

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

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MELTING AND RECRYSTALLIZATION OF PA-6/PA-66 BLENDS

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ABSTRACT

The morphology of a number of polyamides (PA) of current and potential use for mobile air conditioning and refrigerant tubing, namely PA-6, PA-66, PA-6/PA-66 blends and PA-6/PA-66 copolymers, as prepared from the melt and from HCOOH solution and the effect of annealing thereof has been examined. In the blends the PA-6 crystallizes within the PA-66 spherulites, the PA-66 crystallizing first in a loose lamellar framework. The copolymers also crystallize as large spherulites. When prepared from HCOOH solution at 25°C (77°F) 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 either 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 (212°F).

INTRODUCTION

In the 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 co-crystallize 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 the PA-6, however, increased with increasing PA-66, a feature attributed to nucleation of the PA-6 by the 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 between roughly 130-230°C (265-445°F) 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 pseudo-hexagonal 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 (77°F). Similar melting behavior was described by Cojazzi et al. (6) for PA-12, but their

explanation, based on the transition from α to 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 Company and Zytel Du Pont Company) and PA-66 (Du Pont Company). Melt prepared blends of PA-6/PA-66 and copolymers of PA-6 with PA-66 were obtained by courtesy of Dr. A. Elia of the Du Pont Company. Solution crystallized PA-6, PA-66 and PA-6/PA-66 blends were prepared by evaporating fresh HCOOH (85-90%) solutions at 25°C (77°F) or 100°C (212°F) and drying for 16 hrs *in vacuo* at 25°C (77°F).

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 (68°F)/min.

X-ray diffraction. X-ray diffraction scans were done using a Scintag x-ray goniometer with heating stage. The $\text{CuK}\alpha$ radiation was Ni-filtered and detected by a Ge solid state detector. Measurements at higher temperatures were performed in 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 (77°F), shadowed by Pt/C and, in case of the glass slide, the replica (shadowing) removed using polyacrylic 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 shows always 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 HCOOH solution at 25°C (77°F). 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 Fig. 1-4. Surprisingly, one can see marked exothermic peaks before melting. This indicates that a crystallization or recrystallization event takes place before melting. With slower heating rates (<20°C (68°F)/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 Figs. 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 which competes with the endothermic melting peak of PA-6 (which takes place in the range 190-

220°C (374-430°F)), 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, 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 (50°F)/min from 25 to 300°C (77 to 570°F). 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 (77°F) by adding excess of water, it is absent when precipitating a solution of PA-66 in concentrated H₂SO₄ in a similar fashion. In addition, by evaporating HCOOH from PA-66 (or PA-6/PA-66) solutions at temperatures of 100°C (212°F) and higher, no exothermic peak during melting could be observed. Annealing the sample prepared at 25°C (77°F) at temperature above 100°C (212°F) leads to the diminishing and finally 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 (77°F). The PA-66 structure formed at 25°C (77°F) 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 homopolymer and in its blends and copolymers with PA-6, we have measured the wide angle x-ray diffraction spectra of PA-6, PA-66 and of 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 (77-480°F). 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 2θ positions of the two main polyamide diffraction peaks measured stepwise at various temperatures, starting from 25°C (77°F). Comparing the samples prepared from the melt and from 25°C (77°F) HCOOH solution, one may notice two important differences: the solution prepared samples have the d-spacing which corresponds to the H-bonded sheets (higher 2θ values in Fig. 6) almost 3% smaller than 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 pseudo-hexagonal 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 (320°F). This can be seen in Fig. 6a for melt crystallized samples of both pure PA-6 and PA-66. The points on the lowest line, at temperatures above 220°C (430°F), 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 temperature (225°C (438°F)) than the melt crystallized samples.

When we heated the solution prepared samples to temperatures corresponding to the DSC exothermic peak (205-230°C (397-444°F)) and cooled them down to 25°C (77°F), 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, mainly the c -spacing 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 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 PA-6 and PA-66 melting behavior remains to be explained.

Morphology

Melt crystallized samples of PA-6, PA-66, 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. 4). Crystallization from solutions may lead to lamellar single crystals or more complex fibrillar, lamellar, sheaf-like or spherulite structures according to solvent concentration and crystallization conditions (7).

The morphology of the individual homopolymers, their blends and copolymers prepared by evaporation of dilute (0.01-0.5%) HCOOH solution at 25°C (77°F) 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 (8g). 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 polymer 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 Fig. 8a-d because they closely resemble the structures of melt crystallized samples.

Annealing solution prepared samples

Samples prepared from HCOOH solution at 25°C (77°F) 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 homopolymers did not differ from that of their 1:1 blend shown for various annealing temperatures in Fig. 9. In all cases, the basic spherulite texture remained unchanged. At annealing temperatures of 200 (392°F) and 225°C (438°F), 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 (438°F) there were some void spaces within the spherulite. In no case did we observe larger domains which 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.

In order to locate the relative positions of the PA-6 and PA-66 blend components in common spherulites, we have heated melt prepared PA-6/PA-66 blends to 220-230°C (430-448°F) in a vacuum evaporator and shadowed them at this temperature. In this way we have obtained information on the still crystalline PA-66 component and the molten PA-6 phase. Figure 10 show that the spherulites of the blend are composed at 225°C (438°F) 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 which, 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 components 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 (77°F) 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

