Melting and Recrystallization of PA-6/PA-66 Blends

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SYNOPSIS

The morphology of a number of polyamides (PA)—namely, PA-66, PA-6/PA-66 blends, and PA-6/PA-66 copolymers—prepared from HCOOH solution and from the melt has been examined as well as the effect of annealing. In the blends, the PA-6 crystallizes within the PA-66 spherulites. When prepared from HCOOH solution at 25°C, the PA-66-containing samples show a large exothermic peak before the sample melting peak is observed by DSC. This exothermic peak, which cannot be fully explained by previously known observations, PA recrystallization, and/or the morphology changes we describe here, is not seen for PA-6 or for PA-66 prepared from HCOOH solution at 100°C. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In a previous paper,[1] we discussed the crystallization and melting behavior of laminates and solution-prepared blends of polycaprolactam (PA-6) and polyhexamethylene–adipamide (PA-66). Although they did not cocrystallize readily, their at least partial miscibility in the melt and possible co-incorporation as crystal defects caused reductions of the melting temperatures and heats of fusion of both polymers. The crystallization temperature of PA-6, however, increased with increasing PA66, a feature attributed to nucleation of PA-6 by PA-66.

Structural changes of polyamides have been studied by several authors. Starkweather[2] found that PA-66, crystallized from solution in methanol and in other solvents, exhibits a small diffuse endotherm extending roughly between 130 and 230°C, which he associated with the Brill transition as previously described for melt-crystallized PA-66.[3] Murthy et al.[4] observed in melt-crystallized PA-6 a crystalline relaxation between T_g and T_m, which they suggested to be similar to the Brill transition. Whereas in PA-66 the Brill transition is associated with an expansion of the H-bond plane spacing so that $a = \sqrt{3}c$, i.e., to a pseudohexagonal cell, the transition in PA-6 was suggested to be a transition from a monoclinic structure to a new structure, which they suggested is also most likely monoclinic. Similarly, Xenopoulos and Wunderlich[5] suggested, on the basis of thermal analysis and X-ray diffraction, that a conformational disorder in PA-66 begins gradually above room temperature, characterized by a packing change in the crystal. A small endothermic peak similar to that described by Starkweather was seen only in solution-crystallized samples. No DSC peak associated with the Brill transition has been reported for melt-crystallized PA-66 or PA-6.

In this paper, we describe the unusual melting and recrystallization behavior of PA-66, its blends with PA-6, and its copolymers with PA-6 in samples prepared by evaporating HCOOH solutions at 25°C. Similar melting behavior was described by Cojazzi et al.[6] for PA-12, but their explanation, based on the transition from the α to the γ phase, cannot be applied to our results. We also describe the morphology and behavior of the PA blends crystallized from the melt.

EXPERIMENTAL

Materials

Measurements were performed with commercial samples of PA-6 (Amilan-Toray Co. and Zytel DuPont Co.) and PA-66 (DuPont). Melt-prepared blends of PA-6/PA-66 and copolymers of PA-6 with

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PA-66 were obtained by courtesy of Dr. A. Elia of DuPont. Solution-crystallized PA-6, PA-66, and PA-6/PA-66 blends were prepared by evaporating fresh HCOOH (85-90%) solutions at 25 or 100°C and drying for 16 h *in vacuo* at 25°C.

Melting

The course of melting was investigated using a Perkin-Elmer DSC-4 with sample weights of 4-8 mg and a heating rate that, unless otherwise stated, was 20°C/min.

X-ray Diffraction

X-ray diffraction scans were done using a Scintag X-ray goniometer with a heating stage. The CuKα radiation was Ni-filtered and detected by a Ge solid-state detector. Measurements at higher temperatures were performed in a N_2 atmosphere.

Morphology Examination

For morphology examination, a drop of 0.05% HCOOH solution was evaporated either on a carbon film-coated electron microscope grid or on a glass slide at 25°C, shadowed by Pt/C and, in case of the glass slide, the replica (shadowing) removed using poly(acrylic acid). Annealing experiments were performed with PA samples on glass slides in a mineral oil bath. The free surfaces of melt-prepared PA-6, PA-66, and PA-6/PA-66 blend sheets were examined by replication at room temperature and, in some cases, by shadowing at elevated temperatures *in vacuo* followed by PAA stripping of the replica at room temperature.

RESULTS AND DISCUSSION

Melting of Solution-prepared Samples

Melt-crystallized PA-6/PA-66 blend samples, regardless of their previous history (solution or melt), exhibit separate crystallization and melting peaks, as expected for essentially immiscible polymer blends.[1] The PA-66 component always shows two distinct melting peaks, the smaller one at a lower temperature. However, substantially different behavior was observed when directly measuring the melting course of samples prepared from the HCOOH solution at 25°C. Some typical examples of the 1 : 1, 4 : 1, and 1 : 4 PA-6/PA-66 blends and 1 : 9 PA-6/PA-66 copolymer are shown in Figures 1-4. Surprisingly, one can see marked exothermic
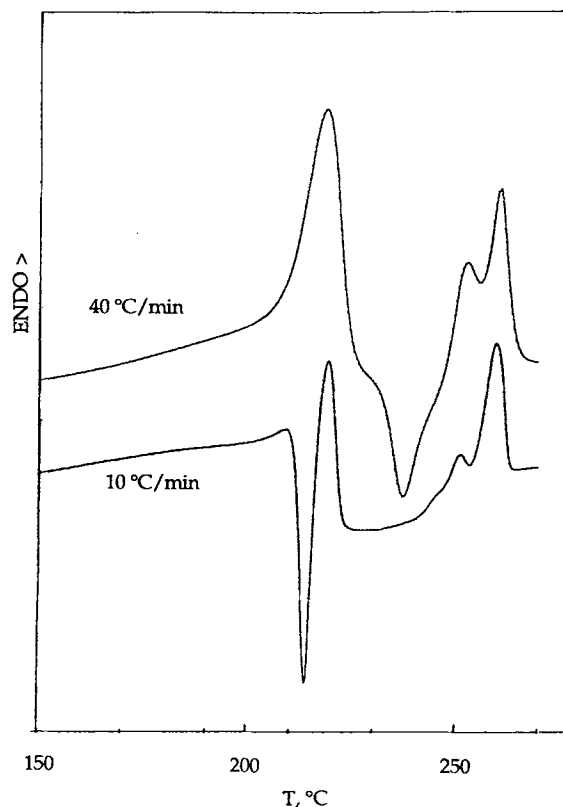

Figure 1 DSC melting scans of the PA-6/66 1 : 1 blend prepared by evaporation of the 0.5% HCOOH solution at 25°C.

peaks before melting. This indicates that a crystallization or recrystallization event takes place before melting. With slower heating rates ($< 20°C/min$), the exothermic peak starts before the PA-6 component melting. At higher heating rates, the PA-6 component melts before the exothermic peak appears.

The shape of the melting curves depends also on the blend composition. As can be seen in Figures 1-4, the area of the exothermic peak(s) is proportional to the PA-66 content. It seems that there is actually one deep and broad exothermic peak that competes with the endothermic melting peak of PA-6 (which takes place in the range 190-220°C), depending on the heating rate and PA-6 content in the blend.

