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Description	

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Anomalous molecular orientation of polypropylene sheet containing *N,N'*-dicyclohexyl-2,6-naphthalene dicarboxamide

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Abstract: Small amount of *N,N'*-dicyclohexyl-2,6-naphthalenedicarboxamide as a β-form nucleating agent is dissolved beyond 280 ºC in a molten isotactic polypropylene (PP) and appears as needle crystals around at 240 ºC during cooling procedure. Further, PP molecules crystallize on the surface of the needle crystals, in which *c*-axis of the β-form PP crystals grows perpendicular to the long axis of the needle crystals. Under flow field at extrusion processing, the needle crystals orient to the flow direction prior to the crystallization of PP. As a result, *c*-axis of the β-form PP crystals orients perpendicular to the applied flow direction with a small amount of α-form PP. Moreover, the vertical molecular orientation of the extruded sheet sample is responsible for unique mechanical anisotropy; the fracture occurs along the transversal direction.

Key words: Polypropylene; Structure-Property Relations; Crystalline Form; X-ray Diffraction; Mechanical Properties

Introduction

Recently, considerable attention has been focused on the preparation of β crystalline form for isotactic polypropylene (PP), although conventional processing operation provides the most stable α crystalline form with a sporadic occurrence of β-form. The β crystalline form was firstly identified in 1959 by Keith and Padden,[1] who classified the crystalline modalities of PP, for the sample quenched below 128 ºC. Later, Tuner-Jones et al. reported that high content of β-form is observed in a sample with a mixture of water and glycerine by quenching at 100-120 ºC.[2] Since then, several methods were proposed to generate β-form, as summarized in a review paper by Varga,[3] such as doping nucleating agents,[3-24] directional crystallization in a temperature-gradient field,[25-27] shear-induced crystallization,[28-31] and vibration induced crystallization.[32]

In particular, the most effective way to obtain the samples containing predominantly β-form would be the addition of specific nucleating agents, as well known for *trans*-quinacridone discovered by Leugering.[4] Up to now, several nucleating agents for β modification have been reported, such as various pigments including *trans*-quinacridone,[4-8] a mixture of pimelic acid and calcium stearate,[9] calcium salts of pimelic and suberic acid,[10,11] and *N,N'*-dicyclohexyl-2,6-naphthalenedicarboxamide.[12-24]

The commercialization of *N,N'*-dicyclohexyl-2,6-naphthalenedicarboxamide, designated as NU-100 in this paper, from New Japan Chemical has a great impact on the research and development of β-form PP in industries, because NU-100 has various attractive properties such as thermal stability and effective β nucleating ability. Crystallization kinetics and morphology observation of PP containing NU-100 were carried out by several researchers. Kotek et al. revealed that the concentration should be more than 300 ppm to show the effective β nucleating ability,[18,19] which was also supported by Menyhard et al.[22] Although NU-100 acts as a very efficient β nucleator beyond the critical concentration,[17] the selectivity is slightly poorer than that for *trans*-quinacridone and calcium-salt of suberic and pimellic acid.[22] Further, the slightly poor selectivity is responsible for dual nucleating ability, i.e., both α and β modifications simultaneously, as demonstrated by Varga and Menyhard by means of precise thermal analysis with polarized microscope observation.[24] Furthermore, they also showed that

NU-100 appears in a molten PP as needle crystals which grow with a lot of branch points.[23]

Kawai et al. studied the crystalline structure of NU-100 in detail and proposed the epitaxial matching with PP crystals.[13,14] According to them, *b*-axis of NU-100 is parallel to *c*-axis of PP. Finally, Zhou et al.[20] and Hou et al.[21] concluded by AFM observation that PP lamellae grow perpendicular to the surface of the nucleating agent, suggesting the epitaxial growth of PP.

From the view point of mechanical properties, it has been recognized that the presence of β crystalline form leads to enhanced toughness and higher drawability, but lower stiffness and yield stress[3,12,15,33-41] In particular, great attention has been focused on the enhanced toughness for the industrial application, because fracture of α-form PP occurs in a brittle manner. The marked toughness is attributed to the energy dissipation during the yield process due to the phase transformation from β to α-form. Further, the deformation mechanism has been studied in detail as compared with α-form PP. Karger-Kocsis demonstrated that plastic work term is 3-4 times higher for β-form PP than that for α-form PP, based on "essential work of fracture concept" of the ductile fracture mechanism.[35-37]

The peculiar lamellar morphology of β-form PP would be the origin of the difference in the deformation mechanism.[3] Huy et al. studied the deformation mechanism of α and β-form PP by means of simultaneous measurements of a stress-strain curve and an infra-red dichroic ratio.[39] They revealed that the α-form PP prefers intra-lamellar slippage whereas inter-lamellar slippage is a dominant mechanism for the β-form PP. The mechanism was supported by Lezak et al. by their XRD study employing the sample deformed under plane-strain compression.[40] Moreover, Li et al. investigated the deformation mechanism by an electron microscopic method.[38] They proved that crazing, not yielding, is the dominant cause of the fracture in case of β-form PP. Then the microcrazes are connected together and develop into large cracks. Furthermore, Chu et al. also reported that a number of pores appear during stretching of β-form PP.[12]

In this study, the molecular orientation of PP containing NU-100 as well as the crystalline form is investigated in detail employing sheet samples extruded from a conventional T-die. In general, addition of a nucleating agent enhances the molecular

orientation because of the rapid solidification. This phenomenon is pronounced in case of a fibrous nucleating agent such as a sorbitol-derivative that is often called as a clarifier, as reported by Tenma and Yamaguchi[41] and Tenma et al.[42] Since NU-100 also appears as needle crystals, the molecular orientation of PP would be greatly influenced.

Experimental

Materials

Commercially available isotactic polypropylene (PP) produced by Ziegler-Natta catalyst was used in this study. The melt flow rate is 10 [g/10min] at 230 ºC. Since the sample is a propylene homopolymer, the melting point measured by a differential scanning calorimeter at a heating rate of 10 ºC/min is approximately 165 ºC. Further, *N,N'*-dicyclohexyl-2,6-naphthalenedicarboxamide (New Japan Chemical, NJ Star^{TR} NU-100), referred as NU-100, was employed without further purification.

Sample Preparation

PP and NU-100 were mixed together with calcium stearate as an acid scavenger and thermal stabilizers such as a hindered phenol (Ciba, Irganox1010) and a phosphate (Ciba, Irgafos168). The concentrations of NU-100 were 500, 1000, and 2000 ppm. The amount of the acid scavenger and each thermal stabilizer used in the preparation was 0.05 %. Compounding was performed by a co-rotating twin-screw extruder (Technovel, KZW 15TW-45MG-NH) at a screw rotation speed of 250 rpm. The temperature in the extruder and the die was controlled at either 280 ºC or 200 ºC. The strands extruded from the extruder were immediately quenched in a water bath and then cut by a strand cutter. The reference sample of PP was also prepared by the identical method without the addition of NU-100.

The obtained pellets mixed at 280 ºC were fed into a single-screw extruder having a T-die controlled at 200 ºC to obtain an extruded sheet with a thickness of 200 μm. The temperature of the chill-roll was controlled at 105 ºC. The sample employed for the extrusion contains 500 ppm of NU-100. Further, pure PP without NU-100 was also processed to obtain a reference sheet sample.

Measurements

Dissolution and crystallization behaviors of NU-100 in a molten PP as well as the crystallization of PP were evaluated by an optical microscope (Leica, DMLP) equipped with an automated hot-stage (Mettler, FP82HT). After heating the sample from room temperature to 200 ºC immediately, the sample was heated at a constant rate of 5 ºC/min to 300 ºC. Then the sample was cooled at a rate of 5 ºC/min to 135 ºC and subsequently kept at the temperature. Birefringence of the sheet samples was measured by the optical microscope (Leica, DMLP) with a tilting compensator (Leica, Tilting Compensator B). Thin film specimens with a thickness of 2.5 μm were prepared at -100 ˚C by using an ultra microtome (Leica, FCS).

