NOTES

Morphological Study by TEM on Thin Films of Nylon-6, Nylon-6,6, and Their Blends As-cast from Formic Acid Solution

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Nylon-6 (polycaprolactam) (N6) and nylon-6,6 (poly(hexamethylene adipamide)) (N66) are very important commercial polymers in the nylon family.[1] By blending these two polymers, a remarkable improvement on their inherent mechanical properties can be expected. Extensive efforts have been, therefore, made for mechanical, thermodynamic and/or structural studies of the blends.[2−11] N6 and N66 are miscible in their molten state,[1] and are also expected to be miscible in their solution state.[7] Some morphological studies by transmission electron microscopy (TEM) of as-solution-cast crystalline thin films of each pure component have been reported so far (*e.g.*, refs 6, 12, and 13 for N6, and refs 6, 14, and 15 for N66; mostly, cast from solutions in formic acid), but there have been few reports on morphology of their blend films as-cast from solution.[6] In particular, although selected-area electron diffraction (SAED) patterns obtained from the same specimen-area tilted at a series of angles are very important to identify the crystal modifications and/or crystallite orientation in a given specimen film, such SAED experiments by specimen-tilting have been done in a few reports only on N66[14, 15] and in no report on their blends, to our knowledge. In this communication, we report some results on morphology of the thin films of N6, N66 and their blends, all of which were prepared by casting the respective solutions in formic acid onto water surface, and also on a set of SAED patterns recorded from the un-tilted and tilted specimen-area for each of the thin films.

EXPERIMENTAL

Materials and Preparation of Thin Films

N6 ($M_w = 16000$) and N66 ($M_w = 22000$) are respectively the products of Unitika Ltd. (A1030BRL) and BASF Co. (R8270), both of which were kindly supplied by Research and Development Center, Unitika Ltd. and were the same materials investigated by Hirami and his co-workers[7−10] and by Bedia *et al.*[11]

The procedure to make solutions in formic acid is similar to that reported previously:[11] Solutions (0.2 wt%) of N6 and N66 were separately prepared at room temperature (RT) by dissolving each nylon in formic acid (this concentration, 0.2 wt%, was determined by trial and error to be just appropriate for our purpose). In order to make blends of desired wt% compositions (N6/N66 = 30/70, 50/50 and 70/30), the corresponding volume ratios of N6 and N66 solutions were mixed together at RT. Thin polymer films were prepared from each of the resulting solutions by casting onto the surface of water thermostated at 55, 65, or 75°C. Of course, these three temperatures are much lower than the melting temperature of N6 crystal and also that of N66 one.[11]