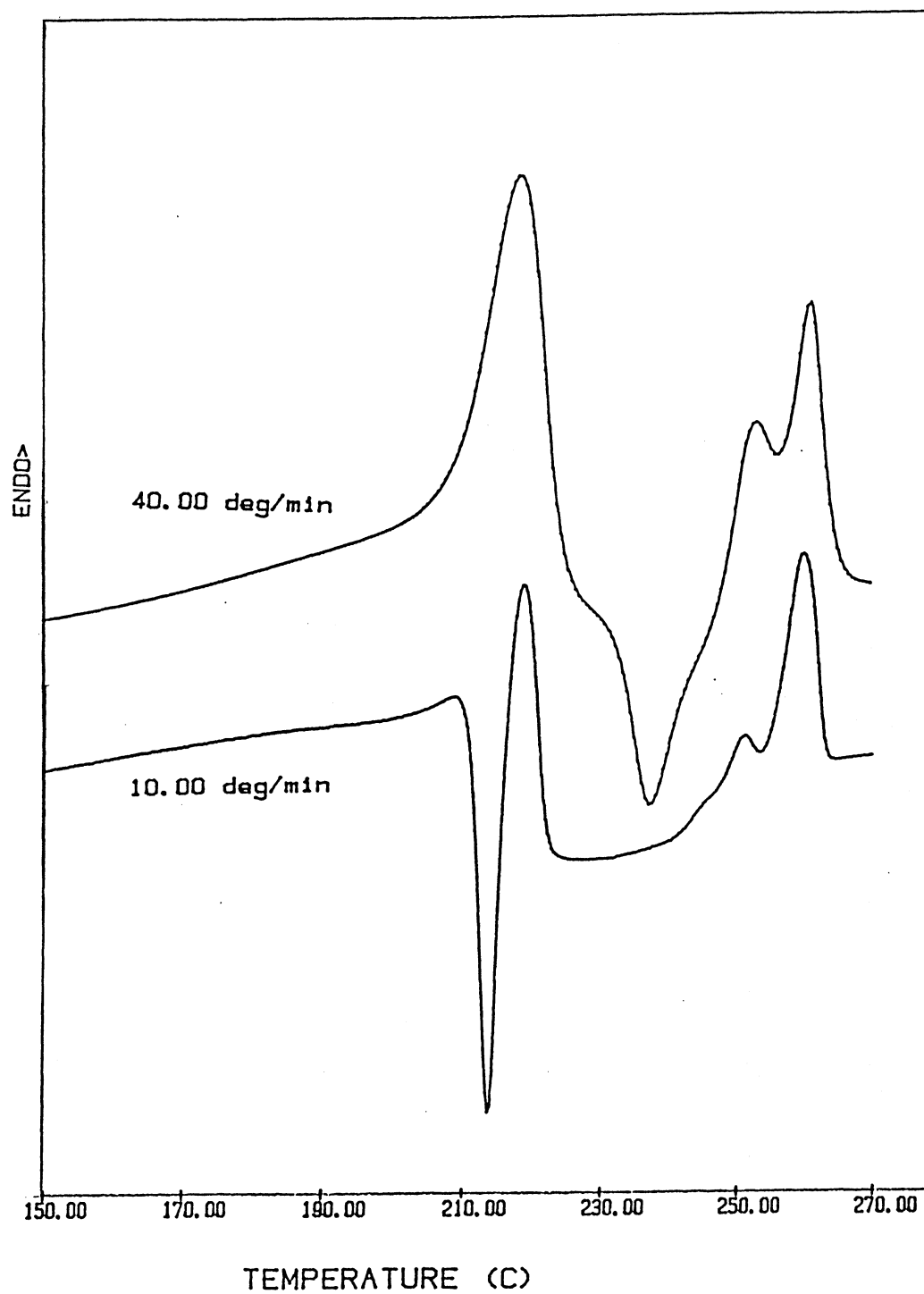
that the PA structure prepared from 25°C (77°F) HCOOH solution differs from that observed in regular melt crystallized samples. However, this new, more tightly packed crystal structure is seen in both PA-66 and PA-6 as well in its blends. Morphological investigations revealed that in blends, crystals 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. The PA6/66 copolymers also crystallize as large spherulites indicating copolymerization does not disrupt the lamellar or spherulitic morphology nor, therefore, their influence on refrigerant diffusion. No morphology differences were observed which 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.

REFERENCES

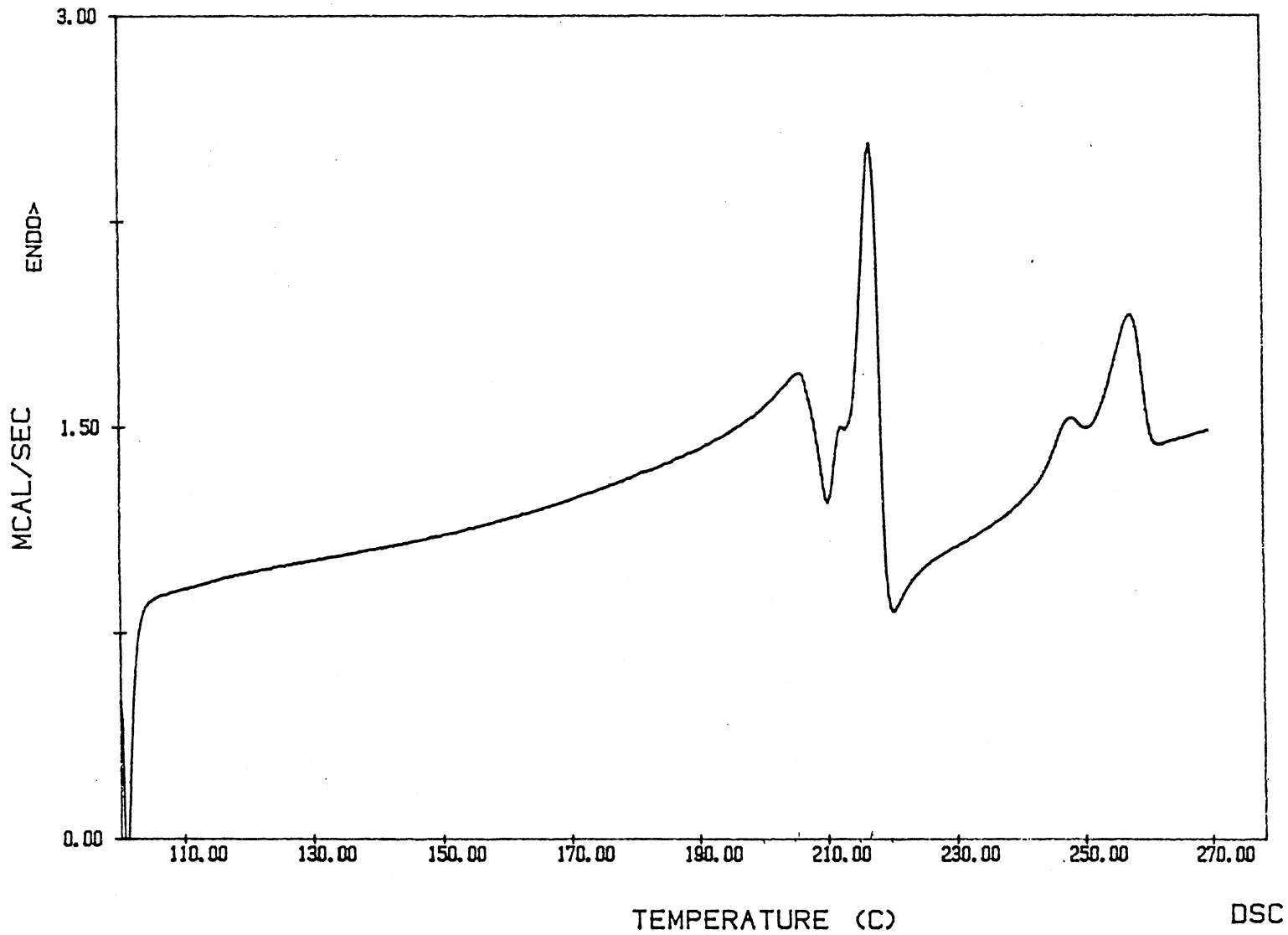
1. F. Rybnikar and P. H. Geil: J. Appl. Poly. Sci., in press.
2. H. W. Starkweather, Jr.: Macromol. 22, 2000 (1989).
3. R. Brill: J. Prakt. Chem. 161, 49 (1942).
4. N. S. Murthy et al.: Macromol. 24, 3215 (1991).
5. A. Xenopoulos and B. Wunderlich: Colloid Polym. 269, 391 (1991).
6. G. Cojazzi et al.: Makromol. Chem. 192, 185 (1991).
7. P. H. Geil: Polymer Single Crystals, Interscience-Wiley, New York, 1963.

