be estimated to be about 0.25 for I0 or 0.25 for I90. Thus, 25% of all the NP molecules are considered to be in oriented positions. This is the nearly same fraction of the NP molecules staying in the oriented

region in SL, namely drawn SPS exposed by NP vapors at room temperature, obtained by Fig. 10. It is quite obvious that the crystallinity of S120 estimated from Figs. 12 and 13 is not expected to be as high as 25%, because the peaks at 7.9 10.5, 17.1, 19.8, and 28.8° corresponding to SPS/NP clathrate cocrystals are quite weak compared with the WAXD pattern of SH. Because the content of NP in S120 is 8.0%, the pattern of Fig. 14E is considered to be not the pattern of SPS/NP clathrate cocrystals but rather that of NP molecules in the amorphous region. The WAXD pattern has shown that the main form of SPS is of trans planar mesomorphic phase. The position of NP molecules should have been influenced by the formation of trans planar mesomorphic phase.

In order to observe whether structural changes occur in S120 by annealing, the S120 film was annealed under vacuum at 60ºC and measured with WAXD and PFR methods every 12 hrs. No changes were observed for 48 hrs. After this procedure, the S120 film was annealed under vacuum at 80°C for 120 hrs. However, no changes were found in the WAXD pattern and the PFR pattern.

These results indicate that (i) the crystallization observed in SH is due to the active motion of NP vapors at 80°C, (ii) the annealing at 80°C is not enough to induce the crystallization of SPS α crystalline form consisting of trans zigzag conformation, because the trans planar mesomorphic form is stable at 80°C, and (iii) the PFR pattern of S120 is of the NP molecules staying in the amorphous region that stepped aside from the oriented mesomorphic phase, resulting that they are also oriented.

The result (ii) is consistent with the experimental results by Petraccone et al. (23), showing that the SPS trans planar mesomorphic form does not change by annealing below 140°C. As for the result (iii), the NP molecules remained in the film even after drying under vacuum at 80°C, so they are considered to have a stable structure in S120. Then, we tried to reproduce the angular distributions of I0 and I90 of NP in S120 in order to determine the position of an NP molecule in the amorphous region coexisting the trans planar mesomorphic form.

(Figure 16)

Fitting of the angular distributions of I0 and I90 of NP in S120

We can calculate the angular distributions of polarized fluorescence intensities in conformity with a theory mentioned before. In our previous papers (7,8,17), we succeeded to determine the perfect arrangement of a guest NP molecule: in particular, we determined the orientation of the NP guest molecule in SPS/NP cocrystals with respect to the axes of the cocrystal unit-cell: angles formed by the short and the long axes of NP with the *c* axis are not far from 80° while the angle between the short axis of NP and the *a* axis is nearly 105° (7). Now is not the case where there was one guest molecule in a cocrystalline unit-cell and almost all the guest molecules had nearly the same orientation all over the film. However, following to our previous papers, we tried to reproduce the angular distributions of I0 and I90 shown in Fig. 14E.

The method is as follows: first, we defined three parameters, *sZ*, *lZ* and *sY*, which are the angles between the short (*s*) and long (*l*) axes of the NP guest molecule with the Z-axis and Y-axis (Fig. 3): Z-axis is the stretching direction of host polymer and Y-axis is perpendicular to Z-axis on film surface plane. We have changed the values of these three angles one by one by every 1° from 0° to 180°, and calculated each I0 and I90. Here the direction of Y-axis perpendicular to Z-axis, namely the stretching direction, can be +90° or -90° against the stretching direction of the film. Thus the I0 and I90 were obtained by averaging the calculated values for both cases. We assessed the validity of the trial fitting by minimizing the sum of the variance.

We could find the theoretical distributions of I0 and I90 that reproduced experimental values relatively well (Fig. 16): the best fitting of I0 and I90 can be obtained for *sZ* = 79º, *lZ* = 167º, and *sY* = 19º. This is the position of an NP molecule against the Z-axis, namely the direction of SPS polymer chains. Because the rotation of SPS chains around Z-axis is not fixed, the simulated positions of NP molecules in S120 were shown as in Fig. 16B. In the case of SPS/NP clathrate cocrystals, *sZ* and *lZ* are 80º, therefore *lZ* of S120 was found to be perpendicular to the case of NP in SPS/NP clathrate crystals. Thus, it is needless to say but most NP molecules of 8% are not clathrated in SPS cocrystals but are oriented in the amorphous region. rather enter between side-chain phenyl groups with an inclination of 79º against the stretching direction, namely the direction of the SPS polymer chains.

The fluorescence spectrum of S120 was found to consist of monomeric fluorescence of NP without its excimer fluorescence. It is quite reasonable because many NP molecules are separated between side-chain phenyl groups of SPS chains as shown in Fig. 16B.

Initial Process of Structural Change of SPS by Exposure of NP vapors at 60ºC

Here let us examine the initial process of structural change of stretched SPS films induced by the exposure of NP vapors at 60ºC. Although the X-ray diffraction measurements could not monitor any change at all during the initial stage up to 12 hrs (S12), the distributions and/or positions of NP molecules following structural change of SPS were found to change even after the exposure of NP for 3 hours by our PFR method.

The results so far can be summarized as follows: (i) the change of I0 and I90 of our PFR method is concluded to take place by one reaction process, (ii) the final stable position of NP molecules in the amorphous region is well simulated by Fig. 16A, and (iii) the exposure of NP molecules to stretched SPS films at 60ºC mainly produced the SPS trans planar mesomorphic phase though it happened to produce just a small amount of SPS/NP δ clathrate cocrystal: no SPS α crystalline form was not produced under this condition.

Since the exposure of NP molecules to stretched SPS films at 80ºC was ascertained to produce SPS/NP δ clathrate cocrystal, the motion of NP vapor at 60ºC is thought to be a bit weak that NP

molecules cannot go into space between SPS chains so much. Many SPS chains are considered to be lining to the parallel direction with the Z axis in Fig. 3. Thus, we assume that the formation of 2_1-helical form of SPS chain would be induced efficiently by the collision of NP molecules from the perpendicular direction of the SPS polymer chain (c axis), namely the Z axis in Fig. 3, and by their entering the free space between side-chain phenyl groups of SPS chain. This assumption corresponds to the position of an NP molecule shown in Fig. 8. If NP molecules stay in the film with the same arrangements as those at their collision with SPS, the angular distributions of I0 and I90 should be the same as Fig. 8B. In Fig. 14, the experimental I0 value at 180º was decreasing with an increase in exposure time of NP vapors. However, the simulated result of Fig. 8 shows that I0 should have the maximum intensity at 180º. Thus, the exposure of NP vapors at 60ºC does not produce the structure shown in Fig. 8, indicating that the NP motion of producing 2_1-helical form of SPS chains or SPS/NP δ clathrate cocrystals was limited so much. However, this motion is considered to be powerful enough to orientate trans zigzag conformation of SPS chains along with the stretching direction of the film: usually a trans planar mesomorphic phase appeared at 130ºC when an SPS film was annealed. Therefore, the motion of NP molecules at 60ºC can be summarized that it can urge SPS chains to form trans zigzag conformation, which is the most stable conformation, but cannot enter deeply so as to be clathrated by SPS chains. Consequently, NP molecules are considered to settle down in the SPS amorphous region so as to avoid a trans planar mesomorphic phase: the direction of an NP molecule is relatively parallel to the stretching direction (the Z axis), namely SPS polymer chain. It is quite interesting but the excimer fluorescence was not observed for S120 in spite of high content of NP molecules, suggesting that each NP molecule is isolated by side-chain phenyl groups of SPS.