In copolymers of PA-6 and PA-66, we see only one melting peak, as expected, but, again, in HCOOH-prepared samples, a broad exothermic peak appears before melting. The assumption that the exothermic peak is due to PA-66 alone was confirmed by measuring pure PA-66 (Fig. 5). PA-6 alone, on the other hand, melts in a normal way. The exothermic peak in PA-66 melting, we suggest,
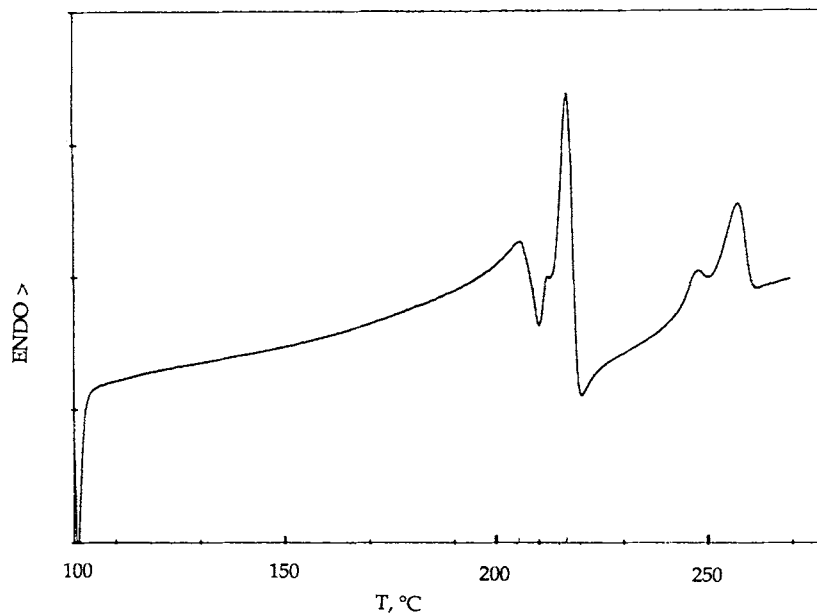
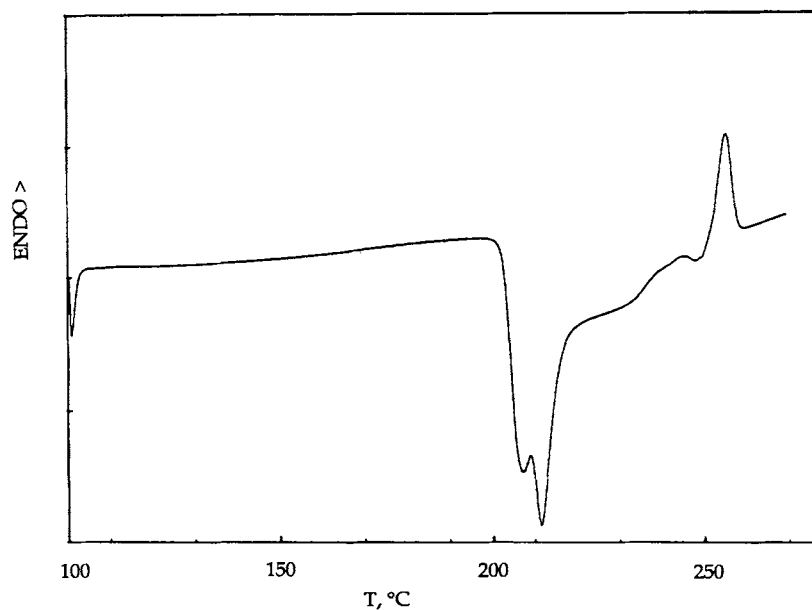**Figure 2**   DSC melting scan of the PA-6/66 4 : 1 blend prepared from HCOOH solution at 25°C. Heating rate 20°C/min.

is due to some specific PA-66–HCOOH interaction. It is found also in PA-66-rich PA-6/66 copolymers. It is not related to eventual differences in residual water or HCOOH because TGA measurements of solution and melt-prepared samples of PA-6, PA-66, and 1/1 PA-6/PA-66 blend did not reveal any substantial differences in weight loss during heating

the samples 10°C/min from 25 to 300°C. The PA-66 exothermic peak in the melting run is also not simply related to the use of an aqueous acidic solvent, because although it was seen in PA-66 samples precipitated from HCOOH solution at 25°C by adding an excess of water, it is absent when precipitating a solution of PA-66 in concentrated H_2SO_4 in a sim-

Figure 3   DSC melting scan of the PA-6/66 1 : 4 blend prepared from HCOOH solution at 25°C. Heating rate 20°C/min.
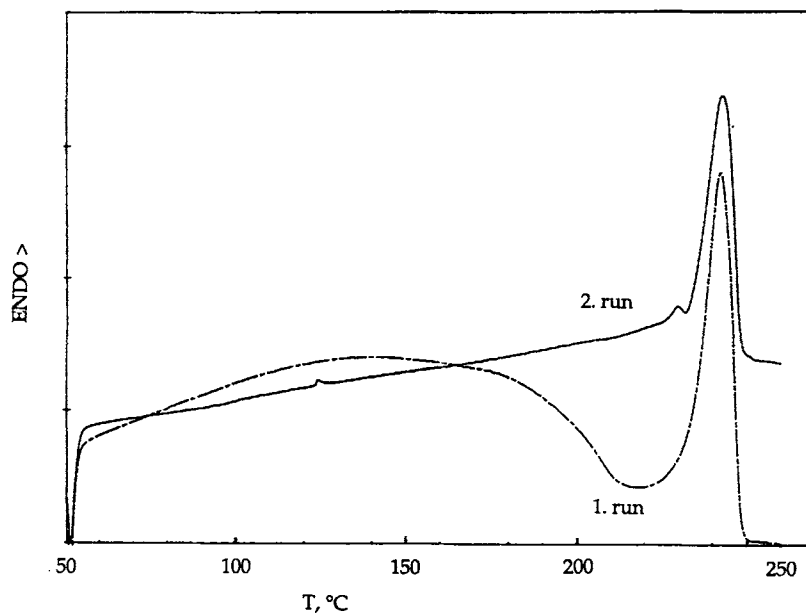
Figure 4   DSC melting scan of the 1 : 9 PA-6/66 copolymer prepared from HCOOH solution at 25°C. Heating rate 20°C/min.

ilar fashion. In addition, by evaporating HCOOH from PA-66 (or PA-6/PA-66) solutions at temperatures of 100°C and higher, no exothermic peak during melting could be observed. Annealing the sample prepared at 25°C at temperatures above 100°C leads to the diminishing and, finally, to the disappearance of the exothermic peak. It is obvious that two main factors play a role in the unusual PA-66 melting: (1) preparation from HCOOH solution

and (2) a temperature close to 25°C. The PA-66 structure formed at 25°C is unstable and changes to the common stable PA-66 structure at higher temperatures.

X-ray Diffraction

To obtain more information on the unstable structure of PA-66 as a homopolymer and in its blends and copolymers with PA-6, we measured the wide-
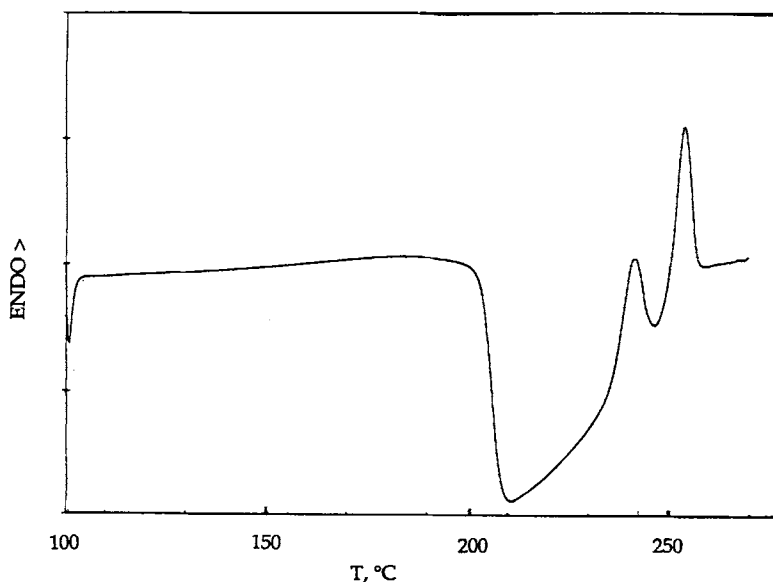