Rybnikár and Geil[6] prepared a specimen film for TEM by evaporating a drop of solution directly on a carbon-coated TEM grid or on a glass slide. Direct evaporation of a solution in formic acid on the TEM grid, however, may leave a residue of formic acid in the resulting film, and such a residue is harmful to a TEM column. In order to minimize this danger and for in-
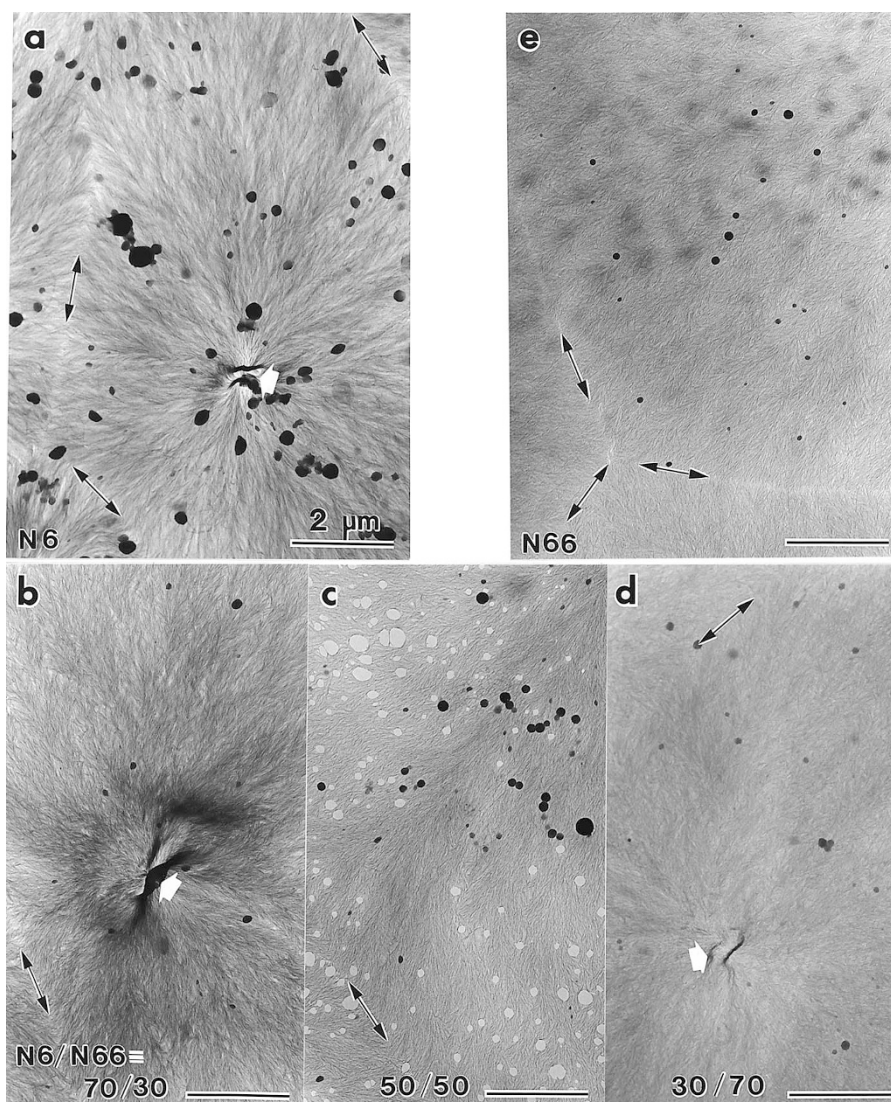
Figure 1. Thin films of N6, N66 and their blends, which were as-cast from respective 0.2 wt% solutions in formic acid onto the surface of water thermostated at 65°C and were not metal-shadowed or stained. In each TEM photograph, the scale bar expresses 2 μm and a double-headed arrow designates the boundary between impinged spherulites. The white thick arrow indicates the center of a spherulite in each of (a), (b), and (d). (a) N6, namely N6/N66 = 100/0. (b) N6/N66 = 70/30. (c) N6/N66 = 50/50. (d) N6/N66 = 30/70. (e) N66, namely N6/N66 = 0/100.

stantaneous judgement of the quality of specimen film, the solution-casting method on the water surface is employed in this study.

Specimen Preparation for Transmission Electron Microscopy (TEM)

A polymer thin film floating on water surface was mounted onto a copper grid for TEM and dried under ambient conditions. The specimens thus prepared were examined by TEM (with a JEOL JEM-100U operated at 80 kV and a JEOL JEM-200CS operated at 200 kV). Ordinary bright-field morphological images were obtained in the amplitude (namely, mass-thickness and/or diffraction) contrast mode mostly with the JEM-100U. SAED patterns were obtained with the JEM-200CS equipped with a conventional specimen-tilting holder

(JEOL EM-SQH): Each of the SAED patterns was taken from a specimen area about 8 μm in diameter and this area contained, roughly speaking, a two-dimensional spherulite or a central part of a larger one (see Figure 1). In order to calibrate the diffraction camera length, the specimens for SAED experiment were coated with vapor-deposited gold (Au). All the images and SAED patterns were recorded on photographic films (Mitsubishi MEM).

RESULTS AND DISCUSSION

Optimal Temperature of Water to Obtain Thin Films for TEM, and Their Morphologies

Figure 1 shows morphologies of the resulting thin films that were all made at the same temperature (65°C)

of water. In all the films of N6, N66 and their blends, long fibrillar entities are clearly observed. (Dark particle-like entities observed in all the films are supposed to be dust particles and/or non-crystalline precipitates of polymer.) As indicated below, SAED patterns revealed that all the films thus prepared are crystalline. All the films have spherulitic textures consisting of closely impinged spherulites whose diametrical size is *ca.* 10 – *ca.* 20 μm, and typical examples of two-dimensional spherulites are well recognized in Figures 1a and 1b. The center of such a spherulite is surely observed in each of Figures 1a, 1b, and 1d, as indicated with a thick white arrow. In Figures 1c and 1e, however, the center of a rather large spherulite appears to be located outside the upper right corner of each photograph. The boundaries between impinged spherulites are clearly recognized, for example, in Figures 1a and 1e where such a boundary is designated with a double-headed arrow.