CONCLUSIONS

We applied Nishijima's method (1, 2) to the clarification of the crystallization process of SPS induced by the exposure of NP vapors at high temperatures. Angular distributions of I0 and I90, intensities of polarized fluorescence, were strongly dependent on the preparation procedure of the films.

In the case of SPS films that were stretched uniaxially and exposed to NP vapors at room temperature, no crystallization occurred at all but the present PFR method clarified that the space for NP molecules able to go into was distributed not uniformly but rather with a sort of orientation in these amorphous films by the stretching procedure. This orientation cannot be obviously monitored by the X-ray diffraction patterns. The distributions of the free space produced by the stretching procedure will be discussed in detail in our future work.

The oriented crystallization was ascertained by the exposure of NP to stretched SPS films at higher temperatures. The NP molecules were clathrated in SPS films in the case of the exposure at

80°C. It is reasonable that a clathrate compound of SPS with NP is formed and leads the crystallization process, because there exists free volume for an NP molecule to enter and stay among SPS chains aggregated even in a gel form (29, 30) and the formation of a polymer-solvent molecular compound, namely a molecular compound between a styrene unit and NP, starts with the formation of fibril structure growing up to a three-dimensional network in a gel system of SPS/NP (31, 32). The cocrystals of SPS/NP are considered to grow up by these SPS chains with NP lining together due to the violent motion of NP vapors.

However, the exposure of NP vapors at 60°C is not enough to produce a perfect SPS/NP clathrate cocrystalline structure, although it was produced with just a small amount. We examined the structural change of stretched SPS films induced by the exposure of NP vapors at 60ºC by the PFR method. Although the X-ray diffraction measurements could not monitor at all, the crystallization or the reaction of forming a mesomorphic structure of SPS with NP (Fig. 16B) were found to proceed even after the exposure of NP for 3 hours. The formation of a trans planar mesomorphic phase was already reported (23-25) but we have succeeded to show the detail of this amorphous region where most NP molecules being absorbed in SPS are staying with an oriented arrangement. The main arrangements of NP molecules in these SPS films such as S120 are first clarified to be shown as Fig. 16 B by PFR method.

In any rate, we have shown the efficiency of our PFR method in the present paper. We really hope that the PFR method can be used more generally as an analysis method to know the orientation of a crystalline form, polymer chains and/or guest molecules in a film.

ACKNOWLEDGMENTS

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TABLE 1. Characterization of the SPS films used.

sample	thickness, μm	content of NP[a], %	temperature of exposure, °C	exposure time, hrs	drawing ratio
SL	113	0.8	23	120	3.0
S3	138	0.1	60	3	3.0
S6	129	0.1	60	6	3.0
S12	138	0.6	60	12	3.0
S48	146	0.3	60	48	3.0
S120	139	8.0	60	120	3.0
SH	58	13.3	80	120	3.0
SX4	103	0.1	60	3	4.0
SX5	105	0.1	60	3	5.0