Figure 5   DSC melting scan of the PA-66 sample prepared from HCOOH solution at 25°C. Heating rate 20°C/min.
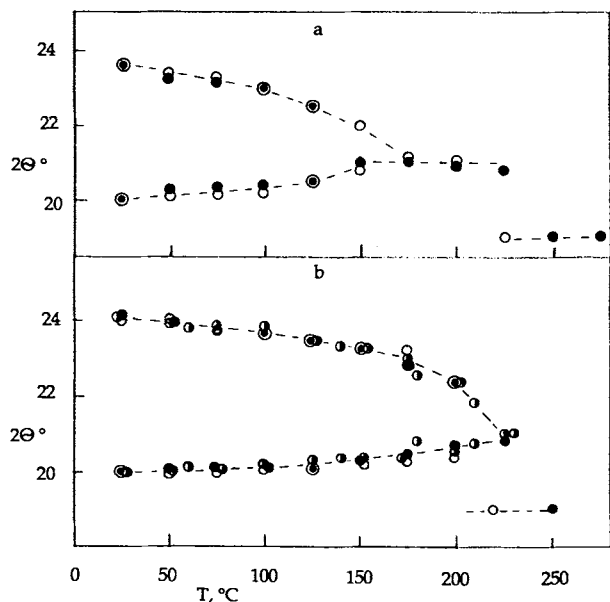
Figure 6 Changes of the 2θ positions of the two strongest PA diffraction peaks with increasing temperature: (a) melt-crystallized (O) PA-6 and (●) PA-66; (b) HCOOH solution-prepared (O) PA-6, (●) PA-66, and (◉) PA-6/66 1/1 blend.

angle X-ray diffraction spectra of PA-6, PA-66, and the PA-6/PA-66 1 : 1 blend prepared both from the melt and HCOOH solution. The diffraction spectra were measured at various temperatures in the range 25–250°C. The spectra of all samples were characteristic of the stable α-modifications (monoclinic for PA-6 and triclinic for PA-66).

Figure 6 shows the changes in the 2θ positions of the two main polyamide diffraction peaks measured stepwise at various temperatures, starting from 25°C. Comparing the samples prepared from the melt and from 25°C HCOOH solution, one may notice two important differences: The solution-prepared samples have the d-spacing that corresponds to the H-bonded sheets (higher 2θ values in Fig. 6), almost 3% smaller than that of the melt-crystallized samples. In addition, it is well known that polyamides, in general, including PA-6 and PA-66, tend to transform at higher temperatures to the pseudohexagonal γ-modification; this is defined as the Brill transition.[3] In PA-66, this transition is characterized by the gradual approaching of the two strongest PA reflections and their merging into a single one at about 160°C. This can be seen in Figure 6(a) for melt crystallized samples of both pure PA-6 and PA-66. The points on the lowest line, at temperatures above 220°C, correspond to melt peaks. The solution-prepared samples, on the other hand,

have a much lower tendency to undergo this transition; PA-6 does not transform completely to γ-modification at all and the PA-66 and PA-6/PA-66 blend samples do so at much higher temperatures (225°C) than do the melt-crystallized samples.

When we heated the solution-prepared samples to temperatures corresponding to the DSC exothermic peak (205–230°C) and cooled them down to 25°C, we obtained d-spacings corresponding to the usual melt-crystallized samples. It is clear that during the process giving rise to the exothermic peaks only the crystal cell dimensions change, i.e., the c-spacing mainly increases. The a and b (molecular axis) spacings remain practically unchanged. The phase change observed by X-ray diffraction proceeds gradually over a wide temperature range and is not visible in the DSC scans. However, we have to realize that the methods of sample heating differ widely in the two cases. The DSC and X-ray results for solution-prepared PA-6 samples differ significantly in that in DSC scans no significant phase change or transformation prior to melting takes place, whereas by X-ray, there is a phase change similar to that observed for the PA-66. This difference between the PA-6 and PA-66 melting behavior remains to be explained.
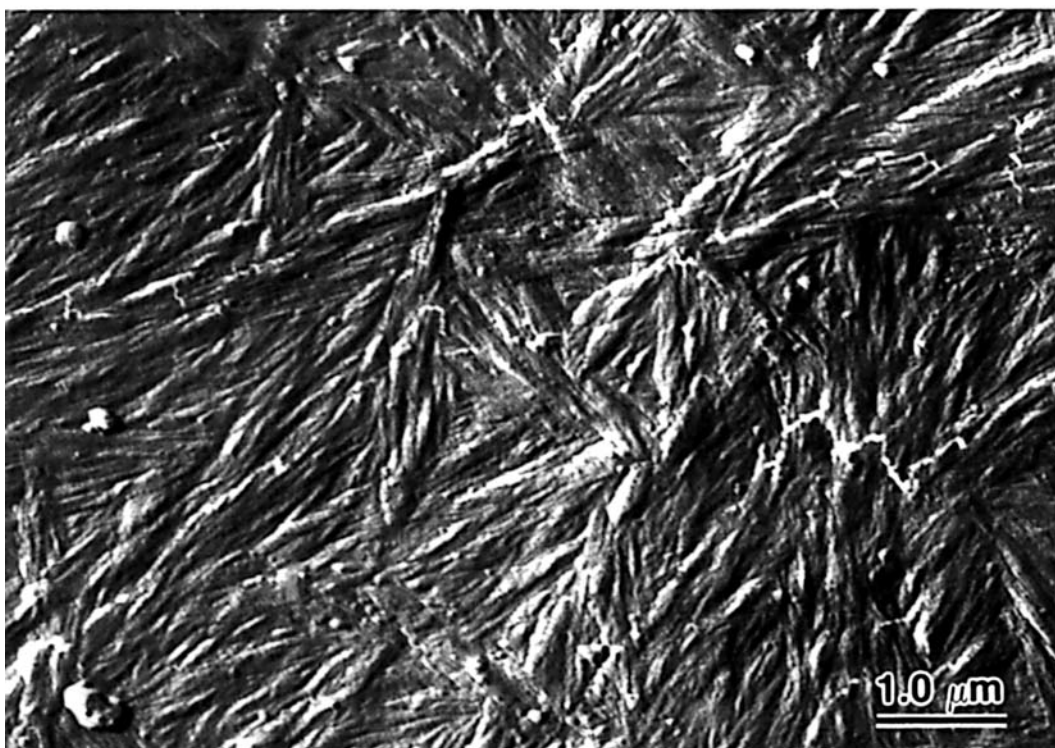
Morphology

Melt-crystallized samples of PA-6, PA-66, and their blends and copolymers are characterized by a lamellar or fibrillar spherulite morphology of similar appearance such that one cannot distinguish the individual polymers (Fig. 7). Crystallization from solutions may lead to lamellar single crystals or more complex fibrillar, lamellar, sheaflike, or spherulite structures according to solvent concentration and crystallization conditions.[7]

The morphology of the individual homopolymers and their blends and copolymers prepared by evaporation of dilute (0.01–0.5%) HCOOH solution at 25°C differs from place to place on the same grid as well as with the sample preparation (Fig. 8). One can observe lamellar spherulites of various shapes and thicknesses and, in addition to this, also globular particles. The same type of structures are observed when the samples are prepared by dropping the PA solution in HCOOH on a water surface (8 g). The shape of the globules may vary from relatively smooth spheres to less regular lamellar stacks and some appear to be hollow.