FIGURES

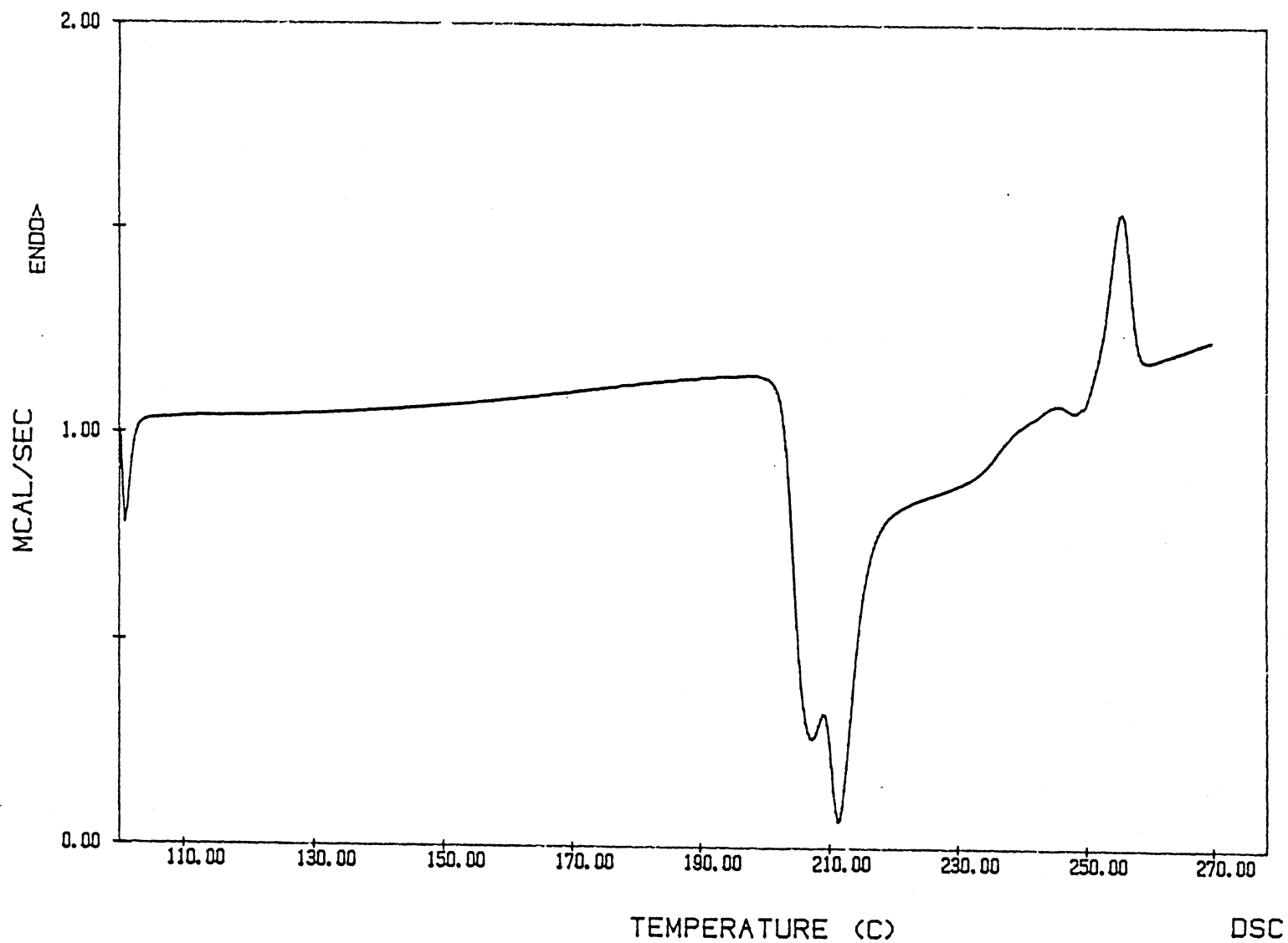
1. DSC melting scans of the PA-6/66 1:1 blend prepared by evaporation of the 0.5% HCOOH solution at 25°C (77°F).
2. DSC melting scan of the PA-6/66 4:1 blend prepared from HCOOH solution at 25°C (77°F). Heating rate 20°C (68°F)/min.
3. DSC melting scan of the PA-6/66 1:4 blend prepared from HCOOH solution at 25°C (77°F). Heating rate 20°C (68°F)/min.
4. DSC melting scan of the 1:9 PA-6/66 copolymer prepared from HCOOH solution at 25°C (77°F). Heating rate 20°C (68°F)/min.
5. DSC melting scan of the PA-66 sample prepared from HCOOH solution at 25°C (77°F). Heating rate 20°C (68°F)/min.
6. Changes of the 2θ positions of the two strongest PA diffraction peaks with increasing temperature: a) melt crystallized PA-6 (○) and PA-66(●), b) HCOOH solution prepared PA-6(○), PA-66 (●) and PA-6/66 1/1 blend (⊙).
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.
8. Morphology of PA samples prepared by evaporating an 0.05 to 0.1% HCOOH solution at 25°C (77°F): 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 and g) PA-6/66 precipitate on a water surface.
9. Morphology of PA-6/66 1:1 blend samples prepared from HCOOH solution at 25°C (77°F) and annealed 5 min at: a) 100°C (212°F), b) 190°C (375°F), c) 200°C (392°F) and d) 225°C (438°F).
10. Morphology of the melt prepared PA-6/66 1:1 blend shadowed at 225°C (438°F).