[a] determined by TG.
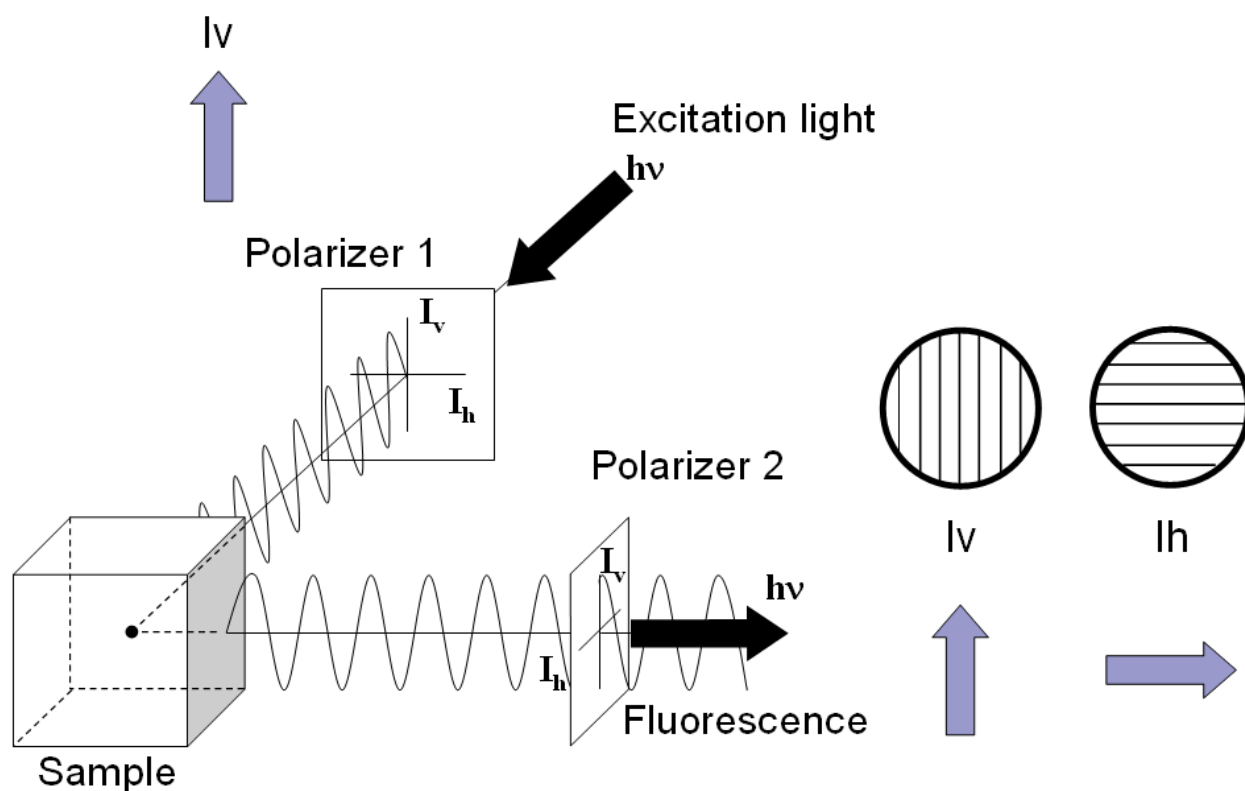
FIGURE 1   Sketch of polarized fluorescence measurements. Iv and Ih are vectors of electric field for the polarized light selected by a polarizer. Polarizer 1 is set as to choose a polarized light whose vector of electric field is Iv as the excitation light, while polarizer 2 are automatically set to be either parallel or vertical to polarizer 1.
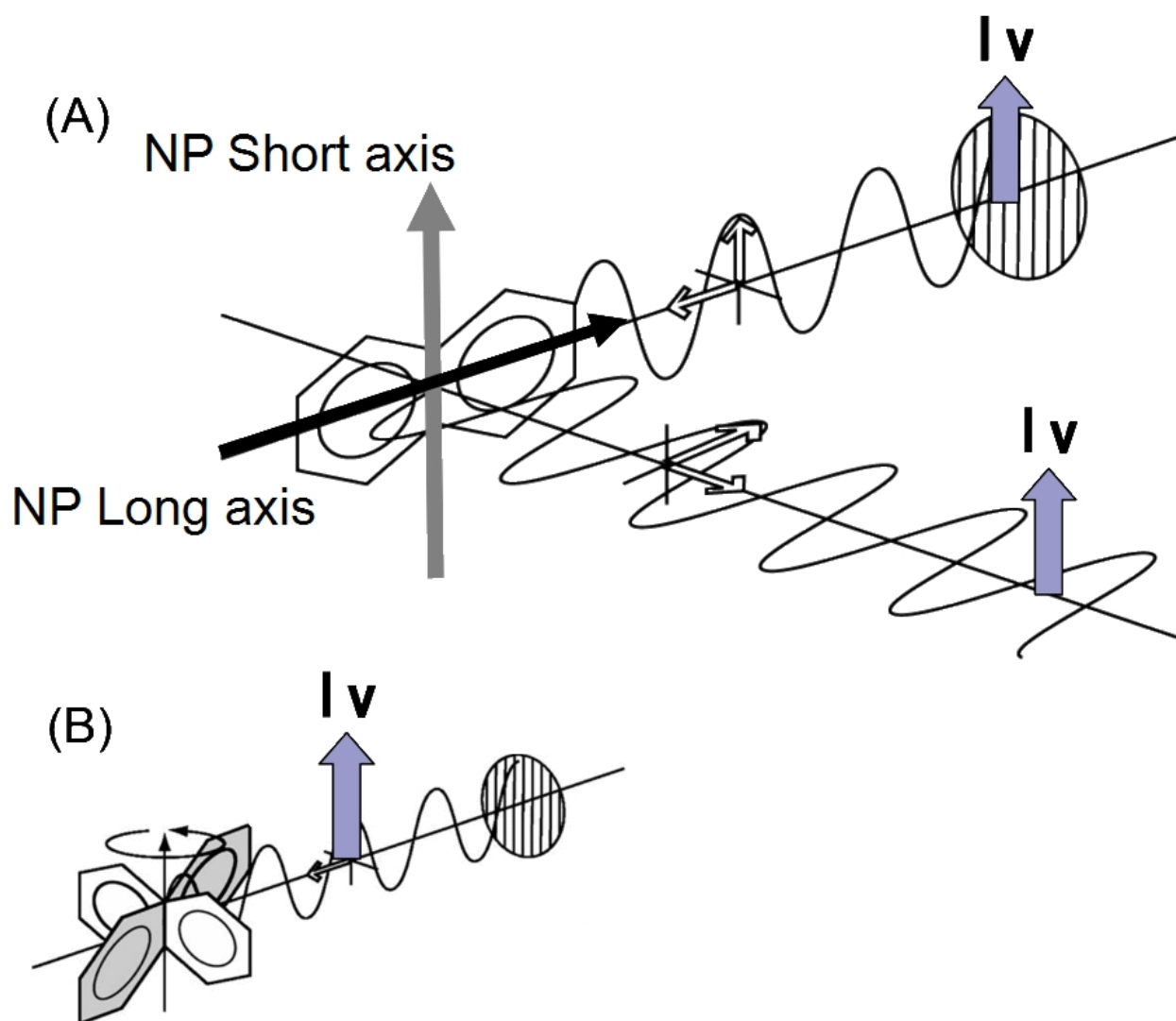
FIGURE 2   Sketch of absorption and fluorescence of naphthalene (NP). Transition moment of NP, 1 $^1B_{1u}$, to absorb 280-nm light is parallel to the short axis of NP, while transition moment of NP, 1 $^1B_{2u}$, of fluorescence is parallel to the long axis of NP. If an NP molecule has an arrangement against Iv shown in (A), I0 is 0 and I90 has a maximum value. All the NP molecules whose short axes are parallel to Iv can absorb the polarized light most shown in (B).