As both PAs can form both lamellar or globular morphologies, it is not possible to simply attribute a specific type of morphology to an individual poly-
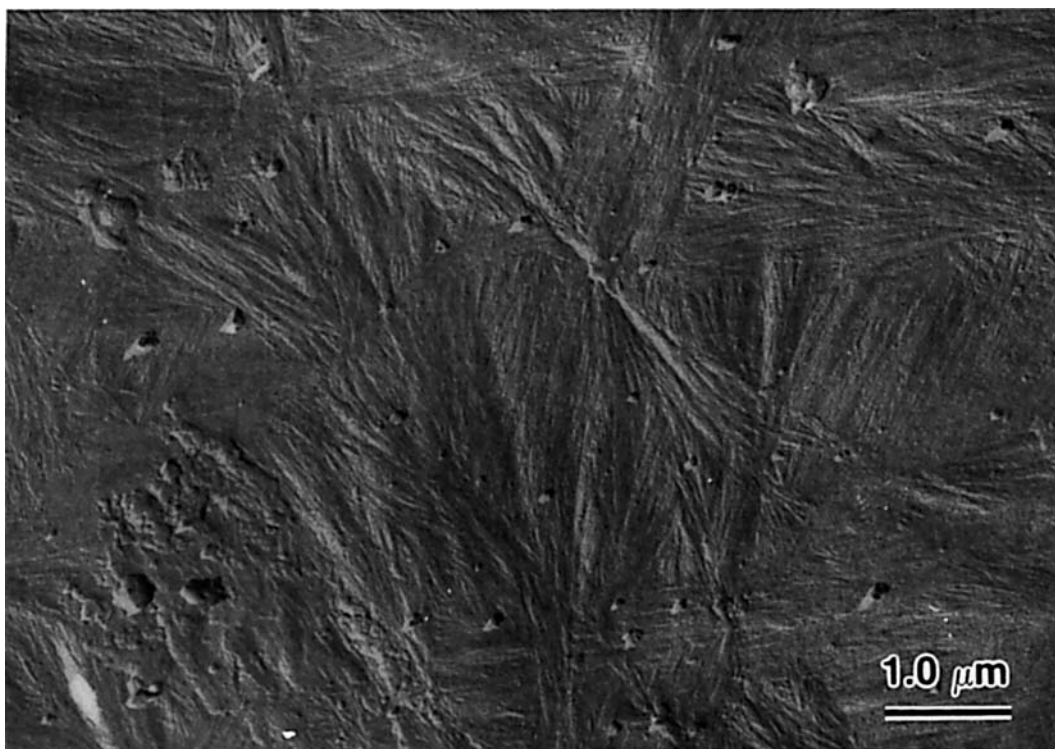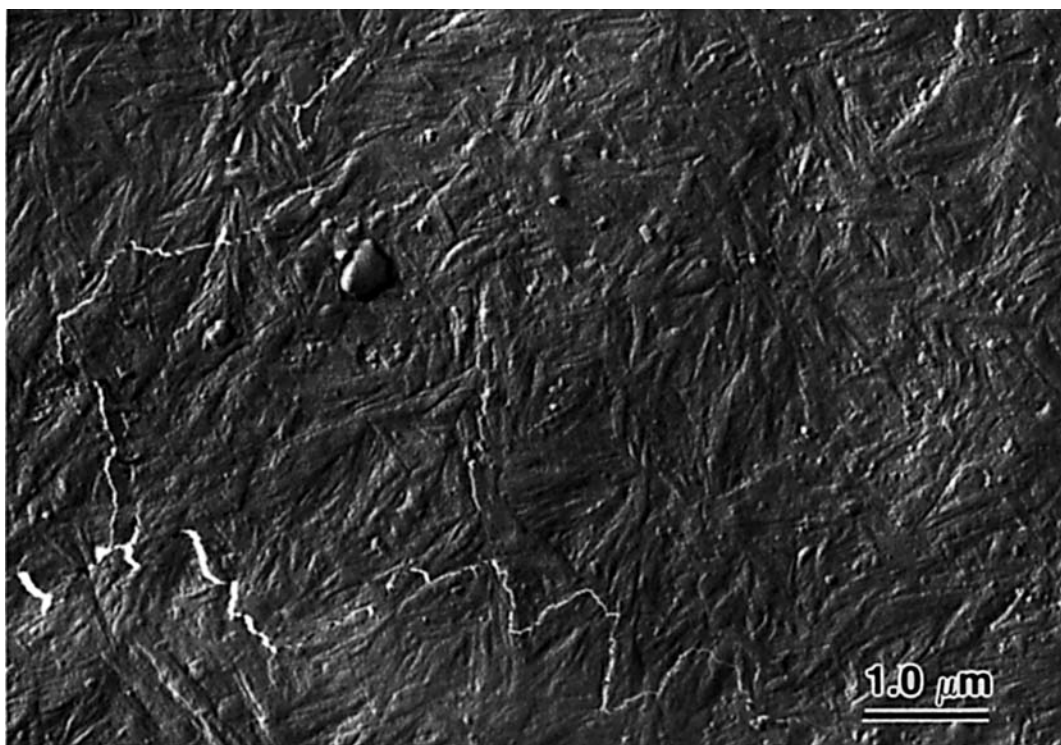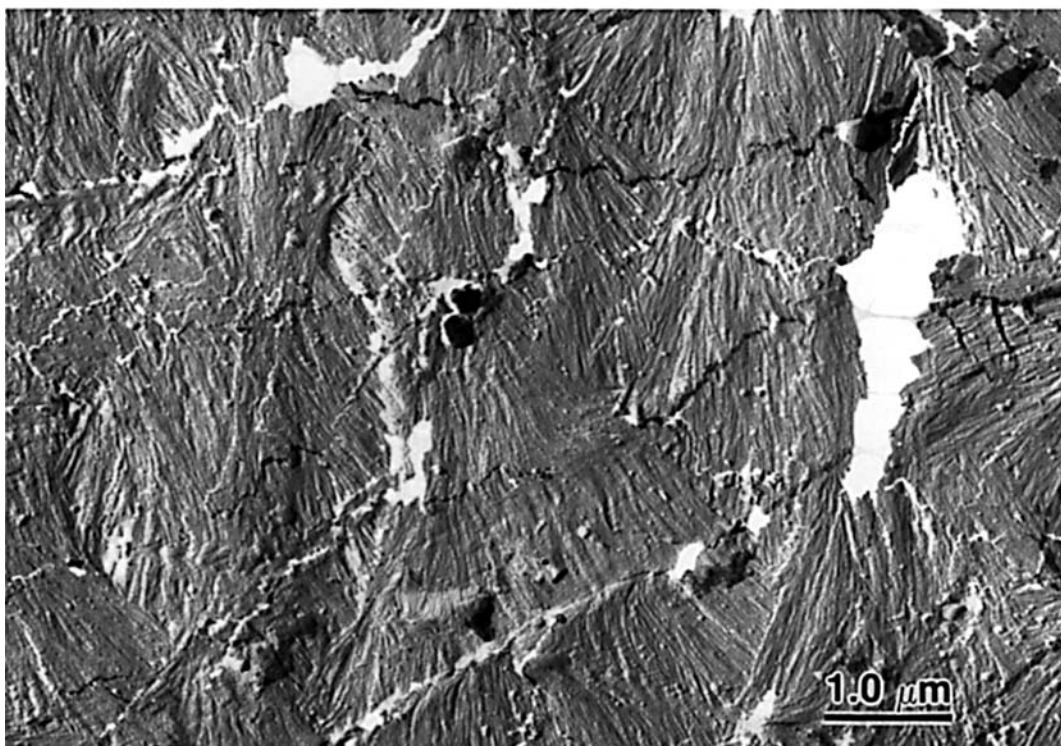
(a)

(b)