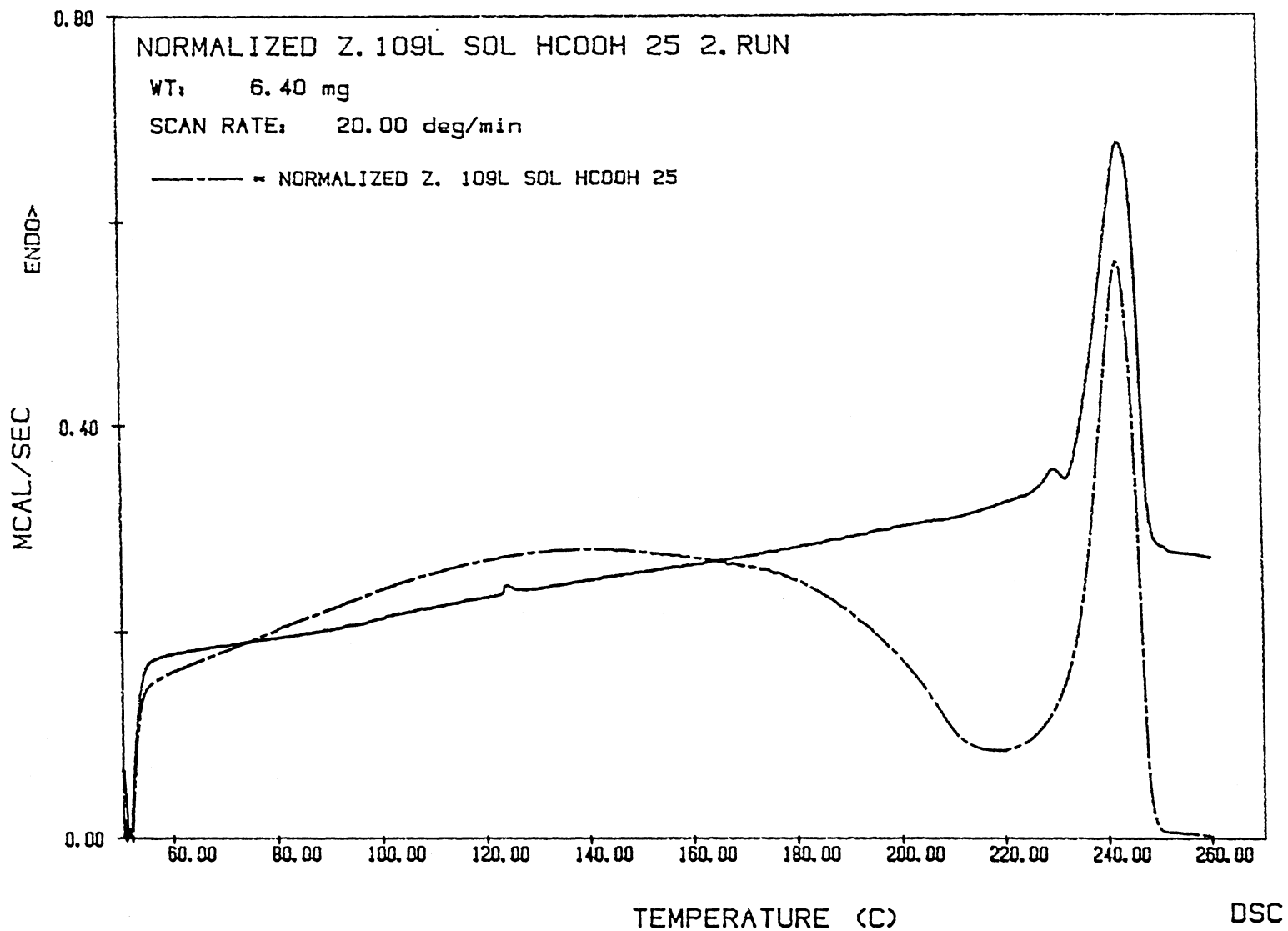
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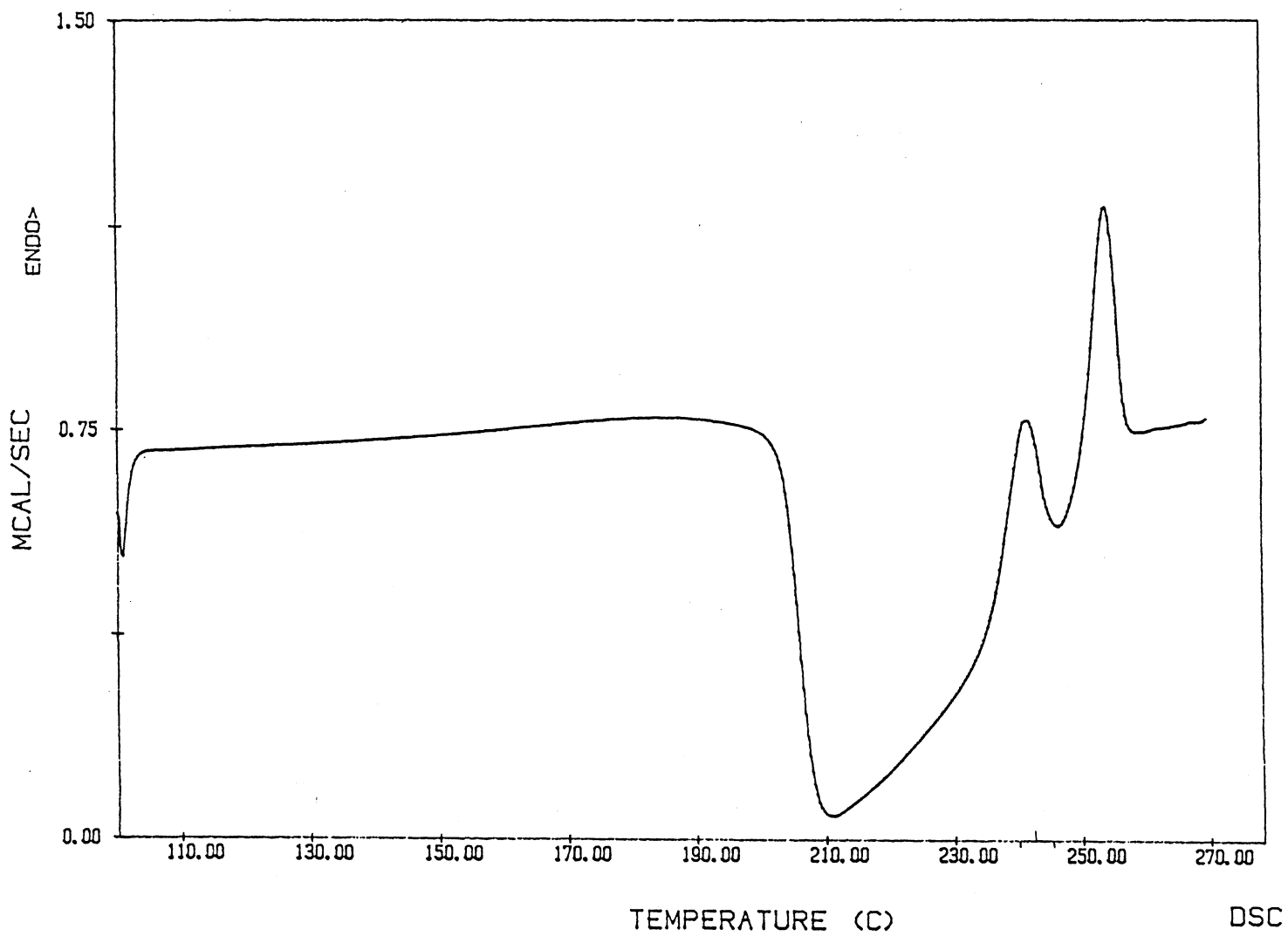
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