Wide-angle X-ray diffraction (WAXD) patterns were measured by using a graphite-monochromatized Cu Kα radiation beam focused via 0.3-mm pinhole collimator with a flat 20×20-cm^2 imaging plate (IP) detector of 1900×1900 pixels (Rigaku, R-AXIS IIc). A small piece of the sample with edge sizes less than 1 mm was mounted with the sample-IP distance 10 cm. As is shown in Figure 1, the exposure was performed with 7 min a shot in three geometrical conditions by directing the X-ray beam in the normal direction (ND) (through view: TV), in the transverse direction (TD) (edge view: EV), and in the machine direction (MD) (end view: DV). For the profile analysis, the crude intensity data recorded on IP were transformed into the curve (*vs*. the diffraction angle 2θ) corresponding to that measured with a conventional powder diffractometer, by correcting for the various effects, such as the dark noises of the IP system, the intensity decrease dependent inversely on square distance from the sample to each pixel, the oblique incidence of the diffracted light onto IP, and the air scattering. In the data files, two bytes were allotted to save each pixel intensity, and by bit-shift storage technique the maximum recording intensity was 8×7FFF (hexadecimal) = 262,136 in the range of the linear sensitivity. All the treatments of the IP data were carried out with PC computers.

[Figure 1]

Mechanical anisotropy was evaluated by a tear test following ISO 6383-1 Trouser tear method using a tensile machine (Tokyo Testing Machine, Little Senster) at room temperature. The sample specimens were cut out from the sheet as shown in Figure 2. The stretching rate was 10 mm/min. The tear-propagation resistance, defined as the force divided by the sample thickness, was measured as a function of the displacement of the

crossheads.

[Figure 2]

Results and Discussion

Dissolution and Crystallization of NU-100

Dissolution and crystallization behavior of NU-100 in a molten PP was evaluated employing pellet samples. Figure 3 shows the optical micrographs for PP containing 2000 ppm of NU-100. There are a lot of particles in the sample mixed at the lower temperature, i.e., 200 ºC, even after melting of PP, as seen in Figure 3(a). The diameter of the particles is approximately 10 μm. The particles are dissolved into the molten PP gradually at a heating process and disappear completely at 280 ºC. On the contrary, the sample mixed at 280 ºC shows homogeneous structure at 200 ºC (Figure 3(d)). As increasing the temperature, however, needle crystals appear in the molten PP (Figure 3(e)). The needle crystals of NU-100 grow until 250 ºC, and then they are dissolved at 280 ºC (Figure 3(g)) as similar to the sample mixed at 200 ºC. The results demonstrate that the dissolution of NU-100 occurs at 280 ºC for the concentration, which is independent of the shape of NU-100. During the cooling process from 300 ºC, the needle crystals appear approximately at 240 ºC and grow with branching as similar to the recent study[23] (Figure 3(i)). Further, NU-100 is not detected at 260 ºC at the cooling process, although they are not dissolved completely at the temperature at the heating process. This is reasonable, because it takes some time for NU-100 to crystallize in a molten PP especially near the dissolution temperature.

[Figure 3]

The temperatures of the dissolution and crystallization of NU-100 in a molten PP were plotted as a function of the concentration in Figure 4. As shown in the figure, the dissolution and crystallization occur at high temperature with increasing the concentration.

[Figure 4]

Figure 5 shows the optical micrograph under crossed polars inserting a full-wave plate that adds 530 nanometers to an optical path. The sample containing 500 ppm of NU-100 is cooled down from 300 ºC. The left figure shows the needle crystals of NU-100

appeared in a molten PP at 210 ºC. The diameter is approximately 10 μm and the length is 100-200 μm. As shown in the figure, the crystals whose long axis orients to Northwest-Southeast are blue, while those orient to Northeast-Southwest are yellow. This result indicates that the refractive index of the long axis is smaller than that of the short axis. Further, crystallization of PP occurs at lower temperature on the needle crystals as shown in the right figure. It is apparent that PP crystal exhibits the same color as the needle crystals. Considering that the refractive index of *c*-axis (fiber axis) is larger than those of the others for PP, *c*-axis of PP orients perpendicular to the long axis of the needle crystals. Although the reason is unknown, the growth direction of PP chains on NU-100, detected in the present study, is different from that proposed by Kawai et al.[13,14] Furthermore, spherulite texture is not detected at the present study, because the needle crystals, as nucleating agents, are too crowded to form spherulites, as similar to PP containing a sorbitol derivative as a fibrous nucleator.[41,42]

[Figure 5]

Structure of Extruded Sheet

Prior to the characterization of molecular orientation and crystalline form of PP in the sheet samples, the dispersion state of the needle crystals in the sheet is examined. Figure 6 shows the optical micrograph of the sheet sample, which is taken immediately after melting of PP. It is confirmed that the needle crystals of NU-100 orient to the flow direction.

[Figure 6]

For the information on the orientation direction of PP molecules, the magnitude of birefringence in the sheet samples were evaluated employing two slices from each sample as shown in Figure 7. Further, the optical micrograph under crossed polars inserting a full-wave plate for a sliced sample is exemplified in Figure 7. It is found from the birefringence measurement that Δn ($=n_{TD}-n_{ND}$) of the TD sample which is shown in the figure is 1.2×10^{-3}, and Δn ($=n_{MD}-n_{ND}$) of the MD sample is 7.5×10^{-4}. The result demonstrates that PP molecules orient perpendicular to the flow direction, i.e., $n_{MD}-n_{TD} = -4.5 \times 10^{-4}$, which is an extraordinary orientation. As a comparison, the birefringence of the extruded sheet of pure PP is also examined. Consequently, the *c*-axis of PP is found to orient to the flow direction slightly; $\Delta n_{TD\text{-}ND}$ is smaller than $\Delta n_{MD\text{-}ND}$, suggesting PP

chains orient to the flow direction, i.e., ordinary orientation, which will be demonstrated in detail by XRD analysis.

[Figure 7]

For the better understanding of the molecular orientation as well as polymorphism, XRD measurements were carried out for the sheet sample containing NU-100. The XRD patterns reveal that the extruded PP sheet comprises both the α- and β-forms and the latter is much predominant. Figure 8 exhibits the assignments of the reflections in the EV pattern, in which the α reflections are shown in the left side and the β reflections are in the right side.

[Figure 8]

The *d* spacings were elucidated by the monoclinic unit cell with the standard dimensions[43] $a = 6.65$ Å, $b = 20.96$ Å, $c = 6.49$ Å, $\beta = 99.3^{\circ}$ for the α reflections, and by the three-chain trigonal unit cell (isochiral-domain model)[44] with $a = b = 11.0$ Å, $c = 6.49$ Å, $\gamma = 120^{\circ}$ for the β reflections. The three isochiral helices assume a frustrated packing, namely, there is no crystallographic symmetry among them.[45] The main reflections hold the indices of $h - k = 3n$, attributable to the one-chain pseudohexagonal subcell with $a' = 6.37$ Å. Figure 9 shows the diffraction curve transformed from the data of the TV pattern and corrected for the Lorentz and polarization (*Lp*) factors. The α reflections are indicated by arrows. The peaks were separated over the amorphous background scattering (Bg), that was approximated by a smooth spline curve. The integrated intensity ratio was nearly α : β : Bg ≈ 5 : 45: 50. The same ratio was obtained for the curve extracted from the EV pattern. In spite of the small 2θ range, it may represent the existence ratio.

[Figure 9]

In Figure 9, the weak reflection A arises from the (110) faces of the monoclinic α crystals, while the strong reflection B arises from the {110} of the trigonal β crystals, including symmetrically equivalent $(2\bar{1}0)$ and $(\bar{1}20)$ faces. The integral widths Δ(2θ) of the reflections A and B were about 0.9º and 0.4º, indicating that the sizes (coherent lengths) of the α and β crystals are about 100 Å, and 220 Å, respectively.

The features of the diffraction patterns claim the preferred orientations of the α and β crystals. The reflections A and B are also designated in patterns of Figure 1. In their

respective narrow 2θ ranges, the pixel intensities of the TV pattern were collected and plotted against the azimuthal angle ϕ defined on the IP plate. The angle ϕ is associated with the azimuthal angle φ_M pointing to the lattice direction [*hkl*], which is defined to be normal to the corresponding (*hkl*) crystal face. In the case of the normal incidence of X-ray beam to the flat IP, the angles are related by

$$\cos \varphi_M = \cos \theta \cos \phi. \quad (1)$$

We describe the direction [*hkl*] by the angles φ_M, φ_N, and φ_T toward MD, ND, and TD, respectively, as shown in the lower left of Figure 1. The data observed in the TV, EV, and DV patterns are limited to particular intersections of the Ewald sphere (reciprocal space) permitted by the Bragg condition, and are contributed only from a fraction of crystals with the corresponding direction [*hkl*] forming an angle $\pi/2+\theta$ with the incident X-ray direction. Allowing for the incomplete data, the azimuthal intensity distributions *vs.* ϕ were transformed into those *vs.* φ_M (Figure 10).