Figure 7   Free surface of melt-crystallized samples: (a) PA-6; (b) PA-66; (c) PA-6/66 1 : 1 blend; (d) PA-6/66 1 : 3 copolymer.
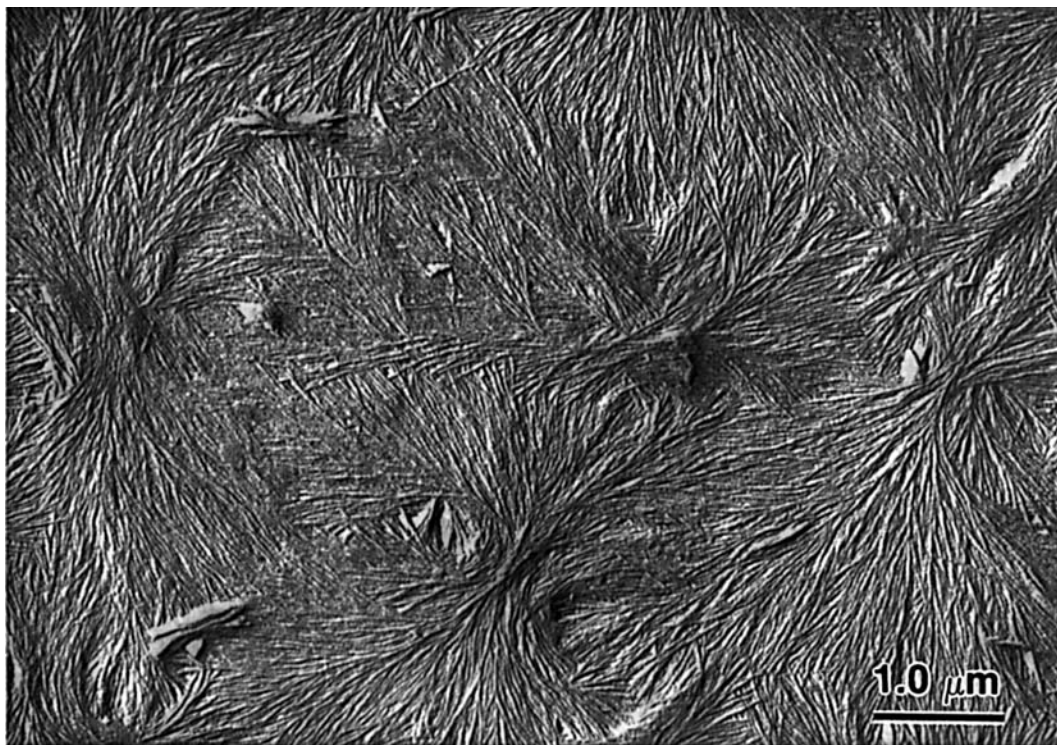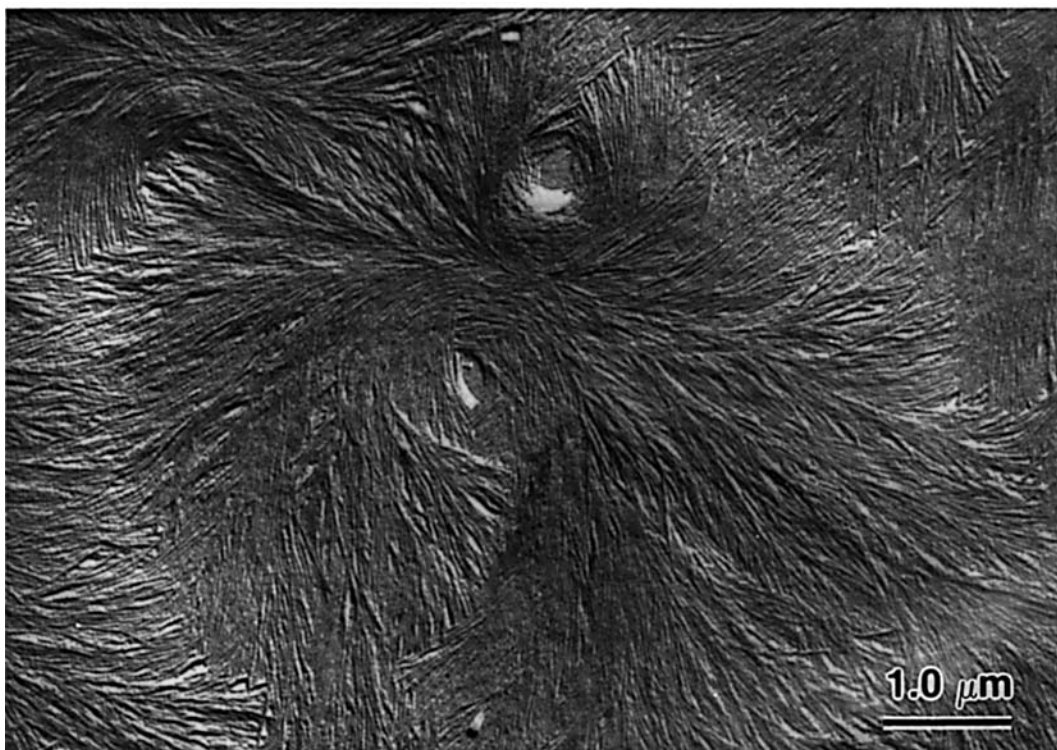
(c)

(d)

Figure 7   (*Continued from the previous page*)

mer in the blend. All this suggests that PA-6 and PA-66 can take part side by side in common morphological formations. In the following, we will be dealing only with spherulite structures such as shown in Figure 8 (a–d) because they closely resemble the structures of melt-crystallized samples.

(a)

(b)