The best temperatures to prepare desired thin films of N6 (N6/N66 = 100/0) and N66 (N6/N66 = 0/100) were 75°C and 55°C, respectively. The second best one for both N6 and N66 was 65°C. The best films of a blend of N6/N66 = 30/70 could be made at 65°C. As for both N6/N66 = 70/30 and 50/50, fairly good films could be prepared at all the three temperatures. In Figure 1c, however, a number of small holes are visible probably because this part of the specimen film of N6/N66 = 50/50 was accidentally very thin.

As mentioned above, 65°C was the second best temperature for preparing N6 films and N66 ones, but it was concluded that 65°C was the optimal temperature for 0.2 wt% solutions of all the blend compositions utilized here. We supposed that the temperature of water should be fixed for comparing the SAED patterns obtained from specimen films of different compositions, and the patterns obtained from the films prepared at 65°C will be shown in Figure 2. Accordingly, the corresponding morphologies of the films made at 65°C have been demonstrated in Figure 1.

SAED Patterns from the Resulting Films

Firstly a SAED pattern was recorded at 0°, namely without specimen tilting (see Figures 2a–2e), after locating the center of a spherulite approximately on the optical axis of the TEM column. Then the specimen area used for taking the "untilted" SAED pattern was tilted in the TEM column by 50° around the vertical axis (*i.e.*, the axis parallel to the meridian, as indicated in Figure 2a), and another SAED pattern was recorded (Figures 2a′–2e′). The lattice spacing for each reflection observed in all SAED patterns was estimated, by calibrating the diffraction camera length with the aid

of the 111 reflection-ring from vapor-deposited Au (see Figure 2a). Major difference in reflection intensity of nylon crystals from pattern to pattern in Figure 2 is attributable to the difference in film thickness.

(1) N6 films (N6/N66 = 100/0). Figure 2a is a SAED pattern obtained at 0° (untilted) in which only one reflection-ring is observed. This reflection-ring is very sharp and has fairly uniform intensity distribution along the Debye-Scherrer circle. The lattice spacing of this reflection-ring was estimated at 0.411 nm. A weak, diffuse ring-like halo is observed just inside the reflection-ring. When the specimen-area used for Figure 2a was tilted around the vertical axis by 50°, the equatorial part of this sharp reflection-ring disappeared and the meridional part still remained, as shown in Figure 2a′. The four off-meridional parts on the same Debye-Scherrer circle increased in intensity, showing a four-point-like reflection. No other reflections, however, are observed in Figure 2a′. The lattice spacing of the reflection observed in Figure 2a′ was estimated at 0.410 nm. On the basis of the X-Ray diffraction experiments, Ohta *et al.*[16] reported that N6 films cast from solution in aqueous formic acid have the γ-form (monoclinic). In this work, the following lattice constants of N6 γ-form reported by Arimoto *et al.*[17] are cited: monoclinic ($P2_1/a$); a = 0.933 nm, b (chain axis) = 1.688 nm, c = 0.478 nm, β = 121°. The reflection ring (measured lattice spacing = 0.411 nm) in Figure 2a and the reflection (0.410 nm) in Figure 2a′ cannot be expected from the N6 α-form (monoclinic ($P2_1$); a = 0.956 nm, b (chain axis) = 1.724 nm, c = 0.801 nm, β = 67.5°),[18] and should be assigned to the 001, 200 and/or 20$\bar{1}$ reflections from the N6 γ-form.[16, 17]