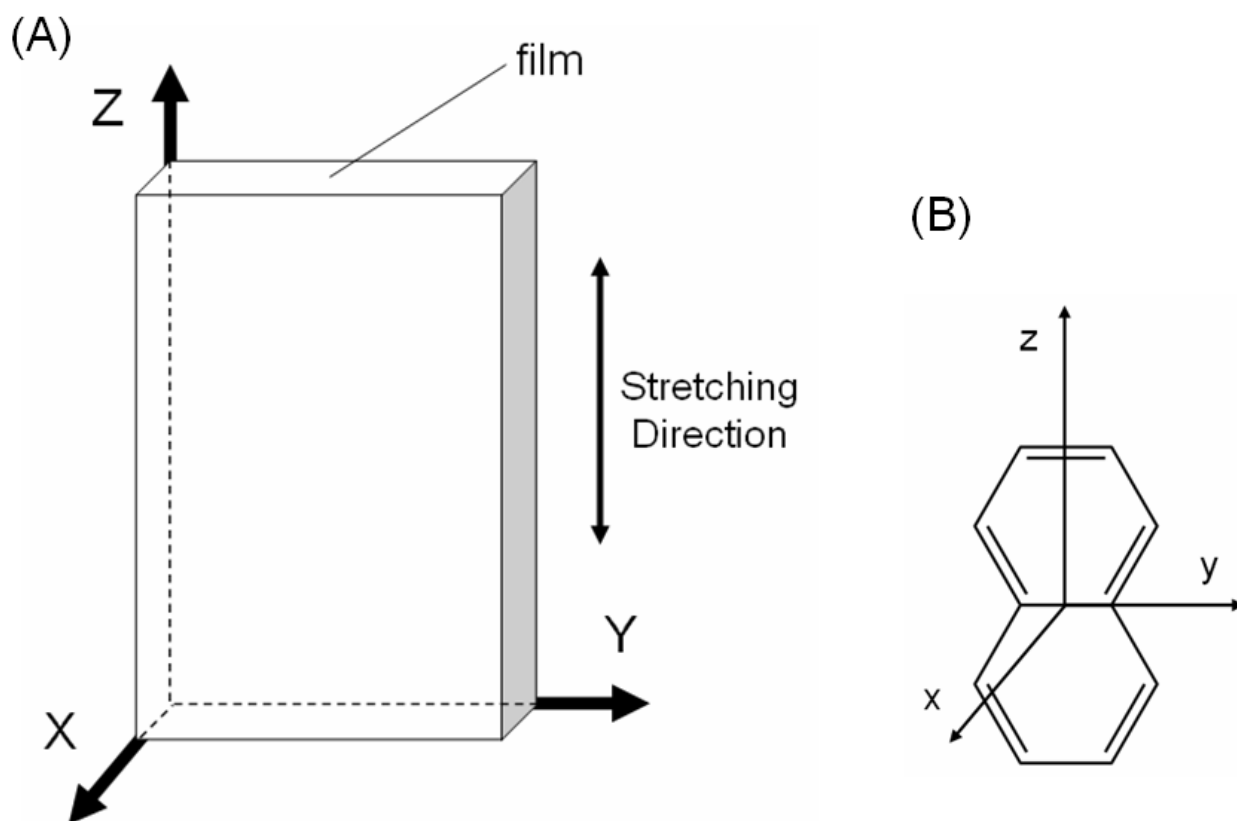
FIGURE 3   (A) is the rectangular coordinate system of an SPS film: the X-axis and the Z-axis are the same as the directions of the thickness and the stretching, respectively. (B) is the rectangular coordinate system of an NP molecule: the y-axis and the z-axis are parallel to the short axis and long axis of NP, respectively.
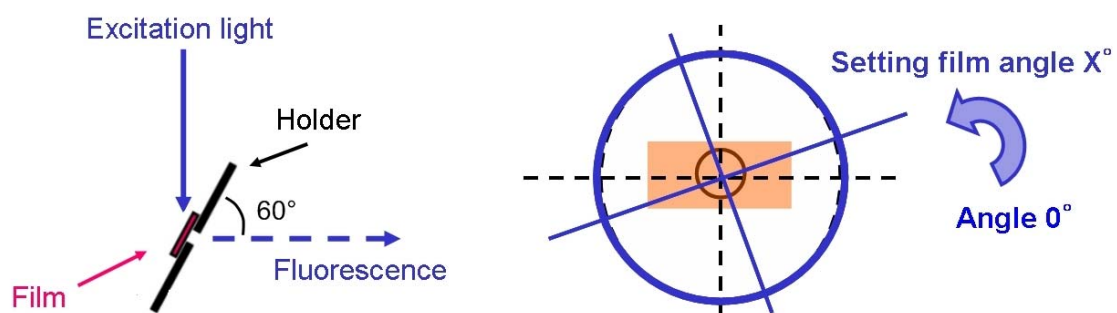
FIGURE 4   Setting way of sample films for the measurements of polarized fluorescence together with the definition of setting film angle. The stretching direction is set to be 0°.
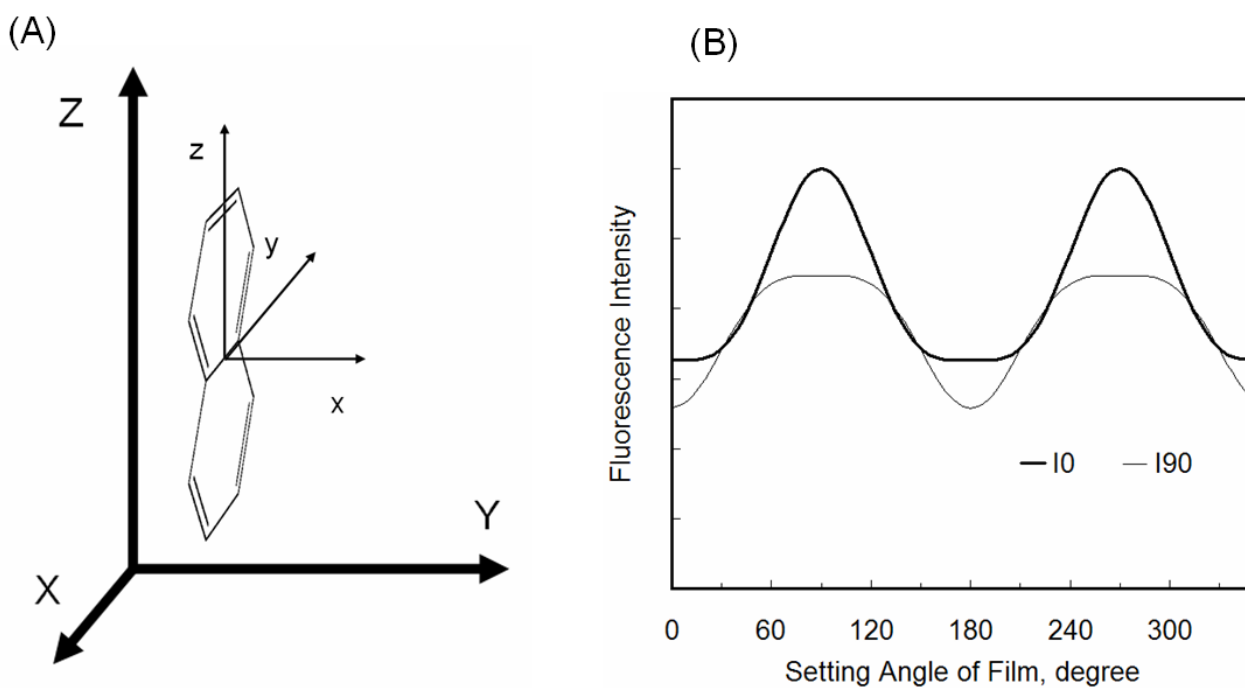
FIGURE 5   (A) is a simulated position of NP molecules in an SPS film. In (A), all the NP molecules have a single arrangement that y//X and z//Z. (B) is the angular distributions of I0 and I90 of NP when NP molecules are located as in (A).