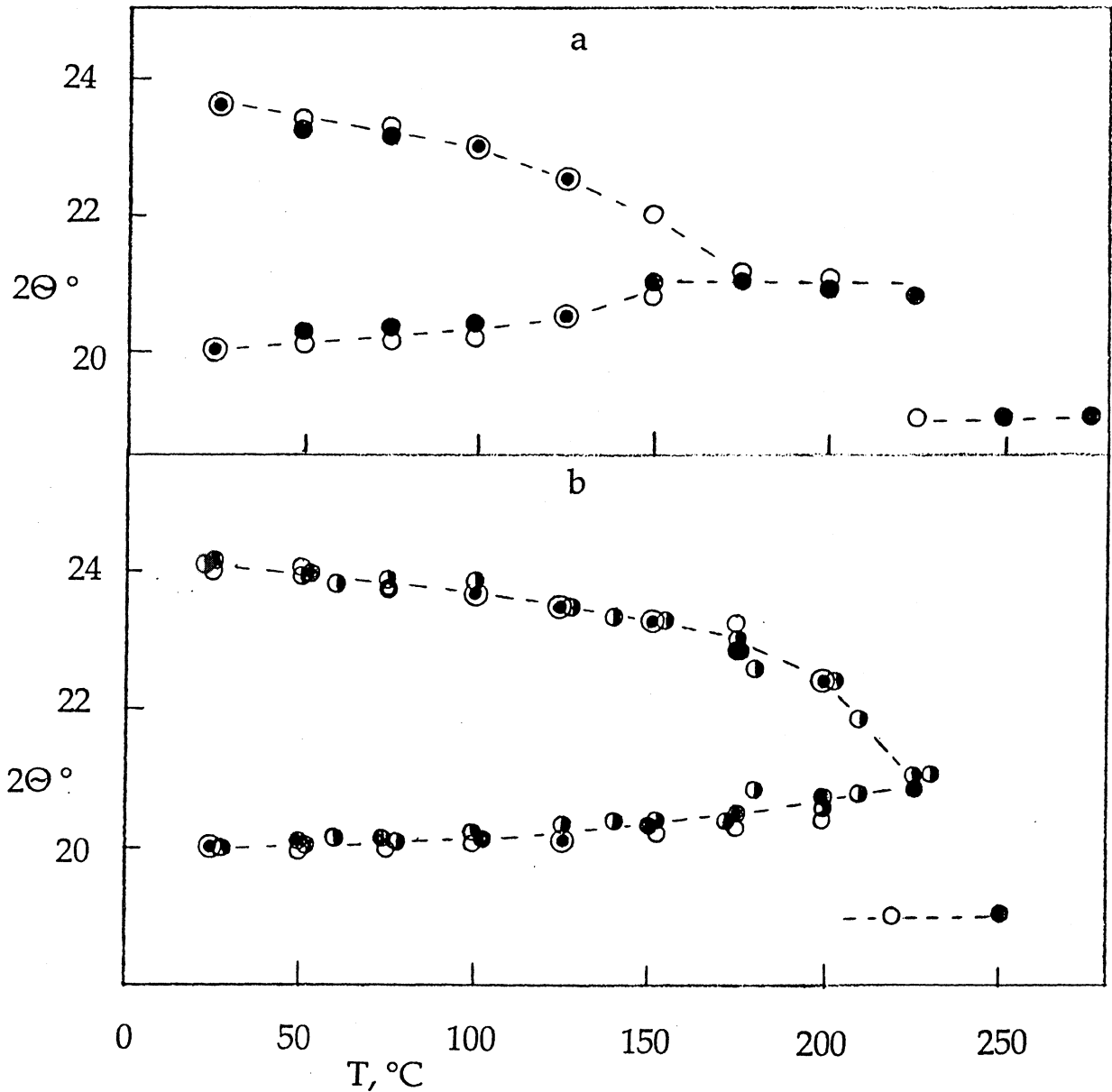
3. DSC melting scan of the PA-6/66 1:4 blend prepared from HCOOH solution at 25°C (77°F). Heating rate 20°C (68°F)/min.