Figure 8   Morphology of PA samples prepared by evaporating a 0.05–0.1% HCOOH solution at 25°C: (a) PA-6; (b) PA-66; (c) PA-6/66 1 : 1 blend; (d) PA-6/66 15 : 85 copolymer; (e) PA/66 1 : 1 blend; (f) PA-66 from 0.005% solution; (g) PA-6/66 precipitate on a water surface.
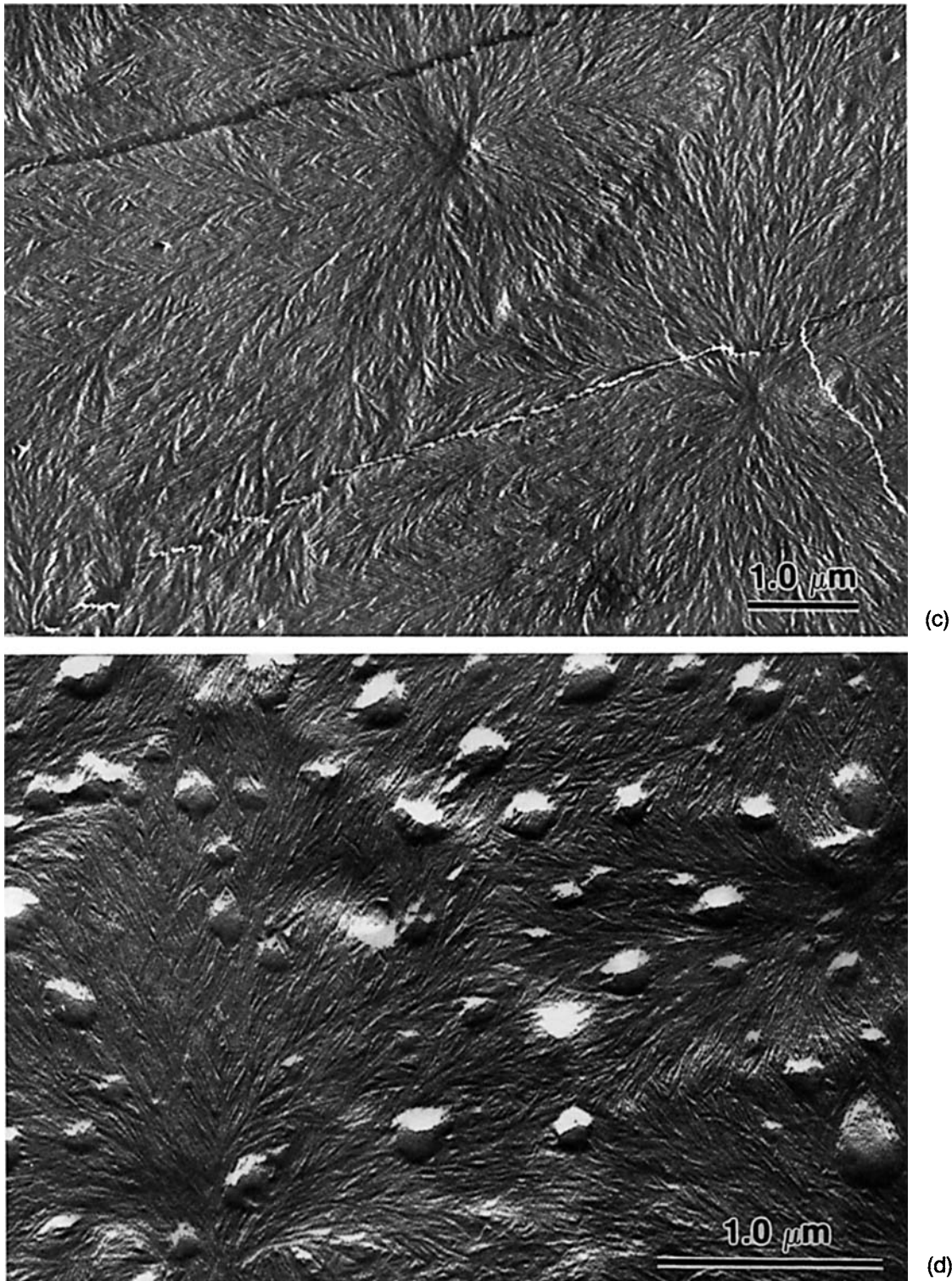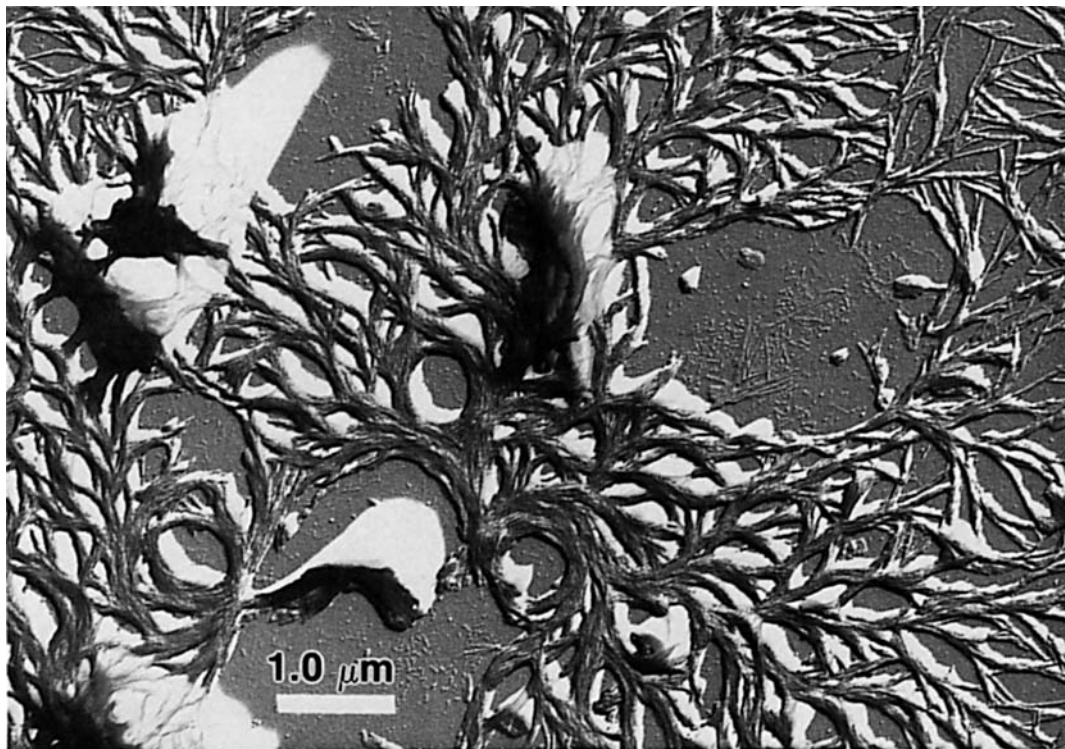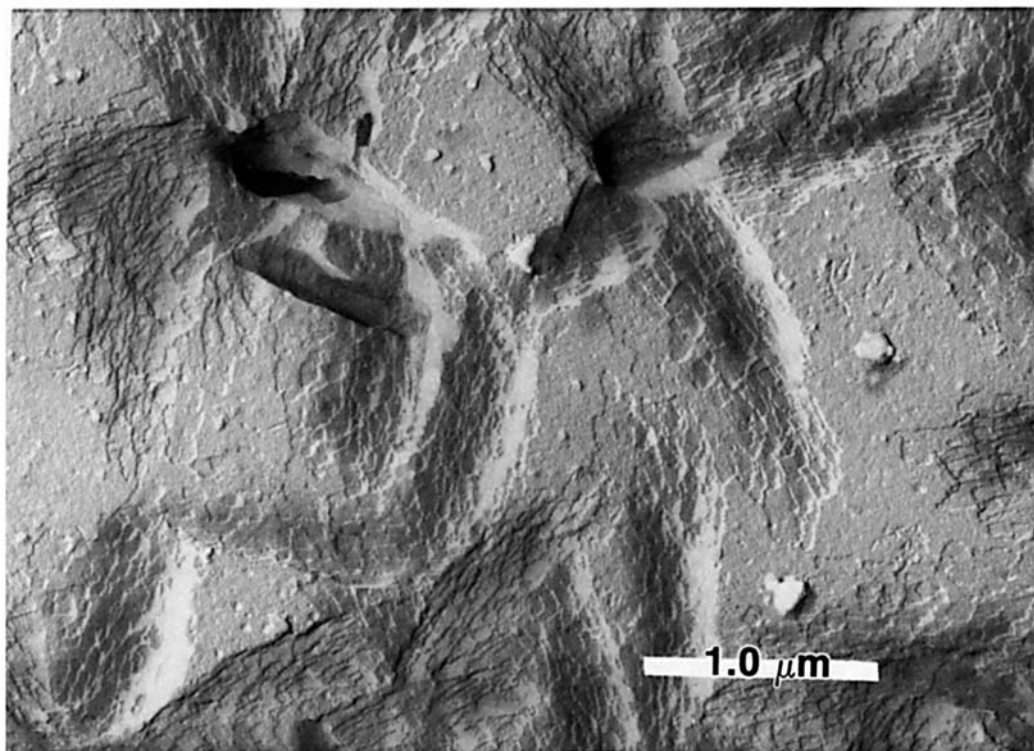
(c)

(d)

Figure 8   (*Continued from the previous page*)

Annealing Solution-prepared Samples

Samples prepared from HCOOH solution at 25°C were annealed 5 min at various temperatures in a mineral oil bath, cooled to room temperature, washed in heptane, Pt/C shadowed, and, after replication, examined in the transmission electron microscope. The morphology of PA-6 and PA-66 ho-

(e)

(f)