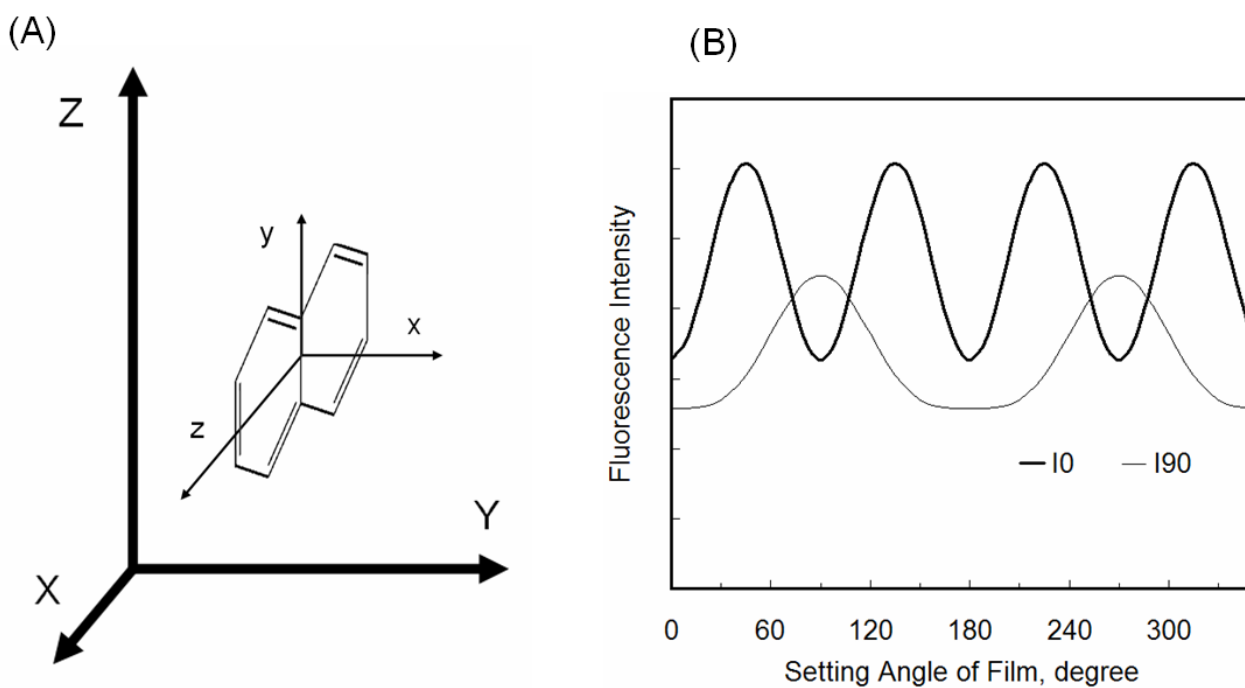
FIGURE 6   (A) is a simulated position of NP molecules in an SPS film. In (A), all the NP molecules have a single arrangement that z//X and y//Z. (B) is the angular distributions of I0 and I90 of NP when NP molecules are located as in (A).
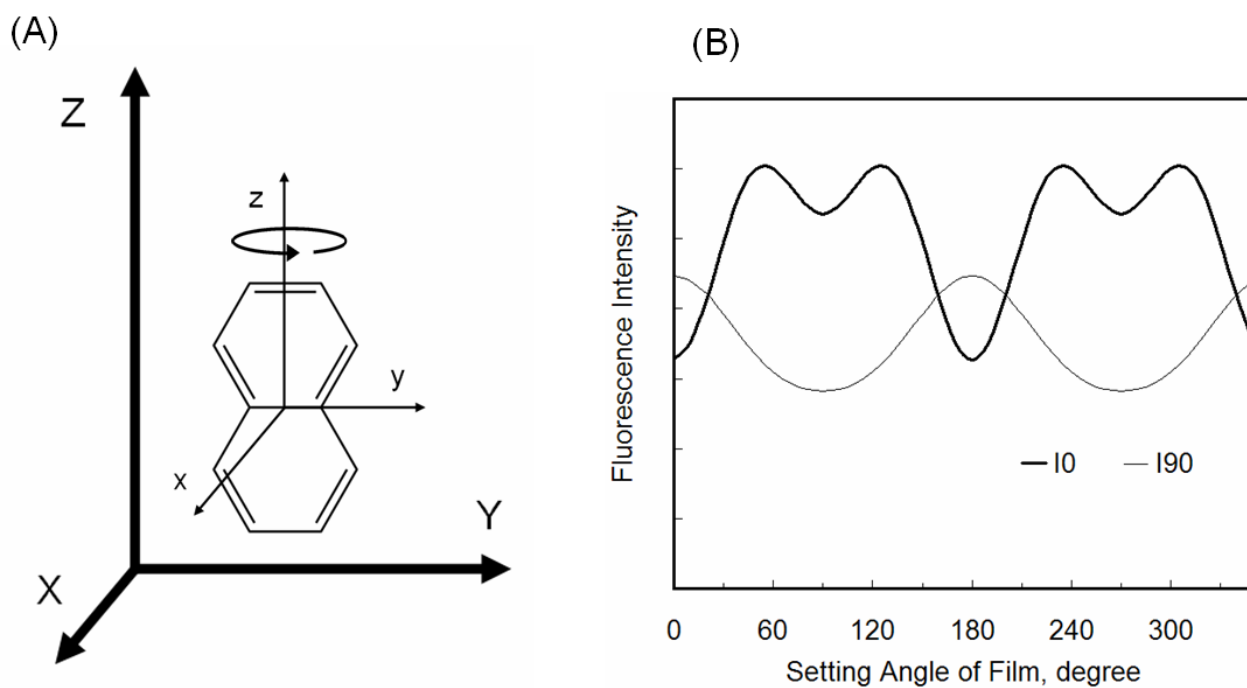
FIGURE 7   (A) is simulated positions of NP molecules in an SPS film where z//Z but the angle between the short axis of an NP molecule and the stretching direction is not fixed. (B) is the angular distributions of I0 and I90 of NP when NP molecules are located as in (A).
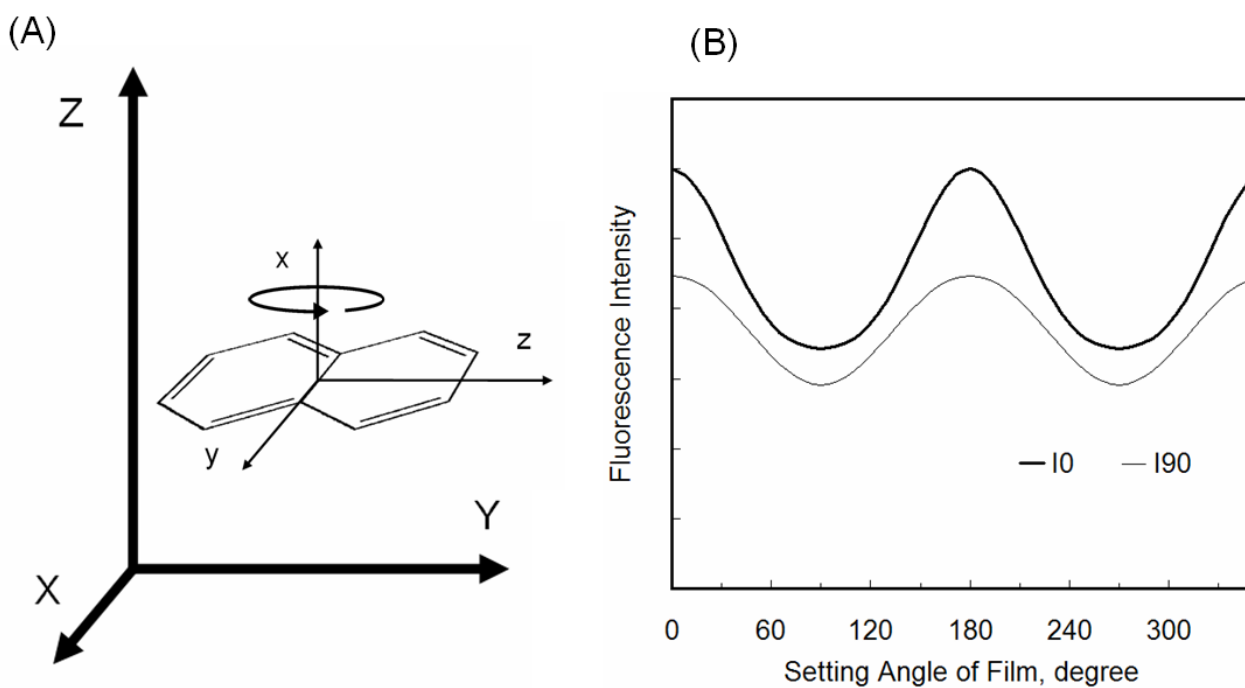
FIGURE 8   (A) is a simulated position of NP molecules in an SPS film: All the NP molecules have the arrangement that their planes are perpendicular to the stretching direction (x//Z). (B) is the angular distributions of I0 and I90 of NP when NP molecules are located as in (A).