4. DSC melting scan of the 1:9 PA-6/66 copolymer prepared from HCOOH solution at 25°C (77°F). Heating rate 20°C (68°F)/min.

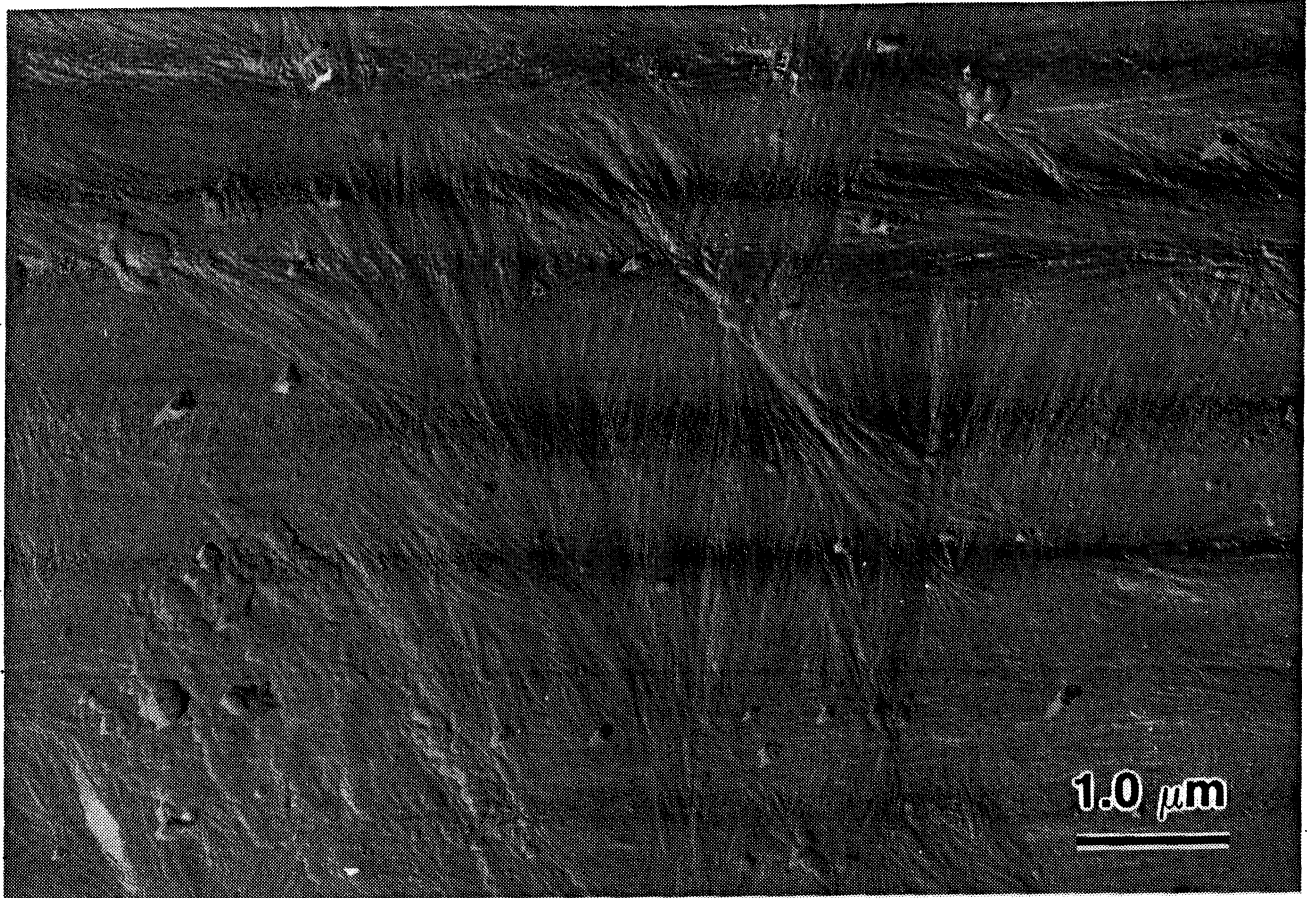


5. DSC melting scan of the PA-66 sample prepared from HCOOH solution at 25°C (77°F). Heating rate 20°C (68°F)/min.

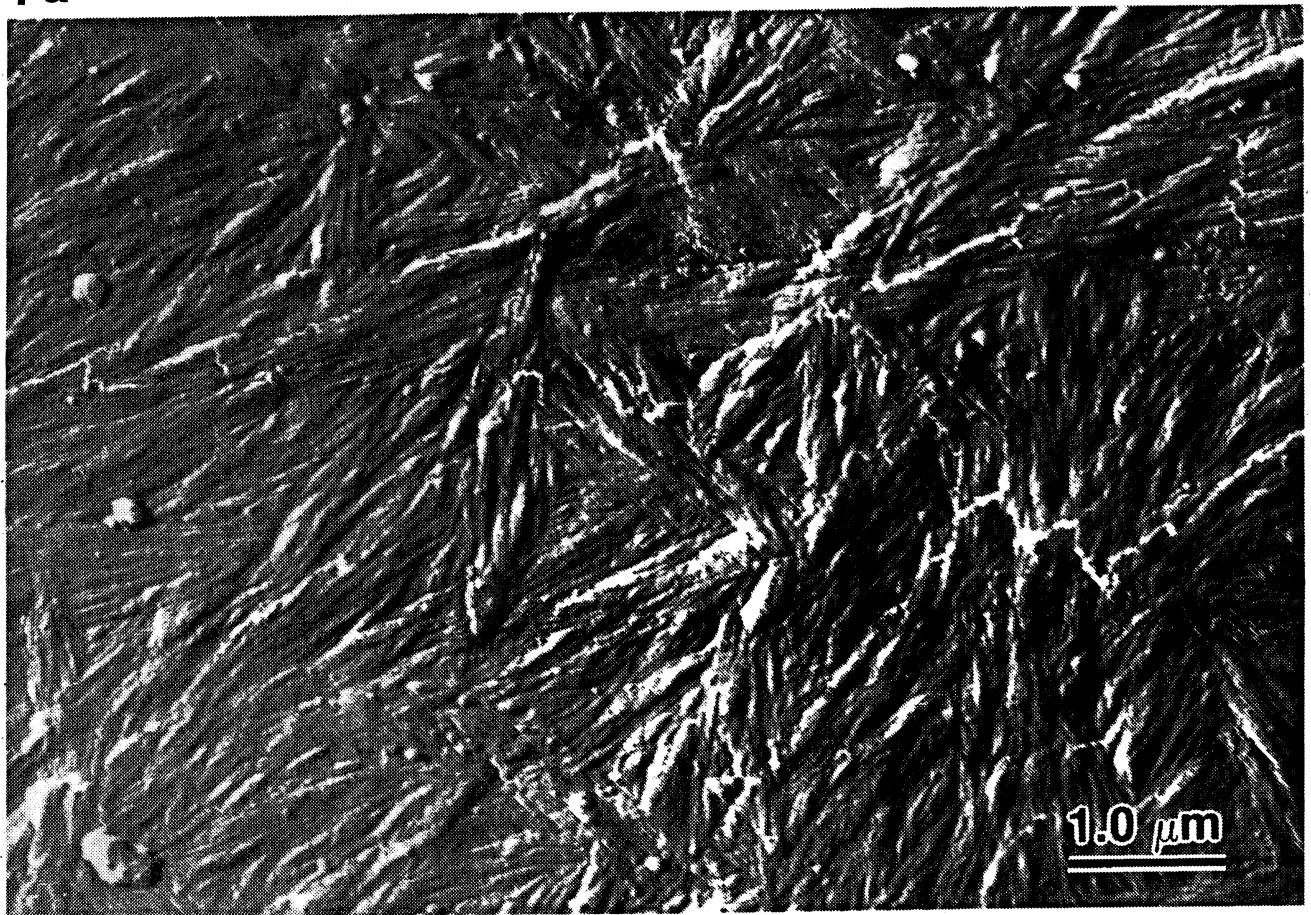


6. Changes of the 2θ positions of the two strongest PA diffraction peaks with increasing temperature: a) melt crystallized PA-6 (○) and PA-66(●), b) HCOOH solution prepared PA-6(●), PA-66 (●) and PA-6/66 1/1 blend (○).