(2) N66 films (N6/N66 = 0/100). Figure 2e is a SAED pattern obtained at 0° in which only one reflection-ring is observed. This reflection-ring is sharp and has fairly uniform intensity distribution along its Debye-Scherrer circle. The appearance of this reflection-ring is similar to that in Figure 2a, but the lattice spacing of this reflection was measured to be 0.438 nm. In Figure 2e, a weak, diffuse ring-like halo located just outside the sharp reflection-ring is recognized. When the specimen was tilted around the vertical axis by 50°, the equatorial part of this reflection-ring disappeared and the meridional part still remained (see Figure 2e′). The four off-meridional parts on the same Debye-Scherrer circle are well recognized in Figure 2e′, showing a four-point-like reflection: its lattice spacing was estimated at 0.433 nm. Weak broad reflection-arcs have appeared off-meridionally at the higher angle end of the halo observed in Figure 2e: the spacing of the arcs was measured to be 0.391 nm. The broad arcs are observable on the equator, but are not
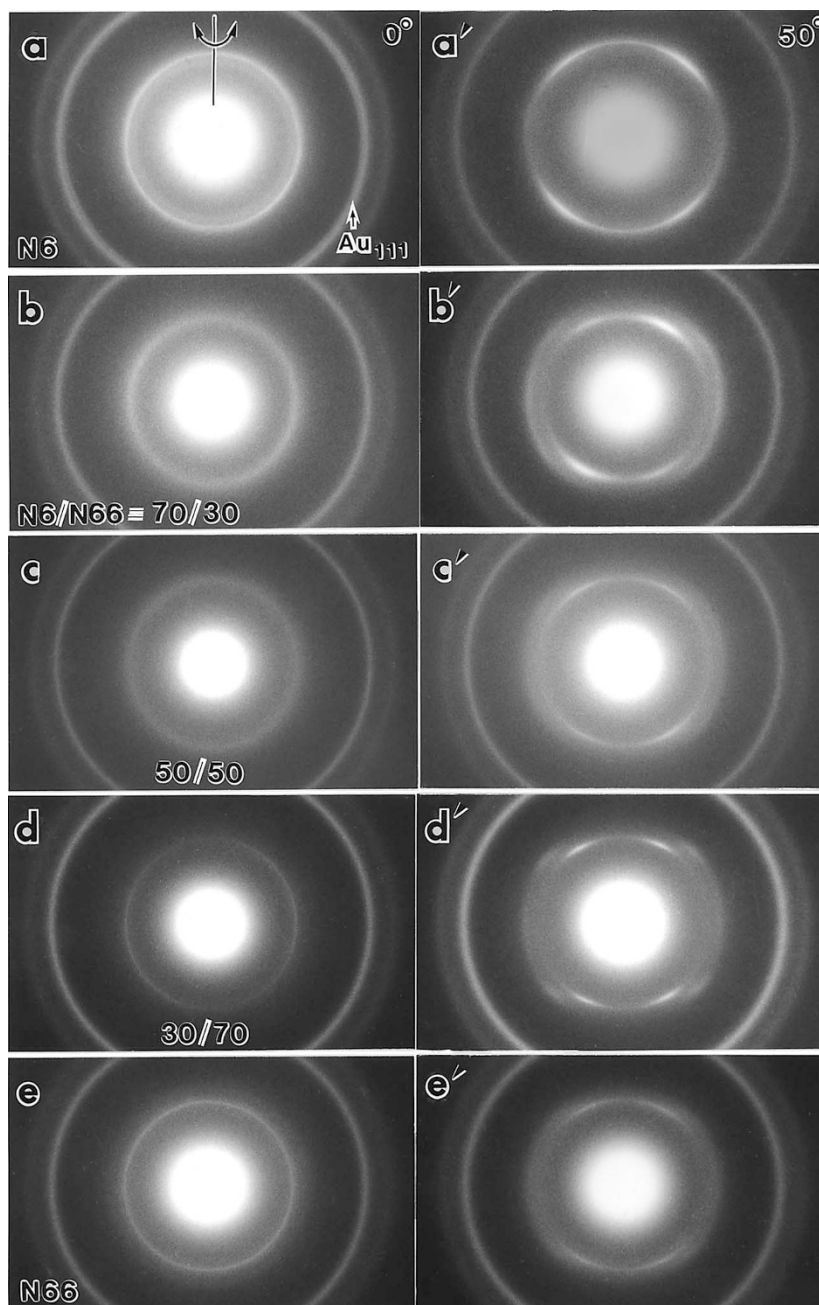
Figure 2. SAED patterns (0° (untilted) and tilted by 50°) taken from an 8-μm diameter specimen-area of each thin film which was as-cast from a 0.2 wt% solution in formic acid onto the surface of water thermostated at 65°C. Because all the specimens here were coated with vapor-deposited Au, the outermost two rings in each pattern are reflections from Au, as marked in (a). Each specimen film was tilted around the vertical axis of the figure, as indicated in (a). (a) N6, namely N6/N66 = 100/0; untilted (0°), (a′) tilted by 50°. (b) N6/N66 = 70/30; untilted (0°), (b′) tilted by 50°. (c) N6/N66 = 50/50; untilted (0°), (c′) tilted by 50°. (d) N6/N66 = 30/70; untilted (0°), (d′) tilted by 50°. (e) N66, namely N6/N66 = 0/100; untilted (0°), (e′) tilted by 50°.