[Figure 10]

The intensity distribution of the reflection A consists of two broad components of the half width $\Delta\phi$ = 50-60º; one is around $\varphi_M \approx 0$º (V component) and the other is around 90º (P component). The former intensity is about twice of the latter. In the EV pattern (Figure 8), the reflection A appears at $\phi \approx 15$º and the 040 reflection at $\phi = 90$º in a narrow range. Therefore, the V-component α crystals orient preferentially with *b*-axis in the ND direction, *a**-axis in the MD direction, and *c*-axis in the TD direction. For *b*-axis, $\varphi_M \cong$ 90º (narrow), while $\varphi_N \approx 0$º and $\varphi_T \approx 90$º (broad). For *a**-axis, $\varphi_N \cong 90$º (narrow), while $\varphi_M \approx 0$º and $\varphi_T \approx 90$º (broad).

As mentioned below, the *b*-axis direction ([010]) of the V component was parallel to [110] of β crystals, and the manner of the mutual orientation was very similar. In the limit-ordered α crystal, the four types of chains, up- and down-pointing right-handed and left-handed helices, are engaged in the $P2_1/c$ unit cell. The disordered modification ($C2/c$) involves the up/down disorder.[46,47] Isotactic PP chain can assume both the right- and left-handed helical conformations, but the helical rewinding reverses the up-down direction. Essentially, the α-forming arrangements of the right- and left-handed helices are not achieved in β-form, but such arrangements may happen sporadically in small

areas, and form less-ordered α crystals. There is a possibility that the V-component α crystals may grow secondarily in the crystallization process of β-form.

The reflection A observed in the DV pattern (the lower right of Figure 1) is associated with the component P, and its azimuthal intensity distribution is almost uniform. Therefore, the P-component α crystals seem to have the uniaxial orientation with the chain axis parallel to the MD direction, and may grow in a minimum quantity by the shear-induced crystallization in the extrusion process.

On the other hand, the intensity maxima of the reflection B appear at $\varphi_M \approx 30^\circ$, 90°, and 150° (Figure 10) in the TV pattern. As shown in Figure 8, the reflection B comprises well-defined six spots in the EV pattern. In the scheme of the axial setting in which the equatorial spot at $\phi = 90^\circ$ (in the ND direction) is assigned to 110, the spots at $\phi \approx 30^\circ$ and 150° are ascribed to $\bar{1}20$ or $2\bar{1}0$. For the direction [110], $\varphi_M \approx 90^\circ$ (narrow), while $\varphi_N \approx 0^\circ$ and $\varphi_T \approx 90^\circ$ (broad). The *c*-axis orients preferentially in the TD direction. Compared to the EV pattern, the broad azimuthal intensity distribution of the reflection B in the TV pattern suggests the small twisting of the β crystals about the [110] axis. From these features, a new morphology depicted in Figure 11 is proposed. The growth direction is along the horizontal [110].[45] The intensity distributions in the DV pattern indicate the [110] orients broadly ($\Delta\phi \approx 50^\circ$) in the ND direction. However, there are still some amounts of the β crystals having the [110] in the TD direction, which may give rise to the small maximum at $\varphi_M \approx 90^\circ$ in the TV pattern. There was no particular evidence for the β crystals with the chain axis aligned in the MD direction.

[Figure 11]

Mechanical Properties

Trouser tear test was performed at room temperature employing two types of the sheet sample containing NU-100; one has a parallel notch to the flow direction (MD), and the other has a vertical notch (TD) as illustrated in Figure 2. Figure 12 shows TPR, tear-propagation resistance, is plotted against the displacement. It should be noted that the MD sample shows ductile behavior whereas the fracture occurs in a brittle manner for the TD sample, which is attributed to the unique molecular orientation of PP. This mechanical anisotropy is completely different from that of conventional polymer

products processed by various processing techniques such as fiber-spinning, film, sheet, blow-molding, and injection-molding.

Furthermore, the appearance of the fractured samples is also significantly different as shown in the figure. The MD sample exhibits a marked stress-whitening behavior with a large plastic deformation area. On the contrary, the brittle failure occurs in the TD sample. The experimental results suggest the possibility to control the direction of the crack propagation.

In case of PP, both MD and TD samples exhibit brittle fracture (but not presented here). The difference between the MD and TD samples is not detected because both samples are so brittle.

[Figure 12]

Conclusion

Structure and properties of PP containing NU-100, as a β-form nucleating agent, were studied employing the sheet samples extruded from a conventional T-die. It is found that dissolved NU-100 appears as needle crystals in a molten PP. Further, the long axis of the needle crystals orient along to the flow direction. Then PP molecules crystallize on the surface of the needle crystals, in which *c*-axis of PP chains orients perpendicular to the long axis of the needle crystals. XRD characterization revealed that there are both α and β forms in the sheet sample with an intense fashion of the β-form. Furthermore, *c*-axis of PP molecules orients perpendicular to the flow direction, which corresponds with the birefringence measurement. The anomalous molecular orientation affects the mechanical anisotropy to a great extent. The sample shows ductile behavior in the TD direction, whereas it fractures in a brittle manner in the MD direction.

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Figure Captions

Figure 1 XRD geometry for the extruded PP sheet

Figure 2 Sample dimension for tear experiments

Figure 3 Optical micrographs with a wave plate for PP containing 2000 ppm of NU-100 at various temperatures: (a)-(c) mixed at 200 ºC and (d)-(i) mixed at 280 ºC: (a)-(g) heating process at a rate of 5 ºC/min and (g)-(i) cooling process at a rate of 5 ºC/min; (a) and (d) at 200 ºC, (b), (e), and (i) at 230 ºC, (c), (f), and (h) at 260 ºC, and (g) at 300 ºC.

Figure 4 Morphology map for PP containing NU-100.

Figure 5 Optical micrographs under crossed polars inserting a full-wave plate; (left) at 210 ºC and (right) at 135 ºC.

Figure 6 Optical micrograph for extruded PP sheet containing 500 ppm of NU-100. The sample was heated to 200 ºC to melt PP. The arrow in the figure indicates the flow direction (MD).

Figure 7 Optical micrograph with a wave plate for extruded PP containing 500 ppm of NU-100.

Figure 8 The EV pattern and the assignments (*hkl* indices and the *d* spacing) of the α reflections (left) and the β reflections (right).

Figure 9 The *Lp*-corrected XRD curve extracted from the TV pattern, and the assignments of the reflections which are indicated by the 2θ angle, *d* spacing, and the *hkl* indices. The reflections indicated by arrows are attributed to the α-form and the others to the β-form. The reflections A and B are those shown in Figure 1.

Figure 10 Azimuthal intensity distributions of the reflections A (α) and B (β) *vs.* φ_M in the TV pattern.

Figure 11 Crystallization mechanism of β-form PP on the needle crystals of NU-100 and the stem packing.

Figure 12 Tear-propagation resistance (TPR) is plotted against the displacement for MD and TD samples. The fractured samples were shown in the figure.