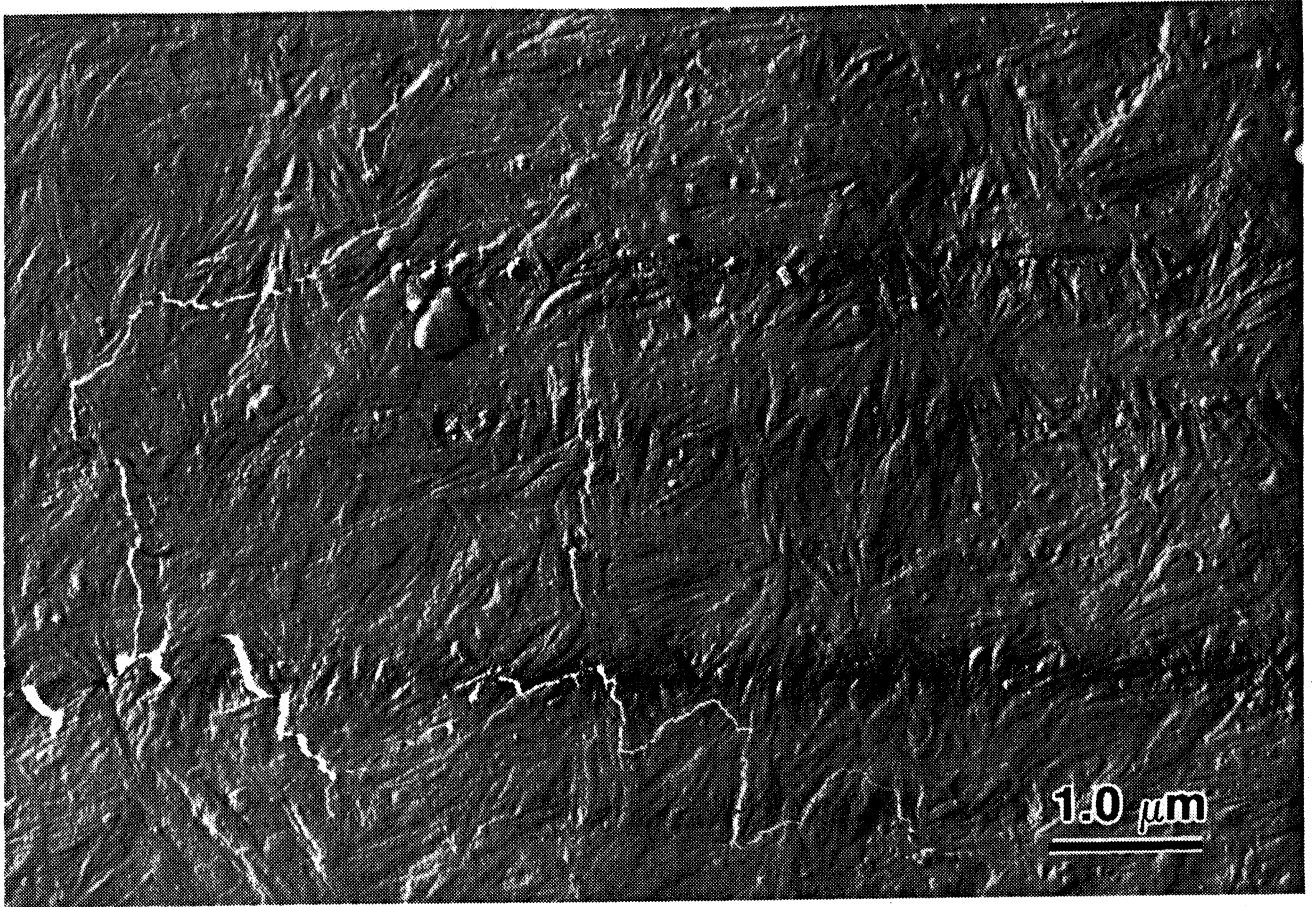
7. Free surface of melt crystallized samples: a) PA-6, b) PA-66, c) PA-6/66 1:1 blend, d) PA-6/66 1:3 copolymer.



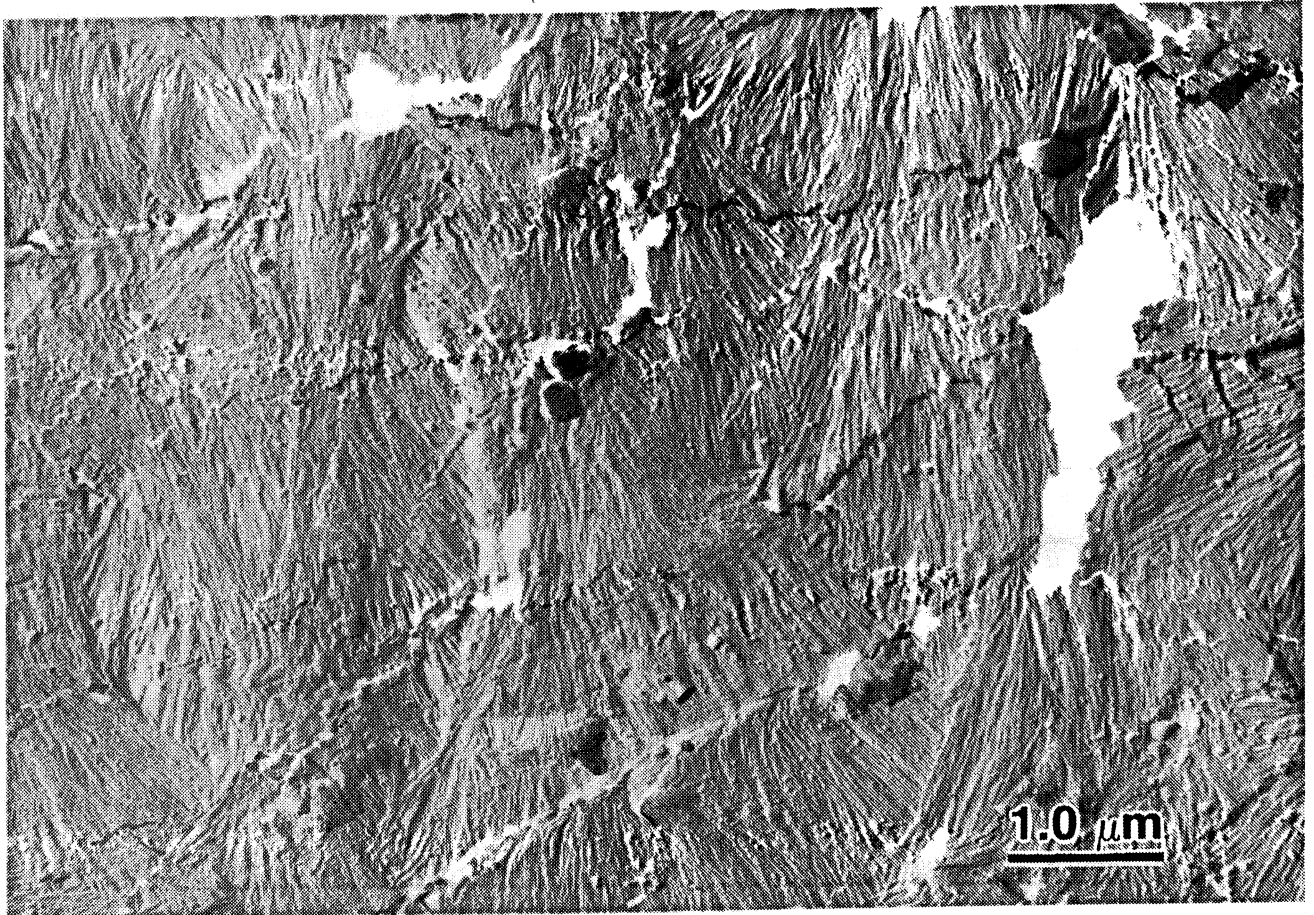
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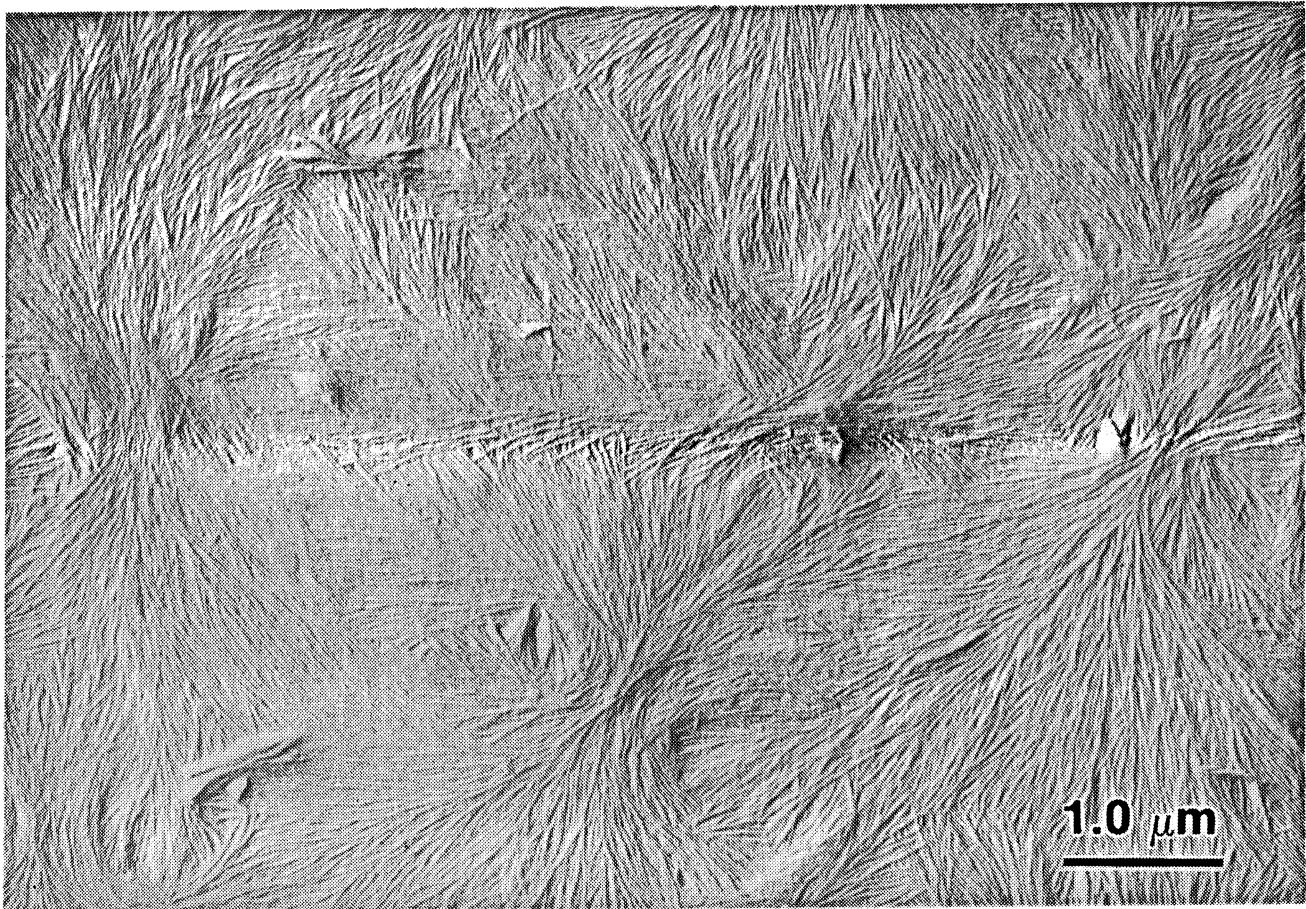