recognized on the meridian.

Judging from the measured lattice spacings of the sharp reflections (0.438 nm at 0° (untilted) and 0.433 nm at 50°) and that of the weak broad arcs (0.391 nm at 50°), it was confirmed that the sharp reflections and the broad arcs are respectively the 100 reflection and the combined $010 + 110$ one of N66 α-form (triclinic ($P\bar{1}$); $a = 0.49$ nm, $b = 0.54$ nm, c (chain axis) $= 1.72$ nm, $\alpha = 48.5°$, $\beta = 77°$, $\gamma = 63.5°$),[19] as already reported in the case of N66 thin films as-cast

from solution[14, 15] and melt-crystallized[11] and also in the case of unoriented N66 prepared for X-Ray diffraction.[19] Our experimental result, as demonstrated in Figrues 2e and 2e′, is basically similar to the results reported before,[14, 15] in which in the case of as-cast N66 films, the outer combined $010 + 110$ reflection weaker than the 100 one was clearly recognized only when the specimen film was tilted, for example, by 45° in a TEM column. On the other hand, melt-crystallized thin films of N66 gave undoubtedly the $010 + 110$ reflection-ring

without specimen tilting although this ring was weaker and somewhat broader than the innermost 100 one.[11] No 00*l* reflections were recognized, even in this study (see Figures 2e and 2e′).

(3) Blend films of N6/N66 = 50/50. Figures 2c and 2c′ are SAED patterns obtained from the same specimen at 0° (untilted) and at 50°, respectively. In Figure 2c, one broad reflection-ring (measured lattice spacing = *ca.* 0.44 nm) is observed. When the specimen was tilted by 50°, a SAED pattern (Figure 2c′) similar to Figure 2e′ was obtained. The spacings of the inner arcs and of the outer broad ones were, respectively, estimated at 0.434 nm and about 0.38 nm. These are here assigned provisionally to the 100 reflection and to the 010 + 110 one of N66 α-form, respectively, by extending the result obtained for N66 (N6/N66 = 0/100) films (this extension is also applied to the other blends (namely, N6/N66 = 70/30 and 30/70)). The broad reflection-ring (*ca.* 0.44 nm) in Figure 2c is also provisionally assigned to 100 of N66 α-form. (As mentioned below in Concluding Remarks, these reflections might come from the N6 α-form[18] and/or the N66 β-form.[19] Such possibility should, of course, be considered also for the blends of N6/N66 = 70/30 and 30/70.) It is, however, noted that no reflections assigned to the N6 γ-form were recognized although several SAED patterns were recorded from the films of N6/N66 = 50/50 in which the content of N6 was 50 wt%.

(4) Blend films of N6/N66 = 70/30. SAED patterns (Figrues 2b and 2b′) obtained from these films are very similar to those (Figrues 2c and 2c′) obtained from N6/N66 = 50/50, respectively. The SAED pattern in Figure 2b′ is similar to that in Figure 2e′, but the inner reflection-arc in Figure 2b′ is broader than that in Figure 2e′. This result seems to indicate the smaller crystallite size and/or the considerable lattice distortion of crystallite in the blends of N6/N66 = 70/30. The lattice spacing of the broad reflection-ring in Figure 2b obtained at 0° (untilted) is about 0.44 nm. In Figure 2b′ obtained at 50°, the spacings of the inner intense arc and of the weak broad one are respectively 0.438 nm and about 0.37 nm. Accordingly, the intense arc-shaped reflection and the weak broad one are provisionally assigned, respectively, to 100 and 010 + 110 reflections of N66 α-form. The broad reflection-ring (*ca.* 0.44 nm) in Figure 2b is also provisionally assigned to 100 of N66 α-form, as in the case of the blend films of N6/N66 = 50/50. No reflections assigned to the N6 γ-form were recognized for the blend films of this composition in spite of the large content of N6 component (70%).