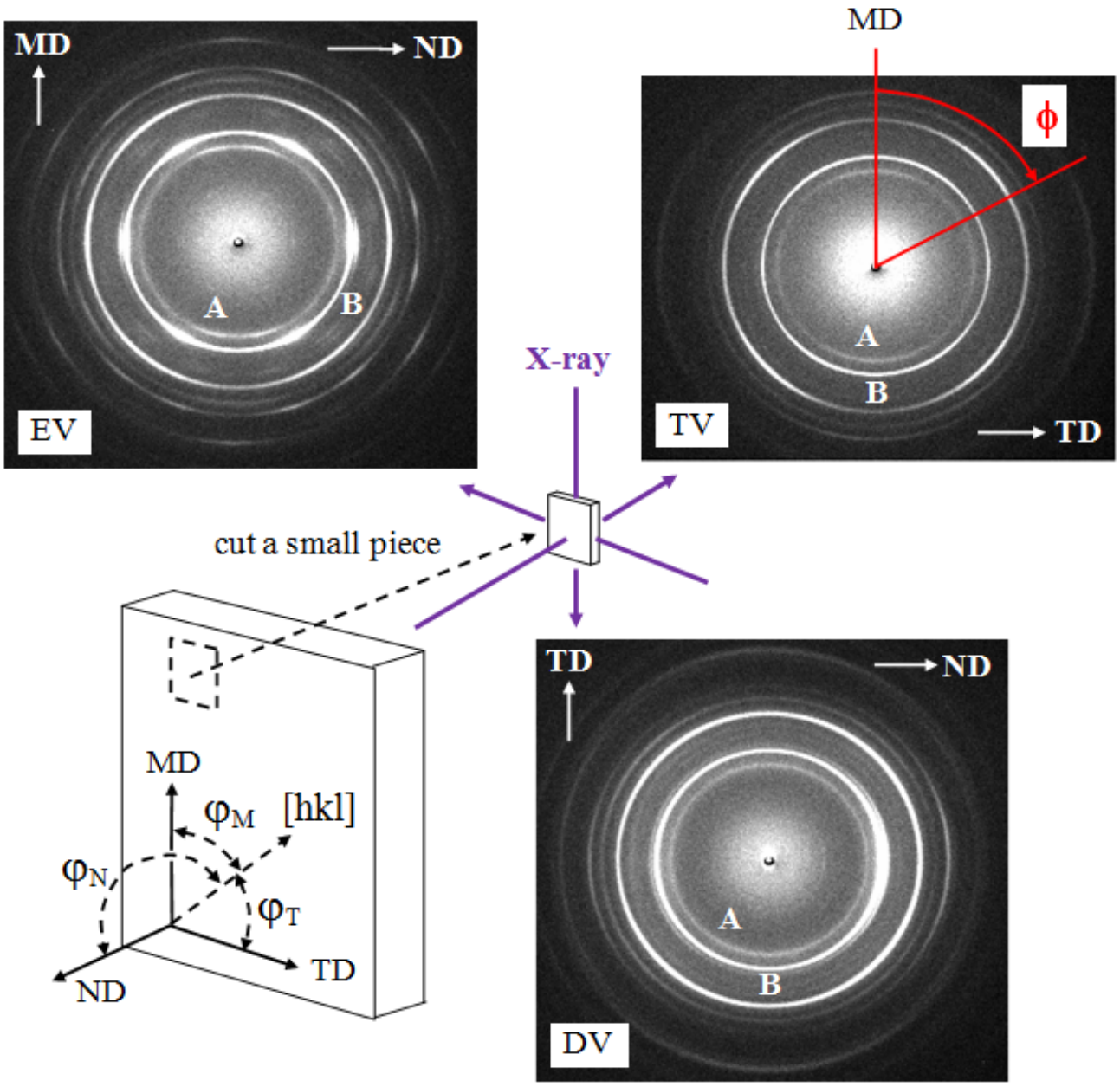

MD
ND
A
B
EV
MD
ϕ
A
B
TV
TD
X-ray
cut a small piece
MD
φM
[hkl]
φN
φT
TD
ND
TD
ND
A
B
DV

Figure 1

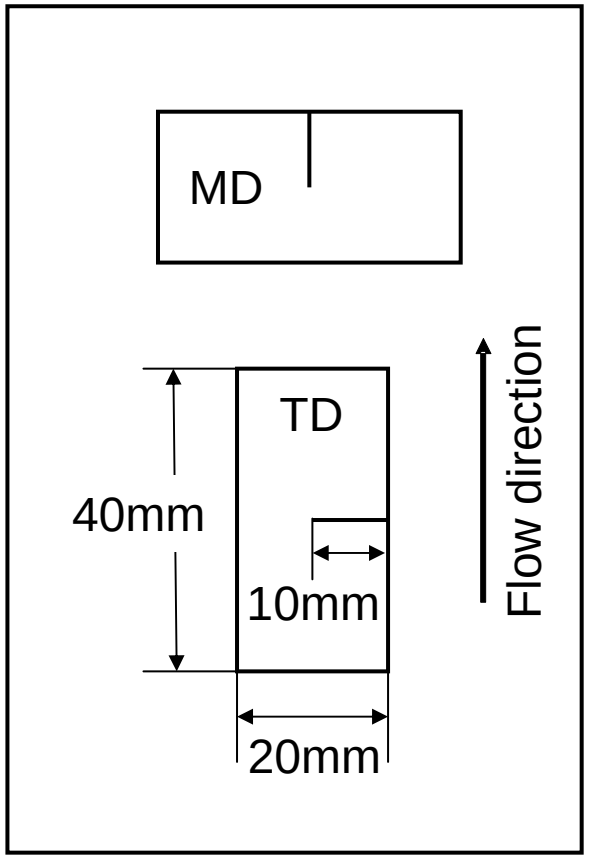


Figure 2

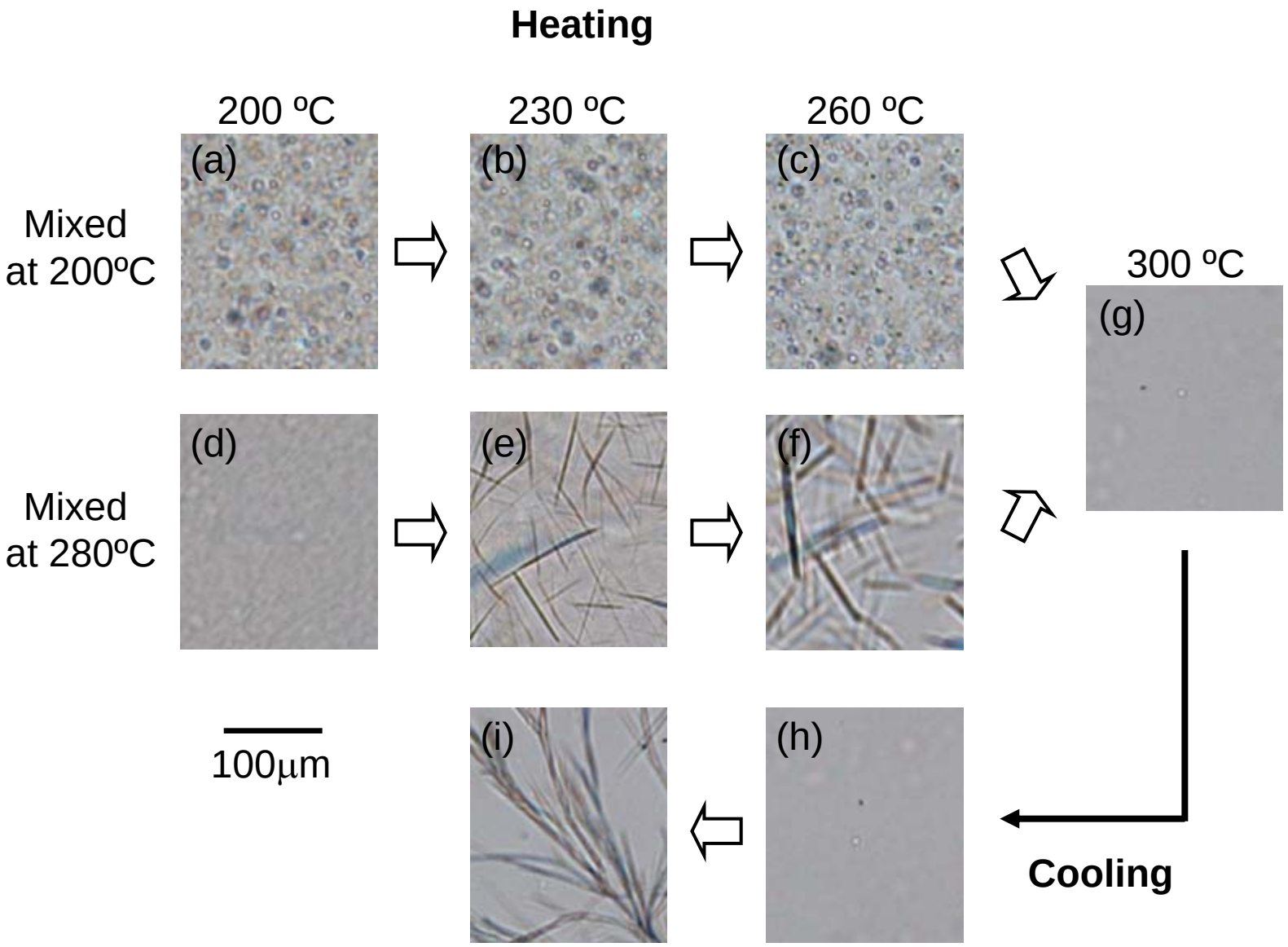

Heating
200 ºC
230 ºC
260 ºC
300 ºC
Mixed at 200ºC
Mixed at 280ºC
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
100μm
Cooling