Figure 8   *(Continued from the previous page)*

mopolymers did not differ from that of their 1 : 1 blend shown for various annealing temperatures in Figure 9. In all cases, the basic spherulite texture remained unchanged. At annealing temperatures of 200 and 225°C, where the PA-6 component was partially or completely melted, only minor changes could be observed after cooling. The lamellar edges were smoothed, and at 225°C, there were some void
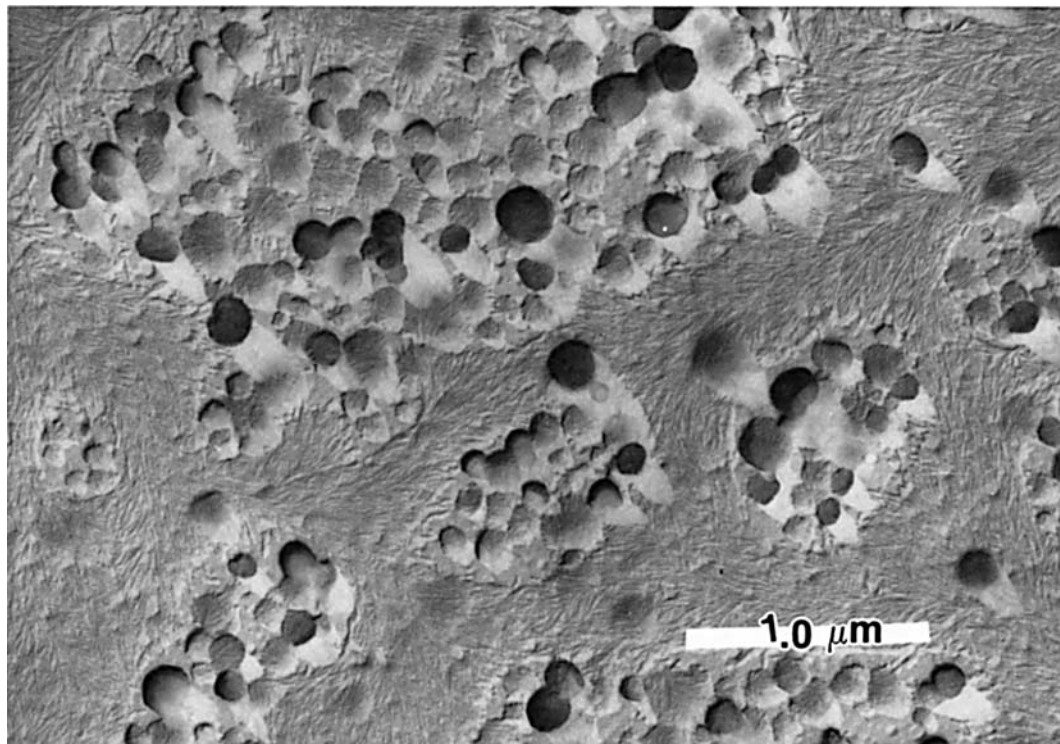
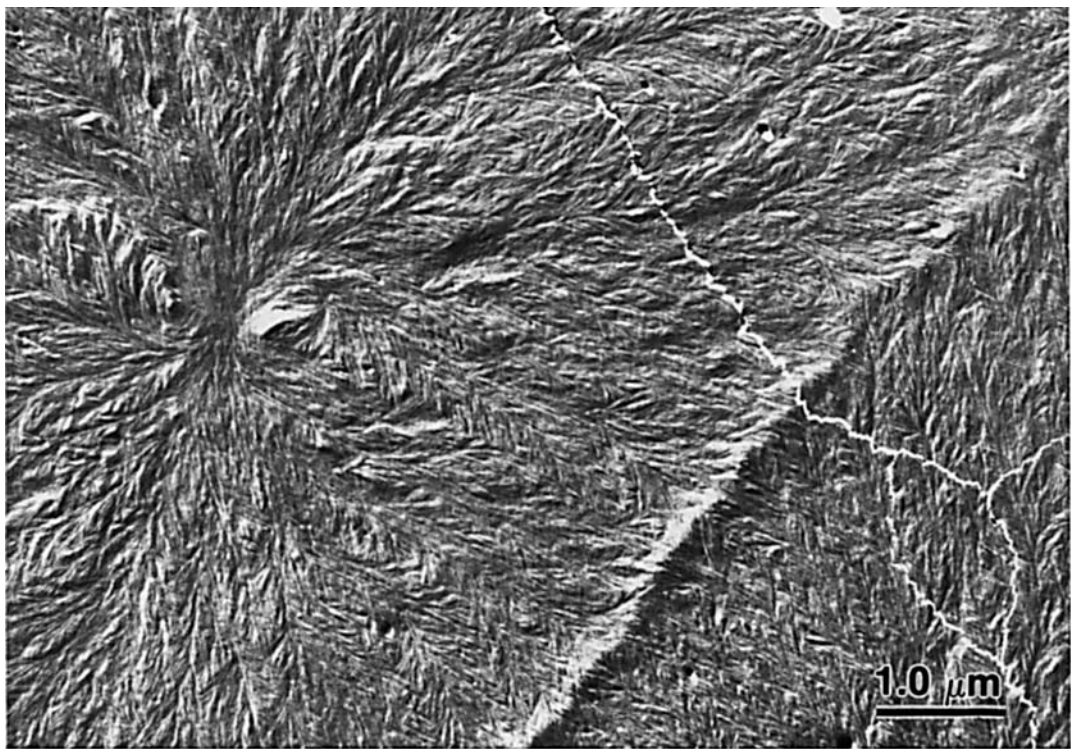**Figure 8** *(Continued from the previous page)*

spaces within the spherulite. In no case did we observe larger domains that could be attributed to the previously molten and separately recrystallized PA-6 component. Apparently, during cooling, the PA-6 crystallized on the surface or in the interstices of PA-66 lamellae.

To locate the relative positions of the PA-6 and PA-66 blend components in common spherulites, we heated melt-prepared PA-6/PA-66 blends to 220–230°C in a vacuum evaporator and shadowed them at this temperature. In this way, we obtained information on the still-crystalline PA-66 component and the molten PA-6 phase. Figure 10 shows that the spherulites of the blend are composed at 225°C of long, relatively isolated PA-66 lamellae with featureless space in between, which we presume is the location of molten PA-6 and lower-melting PA-66 components. This picture is in agreement with our previous results indicating that in melt crystallization of PA-6/PA-66 blends the PA-66 component crystallizes first, forming long, separate lamellae that, at a lower temperature, serve as nucleation substrates for PA-6.[1] In this way, a common spherulitic blend morphology forms. We assume a similar situation exists also in crystallization from solution by solvent evaporation, i.e., one of the com-

ponents crystallizes first, with the other filling intervening spaces.