(5) Blend films of N6/N66 = 30/70. SAED patterns (Figures 2d and 2d′) obtained from these films are apparently similar to those (Figures 2e′ and 2e′) obtained from N66, respectively. In Figure 2d, however, a diffuse halo is not observed. The lattice spacing of the partly oriented but almost ring-like sharp reflection in Figure 2d obtained at 0° (untilted) is estimated at 0.437 nm. In Figure 2d′ obtained at 50°, the measured spacing of the inner sharp arc and that of the weak broad one are respectively 0.433 nm and 0.379 nm. Accordingly, the sharp reflections (0.437 nm at 0° and 0.433 nm at 50°) and the weak broad one (0.379 nm) are assigned, respectively, to the 100 reflection, taking account of the composition (N6/N66 = 30/70), and provisionally to the 010 + 110 one of N66 α-form. For this composition, any reflections assigned to the γ-form of N6 were not recognized.

CONCLUDING REMARKS

Thin films of nylon-6 (N6), nylon-6,6 (N66) and their blends (N6/N66 = 70/30, 50/50, and 30/70) were prepared by casting each solution (0.2 wt%) in formic acid onto the surface of water thermostated at 55, 65, or 75°C. Among the three temperatures, 65°C was found to be the optimal temperature for all the blend compositions when the solution concentration was fixed to be 0.2 wt%. All specimen films (N6/N66 = 100/0, 70/30, 50/50, 30/70, and 0/100) were undoubtedly crystalline, judging from SAED, and had the fibrillar entities. All the films evidently showed spherulitic textures. A tilting series (0° and 50°) of SAED patterns obtained from a film of N6 (N6/N66 = 100/0) revealed that such a film of N6 as-cast from its solution in formic acid consists of γ-form crystallites. SAED patterns obtained from an as-cast film of N66 (N6/N66 = 0/100) were well identified to be the α-form of N66. In the SAED patterns obtained from as-cast blend films, however, no reflections assigned to the γ-form of N6 were recognized. N66 component has a certain depression effect on the formation of γ-form crystallites of N6 in thin blend films as-cast from solution in formic acid.

For all the blend films of N6 and N66, the two reflections corresponding to the lattice spacings of 0.37–0.38 nm and 0.433–0.44 nm were observed, and were provisionally assigned, respectively, to the 010 + 110 reflection and the 100 one of N66 α-form by extending the result obtained for N66 (namely, N6/N66 = 0/100), in Part (3) through Part (5) of Results and Discussion. It should be remembered, however, that the N6 α-form[18] also gives two reflections with comparable lattice spacings of 0.36–0.37 nm (002 + 202 reflection) and of 0.44 nm (200 one).[11] Therefore, the two reflections in question, which were observed for the blend films, most likely indicate that both N6 and N66 crystallized in their respective α-forms in the blend films,

Table I. Crystal forms of N6 and N66 in their blend films as-cast from solution in formic acid onto water surface thermostated at 65°C

Composition (N6/N66)	100/0	70/30	50/50	30/70	0/100
Crystal form[a] N6	γ	(α)	(α)	[α]	—
N66	—	[α]	(α)	(α)	α

[a]A probable crystal form is designated in parentheses, but has not yet been identified crystallographically. An assumed crystal form is indicated in the square brackets. To make this table, the compositions were taken into consideration.

as summarized in Table I by taking the compositions into account. At the present stage, however, the possibility of N66 β-form (triclinic ($P\bar{1}$); $a = 0.49$ nm, $b = 0.80$ nm, c (chain axis) $= 1.72$ nm, $\alpha = 90°$, $\beta = 77°$, $\gamma = 67°$)[19] might not be disregarded for the blend films when they are made by casting from solution in formic acid.[21] Although the β mesomorphic form of N6 has recently been reported for melt-spun fibers,[20] this β-form of N6 was disregarded in this study by judging from our method of specimen preparation (namely, a solution-casting method). More study is, of course, needed for further detailed structural analysis of the blend films.

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