Figure 3

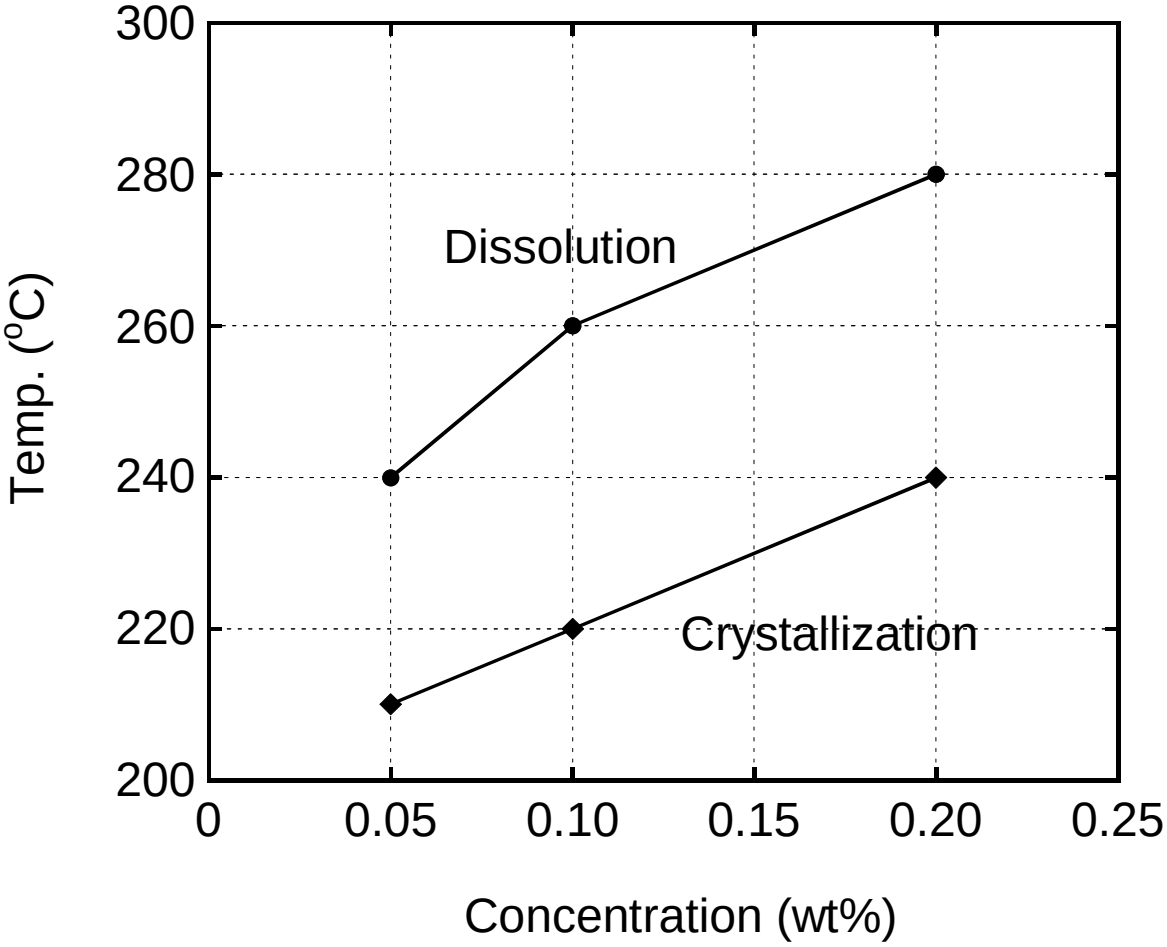
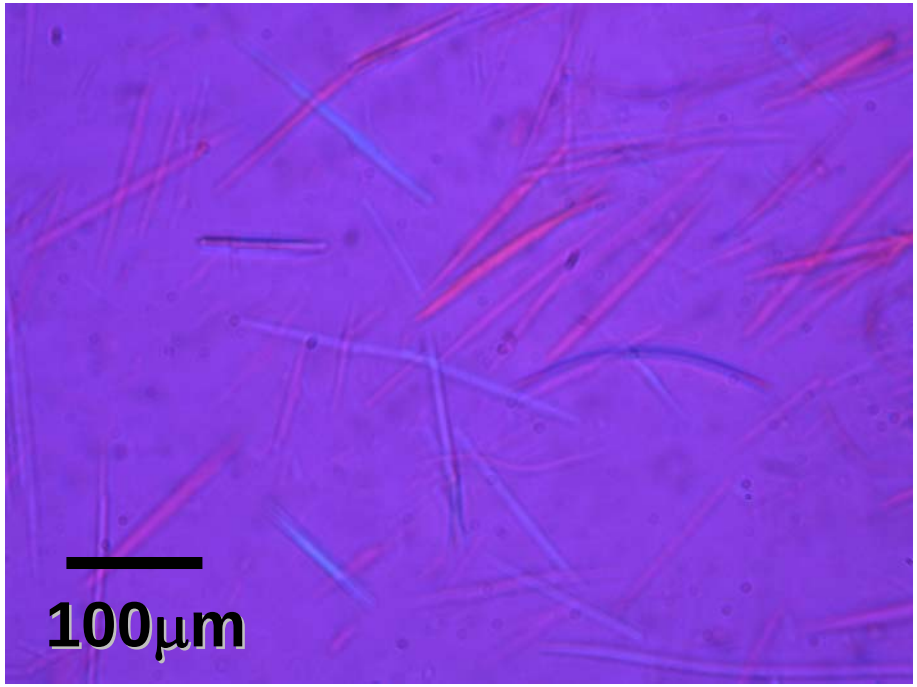

300
280
260
240
220
200
Temp. (°C)
Dissolution
Crystallization
0
0.05
0.10
0.15
0.20
0.25
Concentration (wt%)