(A)

(B)
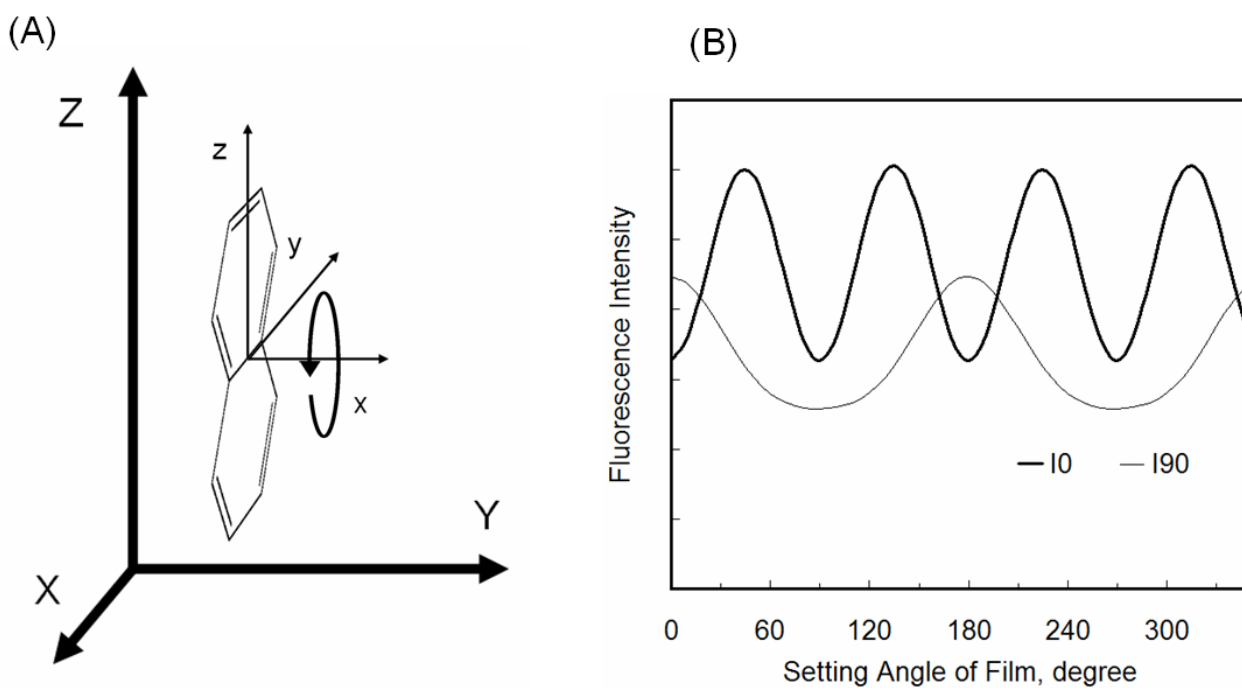
FIGURE 9   (A) is simulated positions of NP molecules in an SPS film. All the NP molecules have the arrangement that their planes are parallel to the stretching direction (x//Y). (B) is the angular distributions of I0 and I90 of NP when NP molecules are located as in (A).
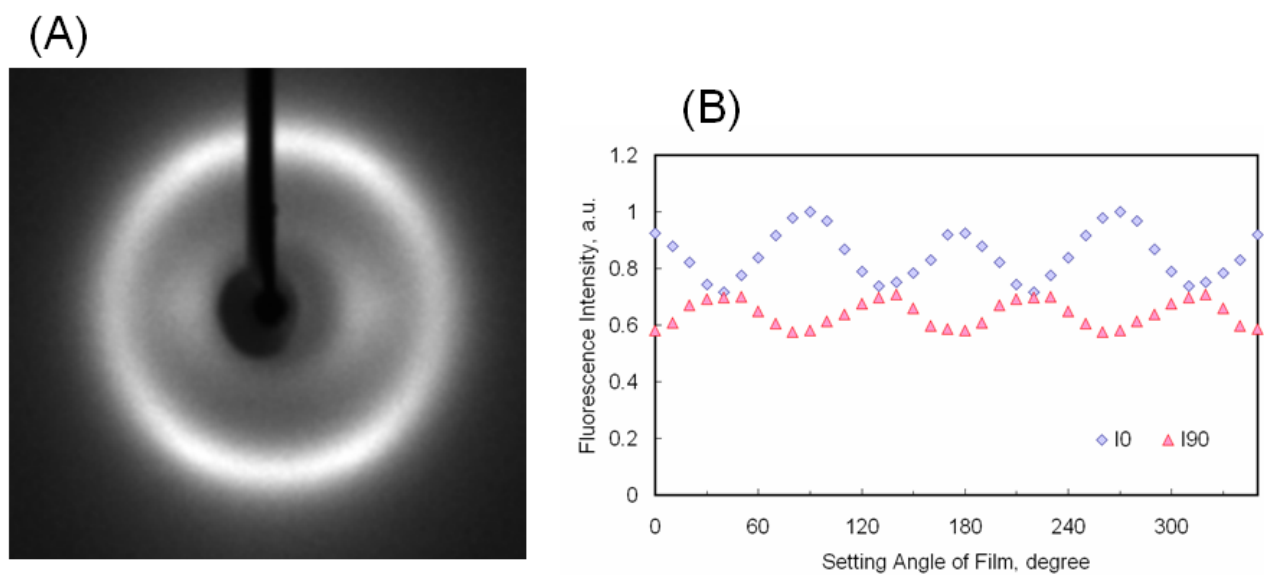
FIGURE 10   (A) X-ray diffraction patterns and (B) angular distributions of I0 (◆) and I90 (▲) of NP in SL. The excitation wavelength of (B) was 280 nm.
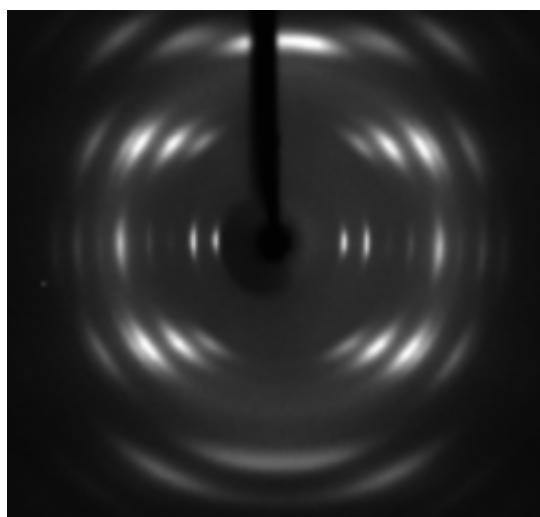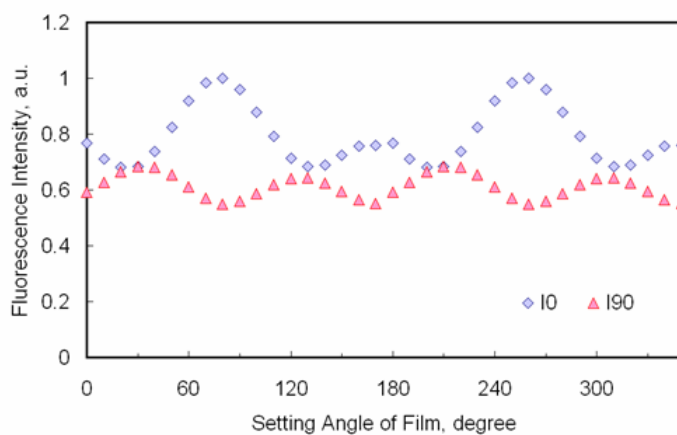
FIGURE 11   X-ray diffraction patterns of SH.
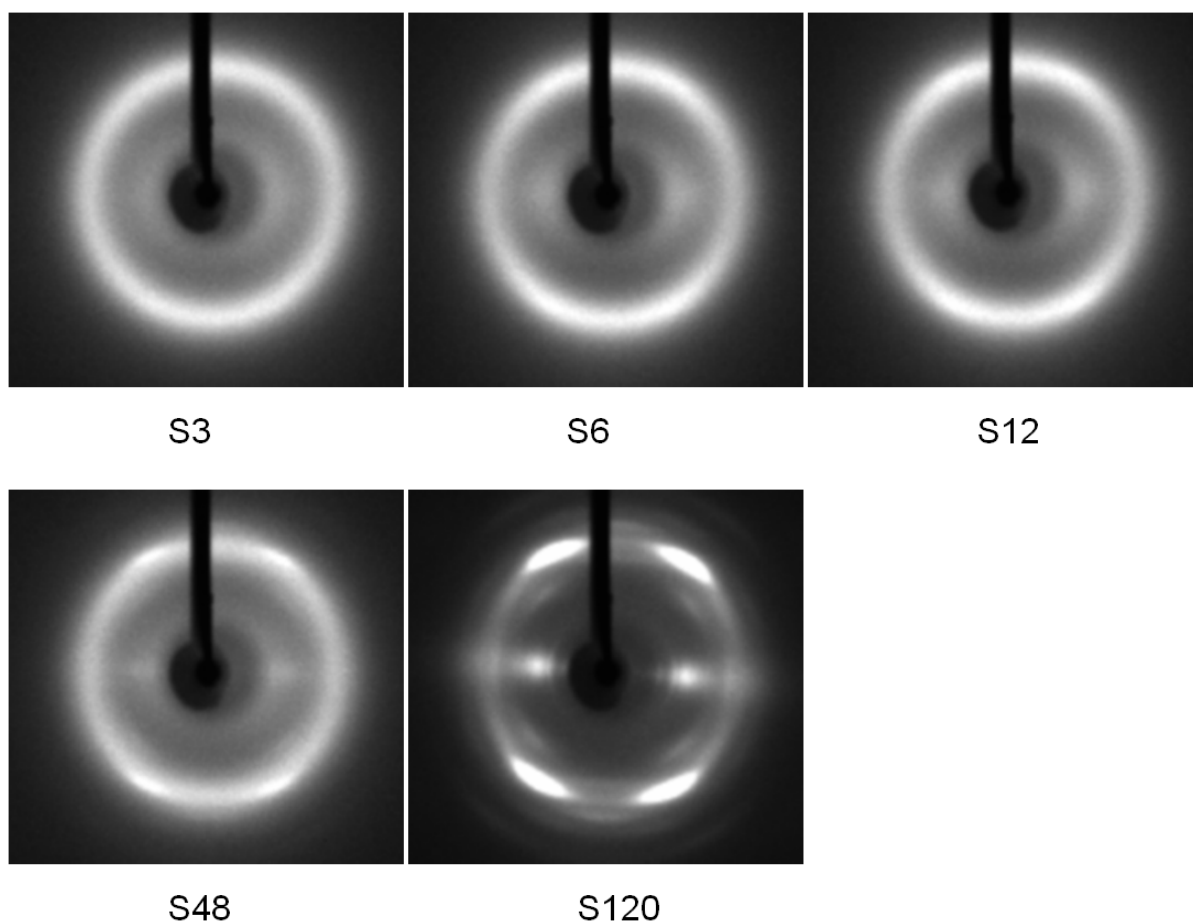
FIGURE 12   Exposure Time dependence of NP vapor to stretched SPS films (at $\lambda \approx 3$) on the oriented crystallization at 60ºC: n of Sn shows the exposure time of NP vapor to stretched SPS films in hrs. All the X-ray diffraction patterns were obtained under the same experimental conditions.