CONCLUSIONS

Our results conclusively show that when samples of PA-66 and its blends or copolymers with PA-6, prepared from HCOOH solution at 25°C, are melted, a large exothermic peak appears before actual PA-66 melting. This behavior is not seen with PA-6 alone. X-ray evidence shows that the PA structure prepared from 25°C HCOOH solution differs from that observed in regular melt-crystallized samples. However, this new, more tightly packed crystal structure is seen in both PA-66 and PA-6 as well in its blends. Morphological investigations revealed that in blends crystals from both the melt and solution PA-66 component crystallizes first in a loose lamellar framework, which, at lower temperatures, serve as nucleation substrates for PA-6. No morphology differences were observed that could be directly related either to the DSC exothermic peak or the crystal change observed by X-rays. Thus, at this time, we have no explanation for the origin of the exothermic peak or differences in cell dimensions of solution-prepared and melt-crystallized polyamides.
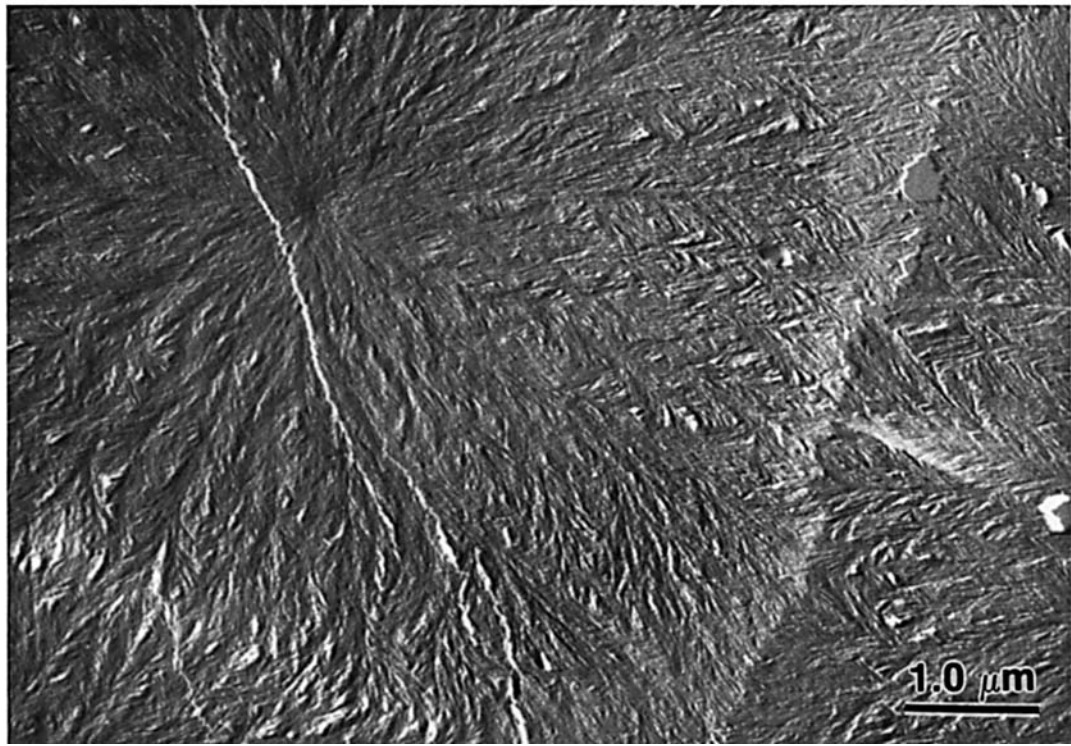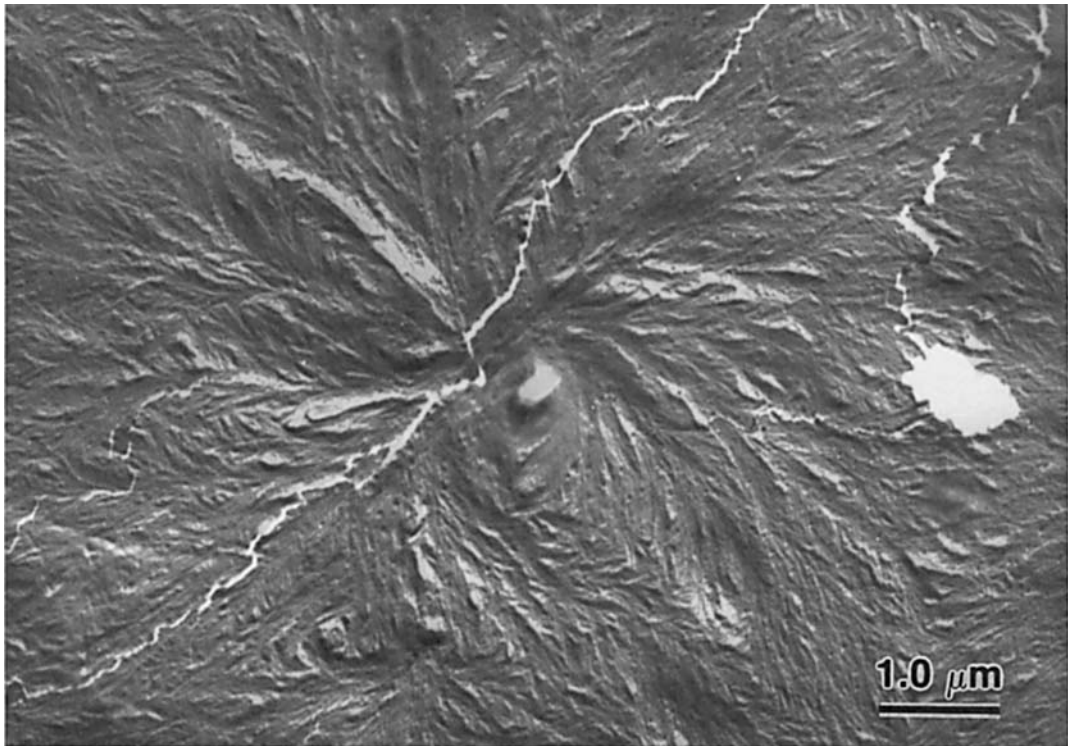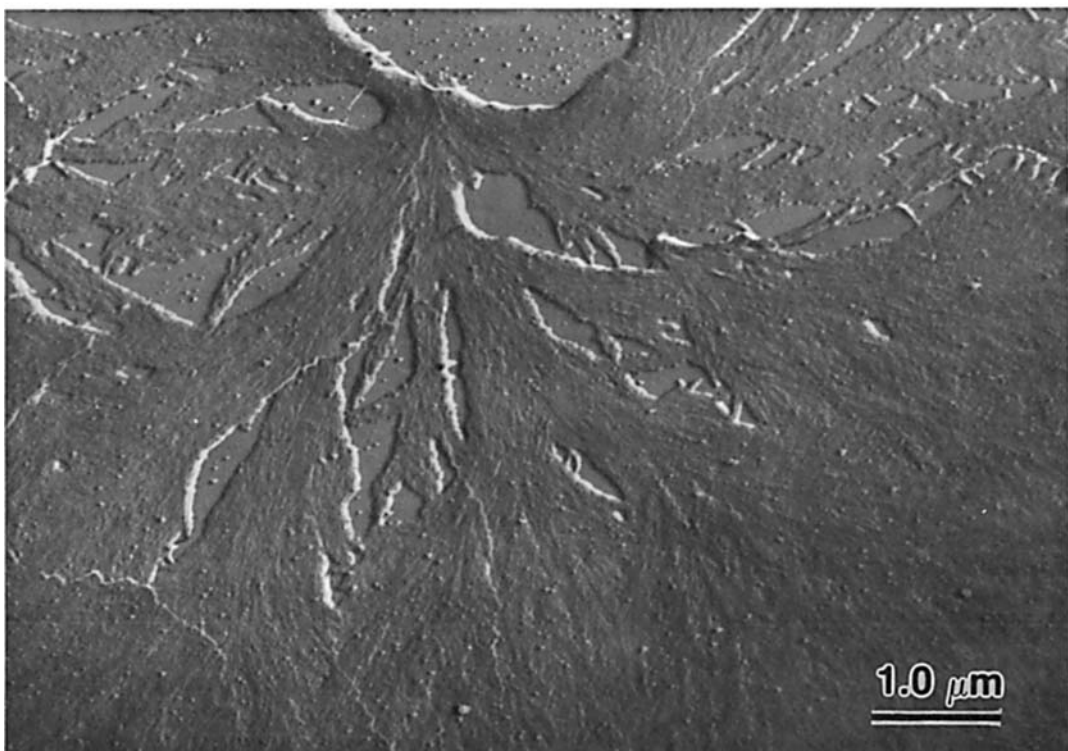
Figure 9   Morphology of PA-6/66 1 : 1 blend samples prepared from HCOOH solution at 25°C and annealed 5 min at (a) 100°C, (b) 190°C, (c) 200°C, and (d) 225°C.

(c)

(d)

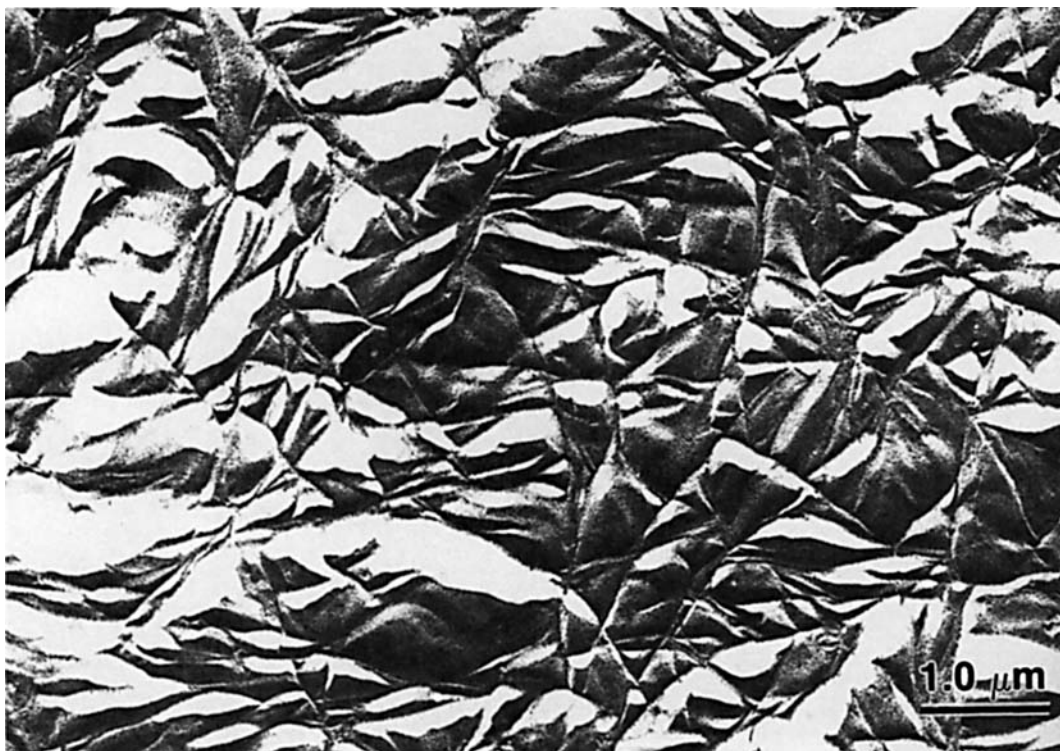**Figure 9** *(Continued from the previous page)*

Figure 10 Morphology of the melt-prepared PA-6/66 1 : 1 blend shadowed at 225°C.

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