Figure 4

210°C



135°C

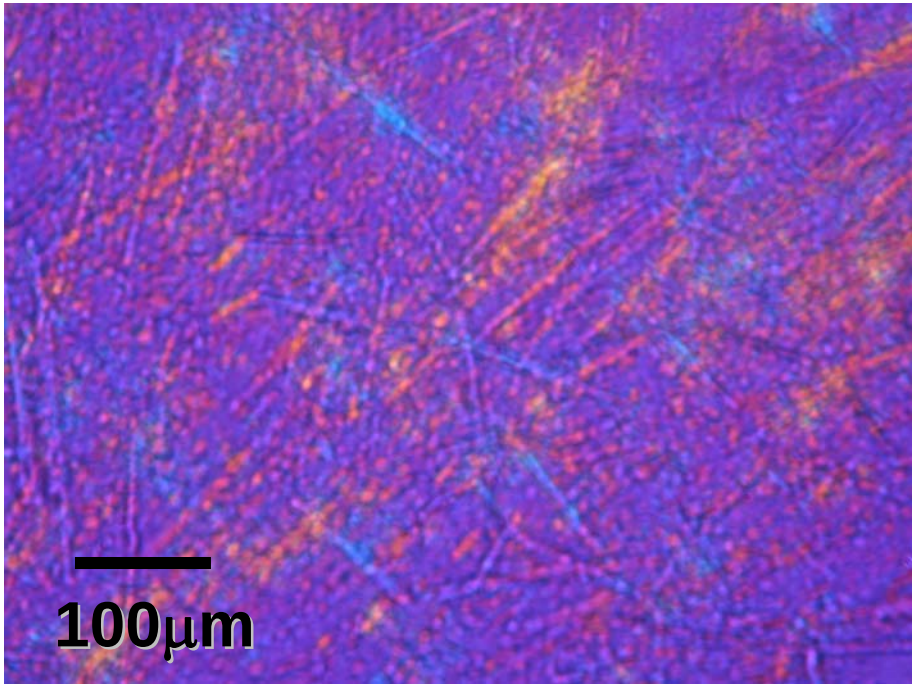


Figure 5

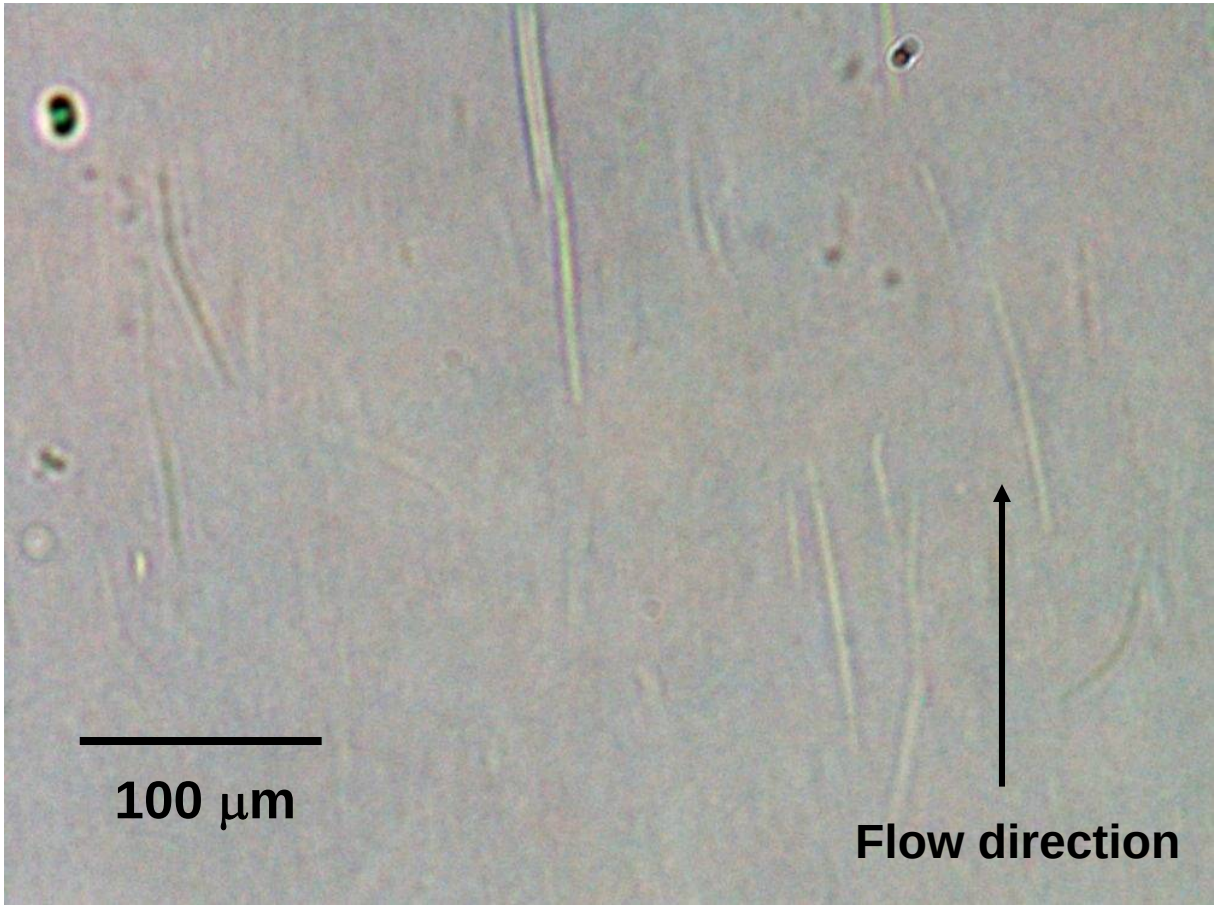
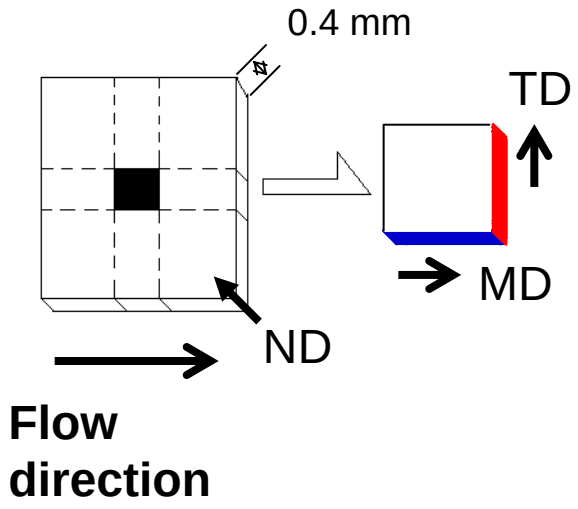