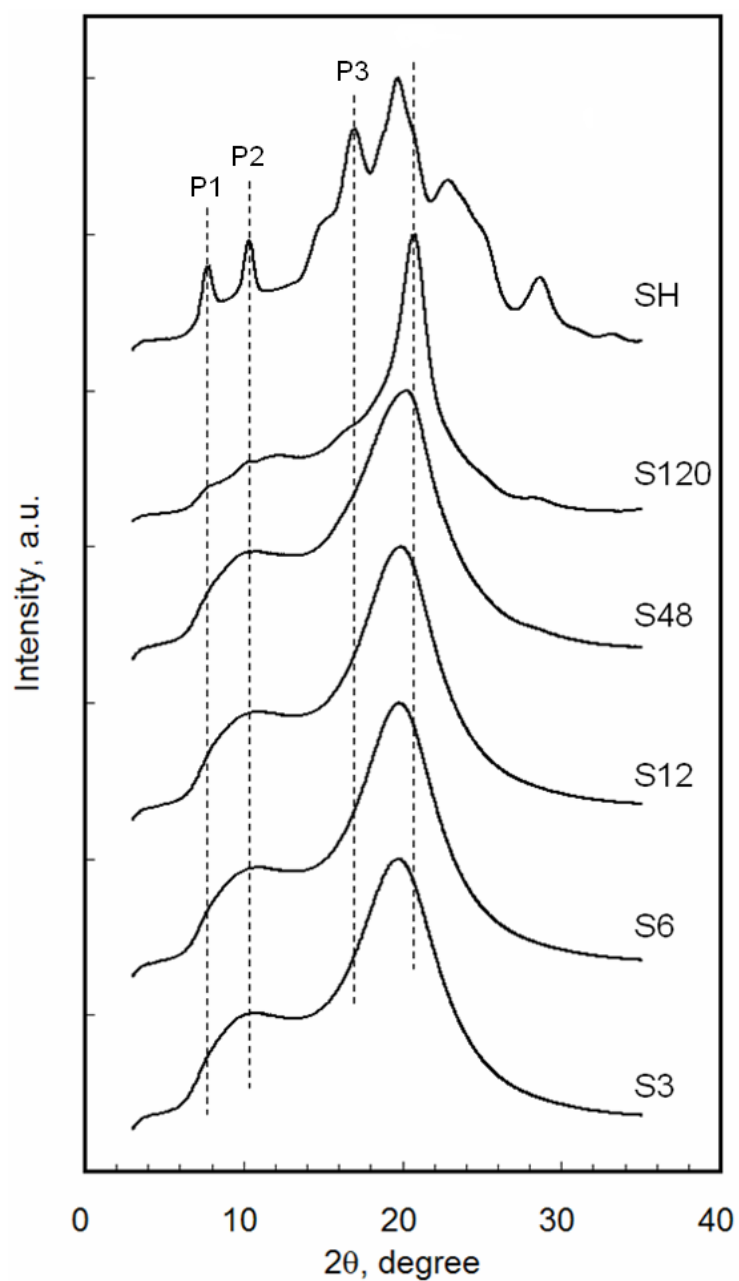
FIGURE 13   X-ray diffraction patterns (Cu Kα) of stretched SPS films (at λ ≈ 3) that were exposed of NP vapor at 80ºC for 120 hrs (SH) and at 60ºC for different hours (S3-S120).
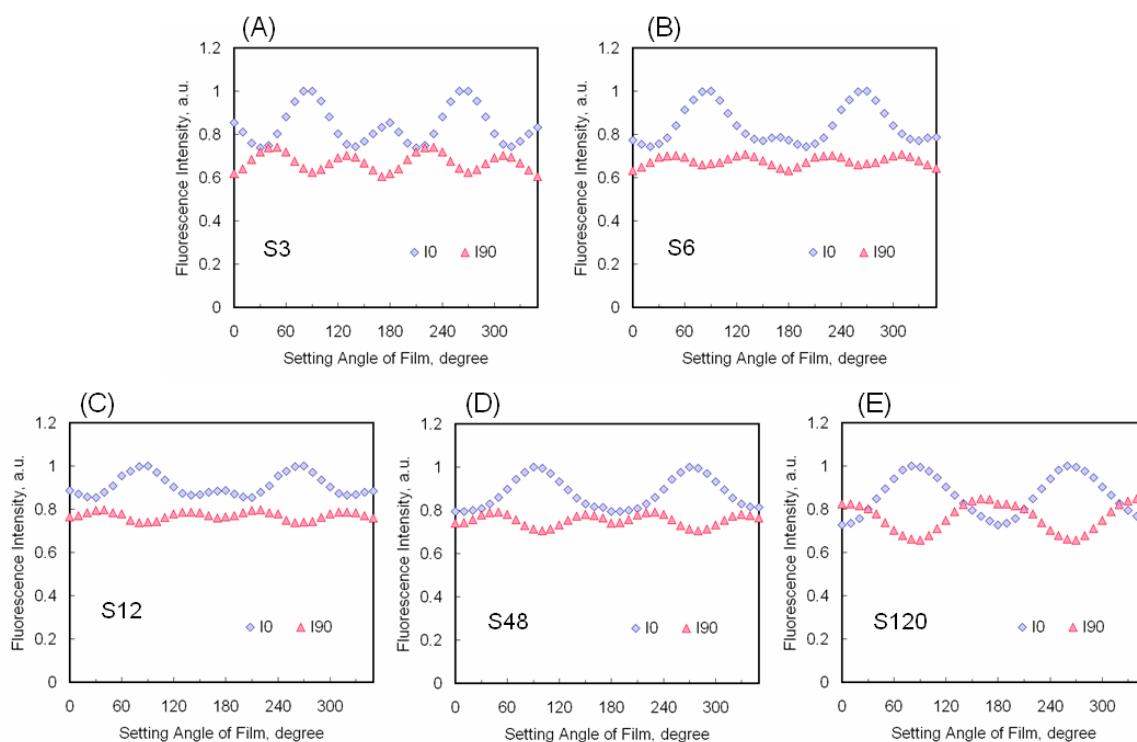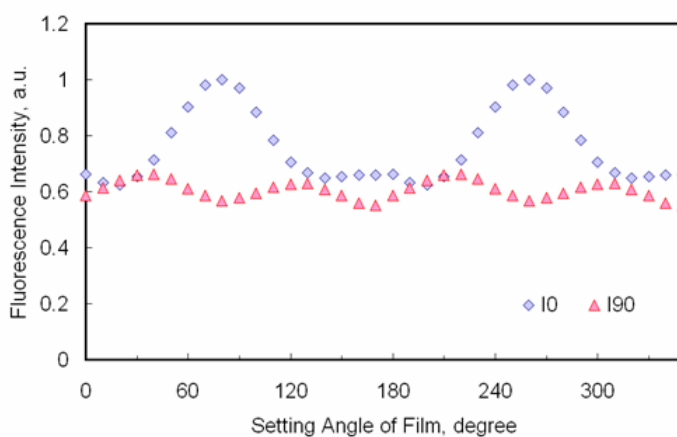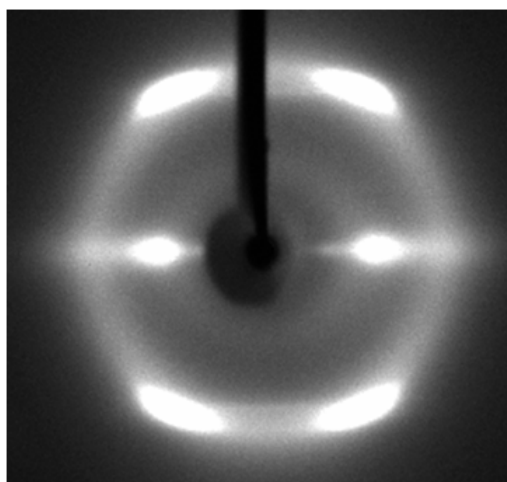
FIGURE 14   Exposure time dependence of NP vapor to stretched SPS films (at λ ≈ 3) on angular distributions of I0 (◆) and I90 (▲) of NP: n of Sn shows the exposure time of NP vapor to stretched SPS films in hrs. All the values of I0 and I90 for each exposure time were normalized to the peak intensity of I0. The excitation wavelength was 280 nm.
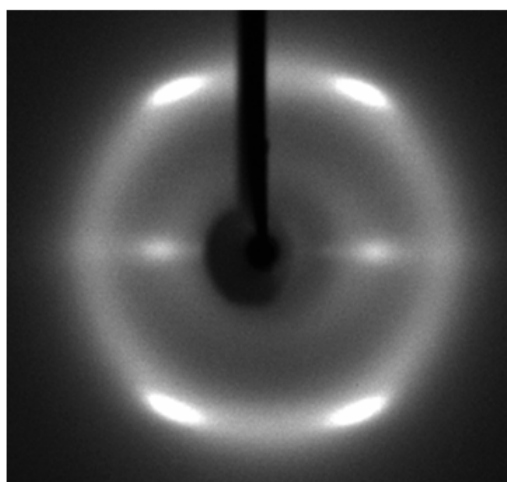
SX4