Figure 6



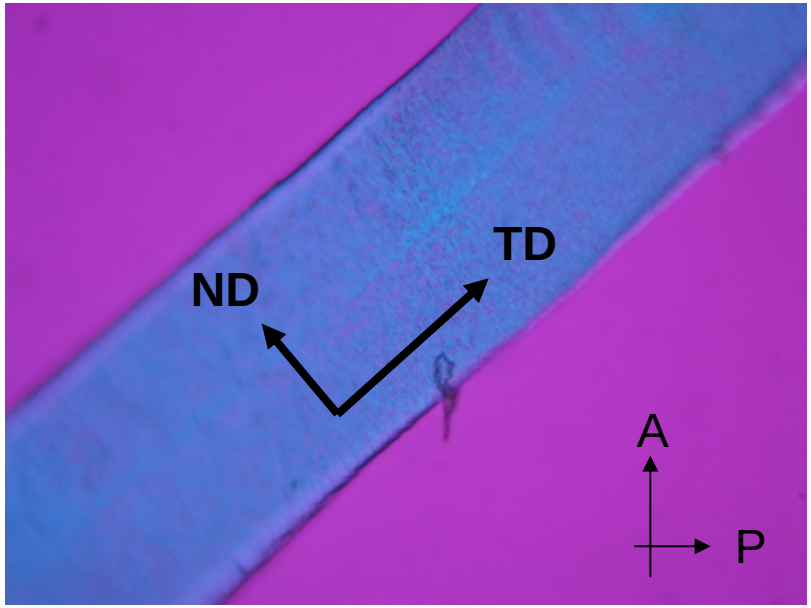


Figure 7

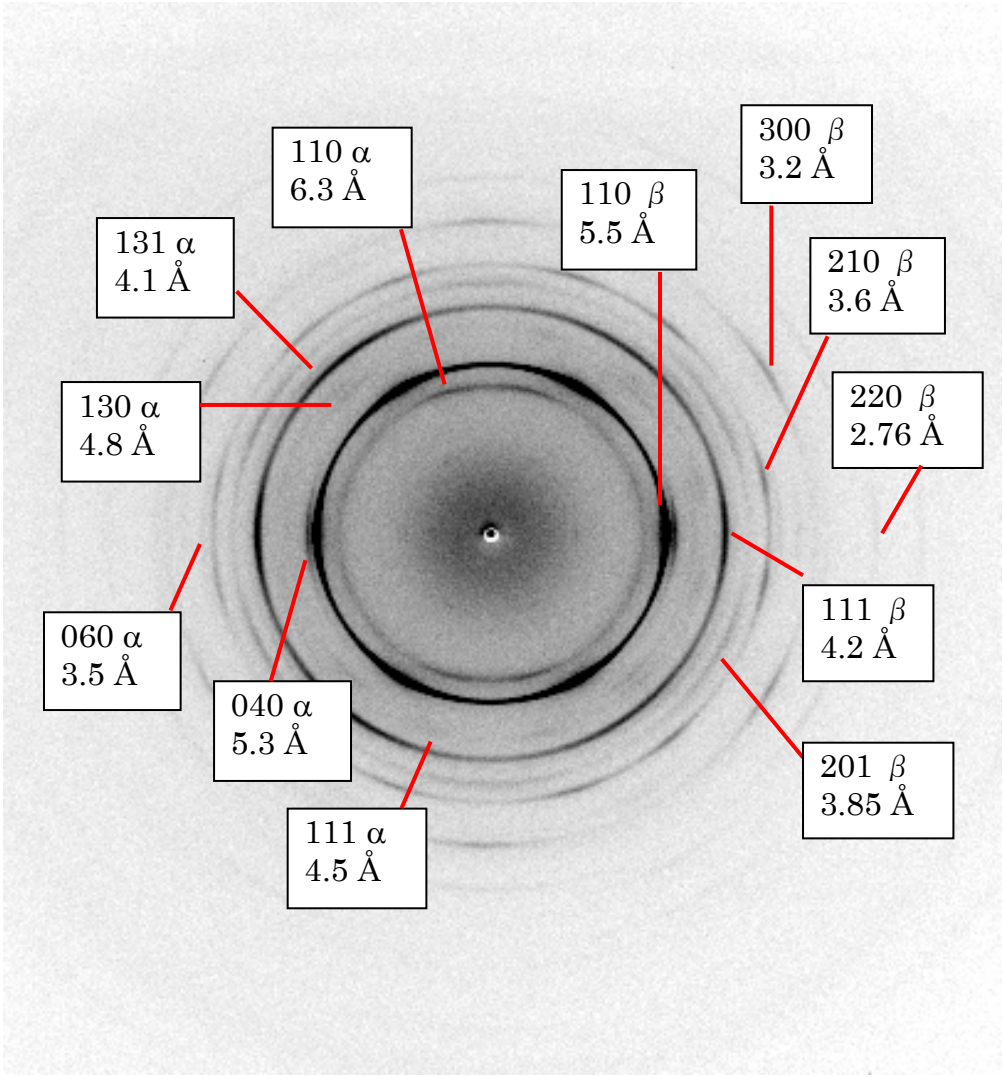

110 α
6.3 Å
131 α
4.1 Å
130 α
4.8 Å
060 α
3.5 Å
040 α
5.3 Å
111 α
4.5 Å
110 β
5.5 Å
300 β
3.2 Å
210 β
3.6 Å
220 β
2.76 Å
111 β
4.2 Å
201 β
3.85 Å

Figure 8

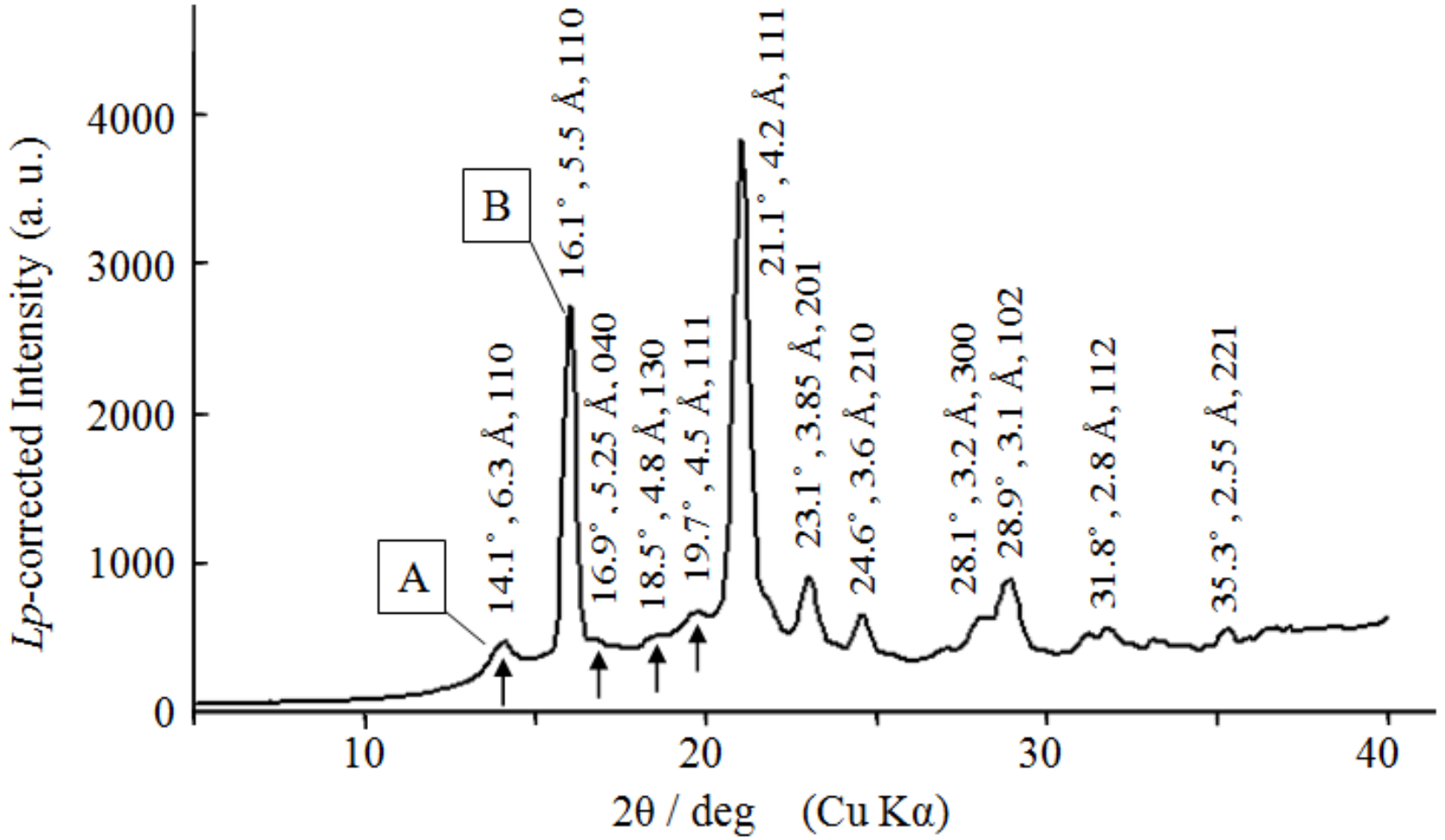

Lp-corrected Intensity (a. u.)
4000
3000
2000
1000
0
10
20
30
40
2θ / deg (Cu Kα)
A
B
14.1°, 6.3 Å, 110
16.1°, 5.5 Å, 110
16.9°, 5.25 Å, 040
18.5°, 4.8 Å, 130
19.7°, 4.5 Å, 111
21.1°, 4.2 Å, 111
23.1°, 3.85 Å, 201
24.6°, 3.6 Å, 210
28.1°, 3.2 Å, 300
28.9°, 3.1 Å, 102
31.8°, 2.8 Å, 112
35.3°, 2.55 Å, 221

Figure 9

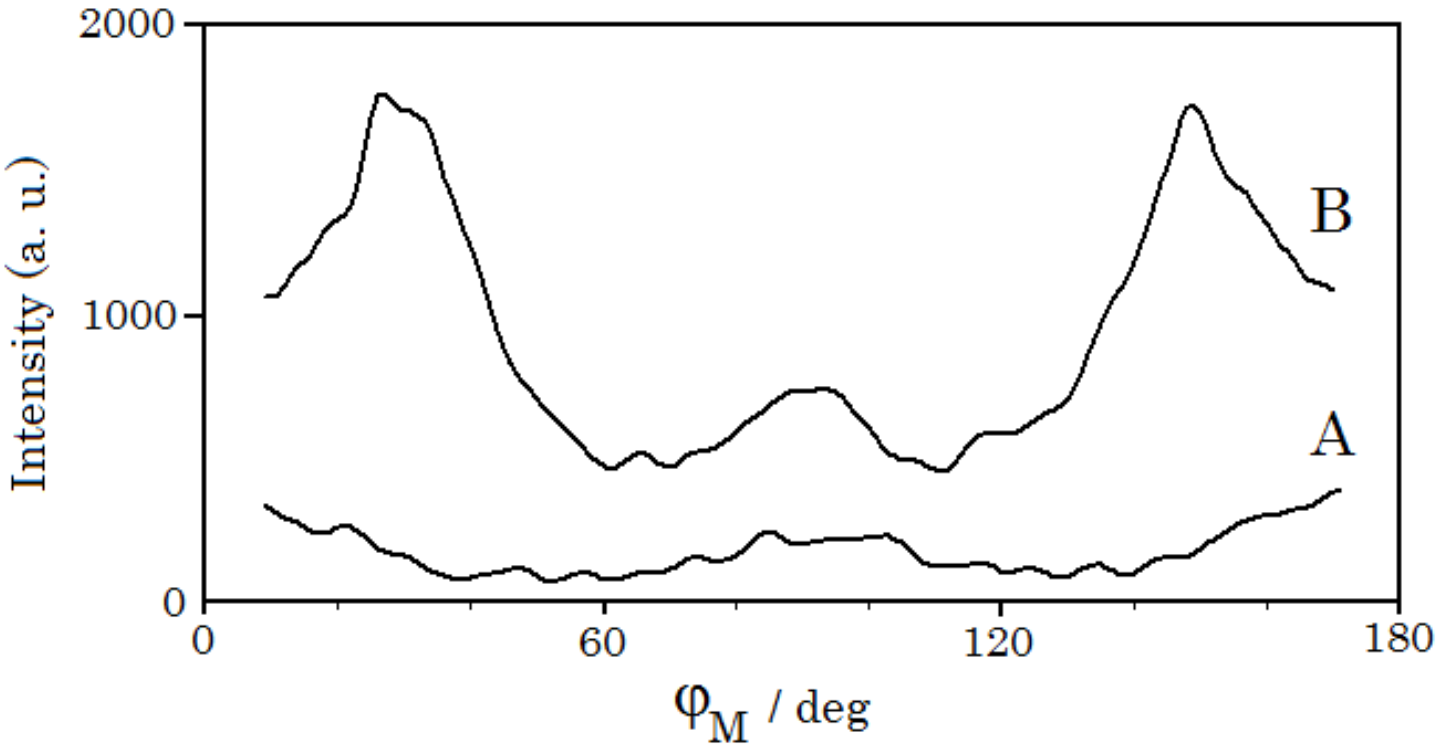


Figure 10

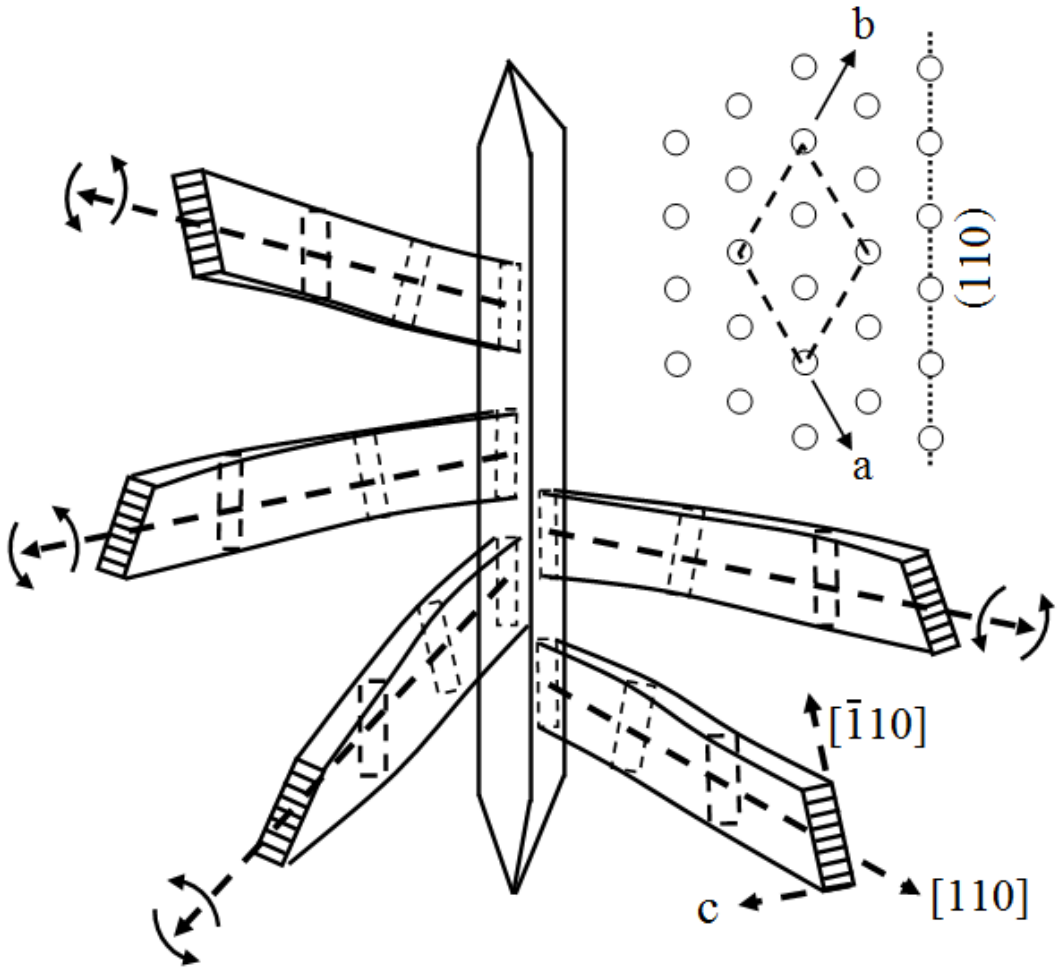


Figure 11

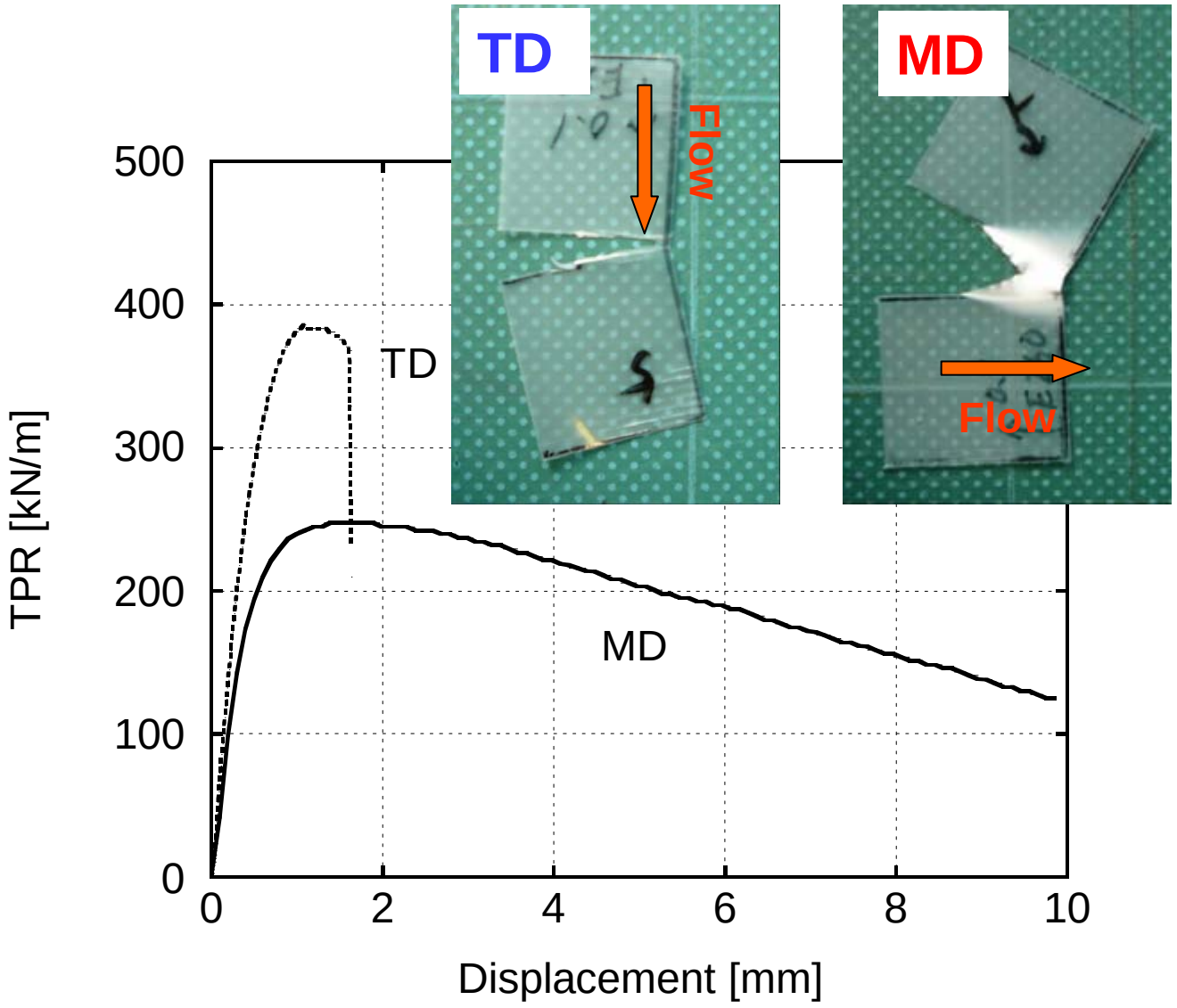

TD
Flow
MD
Flow
TD
MD
TPR [kN/m]
Displacement [mm]
0
100
200
300
400
500
0
2
4
6
8
10

Figure 12