SX5

FIGURE 15   Drawing ratio dependence of the X-ray diffraction pattern and angular distributions of I0 (◆) and I90 (▲) of NP of SX4 and SX5, which were stretched at $\lambda \approx 4$ and 5 then exposed by NP vapor for 3 hrs. All the values of I0 and I90 for each exposure time were normalized to the peak intensity of I0. The excitation wavelength was 280 nm.
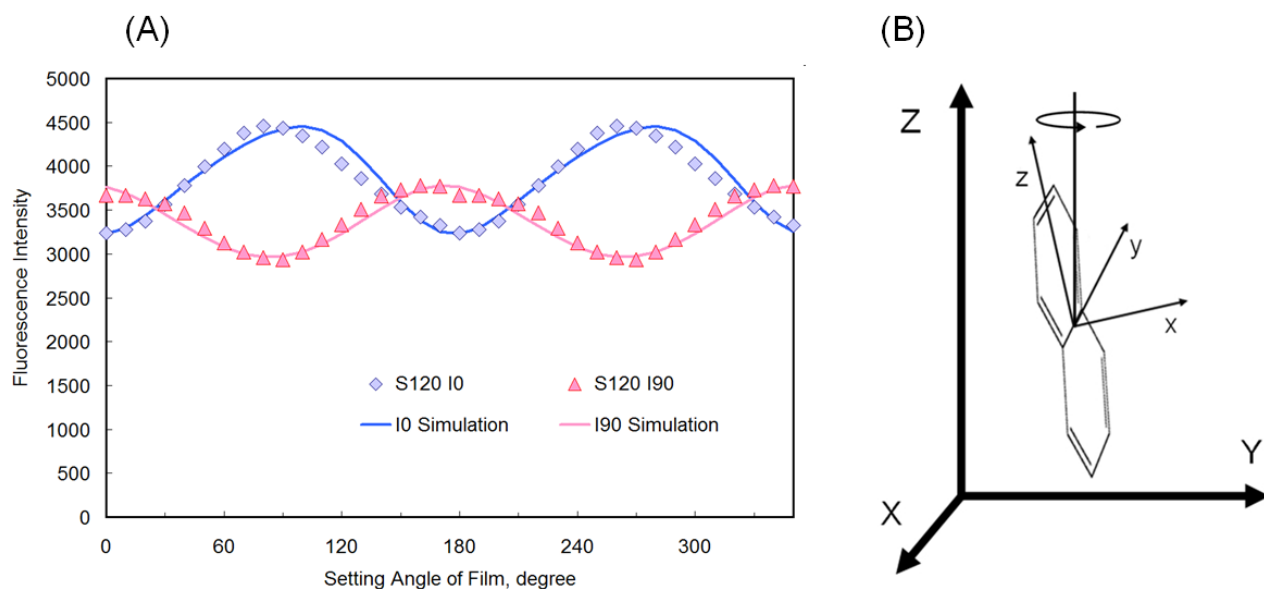
(A)

(B)

FIGURE 16   (A) Angular distributions of I0 (◆) and I90 (▲) of NP in S120, and the solid lines show the fitting curves of I0 and I90 obtained for $sZ = 79°$, $lZ = 167°$, and $sY = 19°$. (B) The simulated positions of NP molecules in an SPS film to reproduce the angular distributions of I0 and I90 of NP shown in (A).