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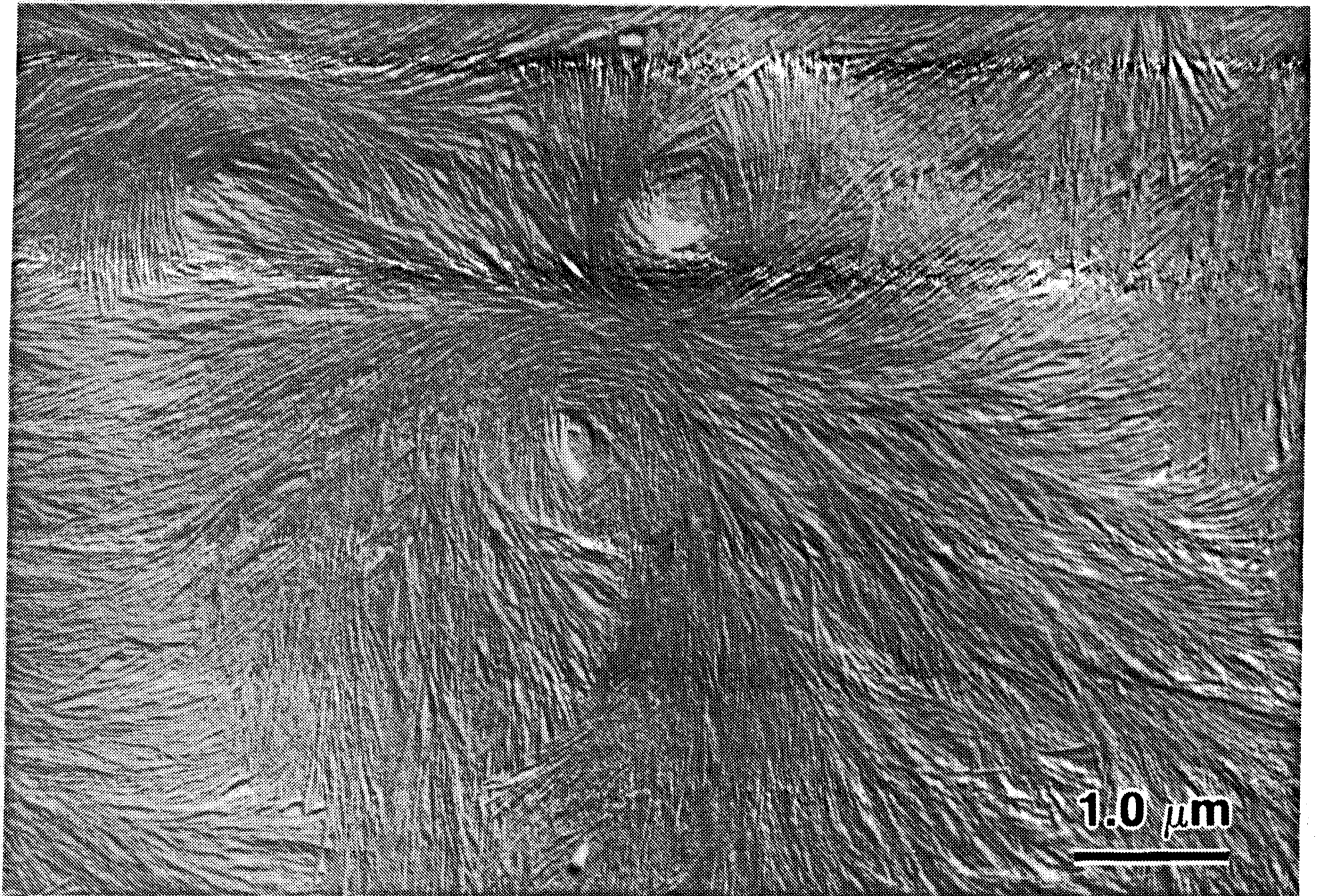


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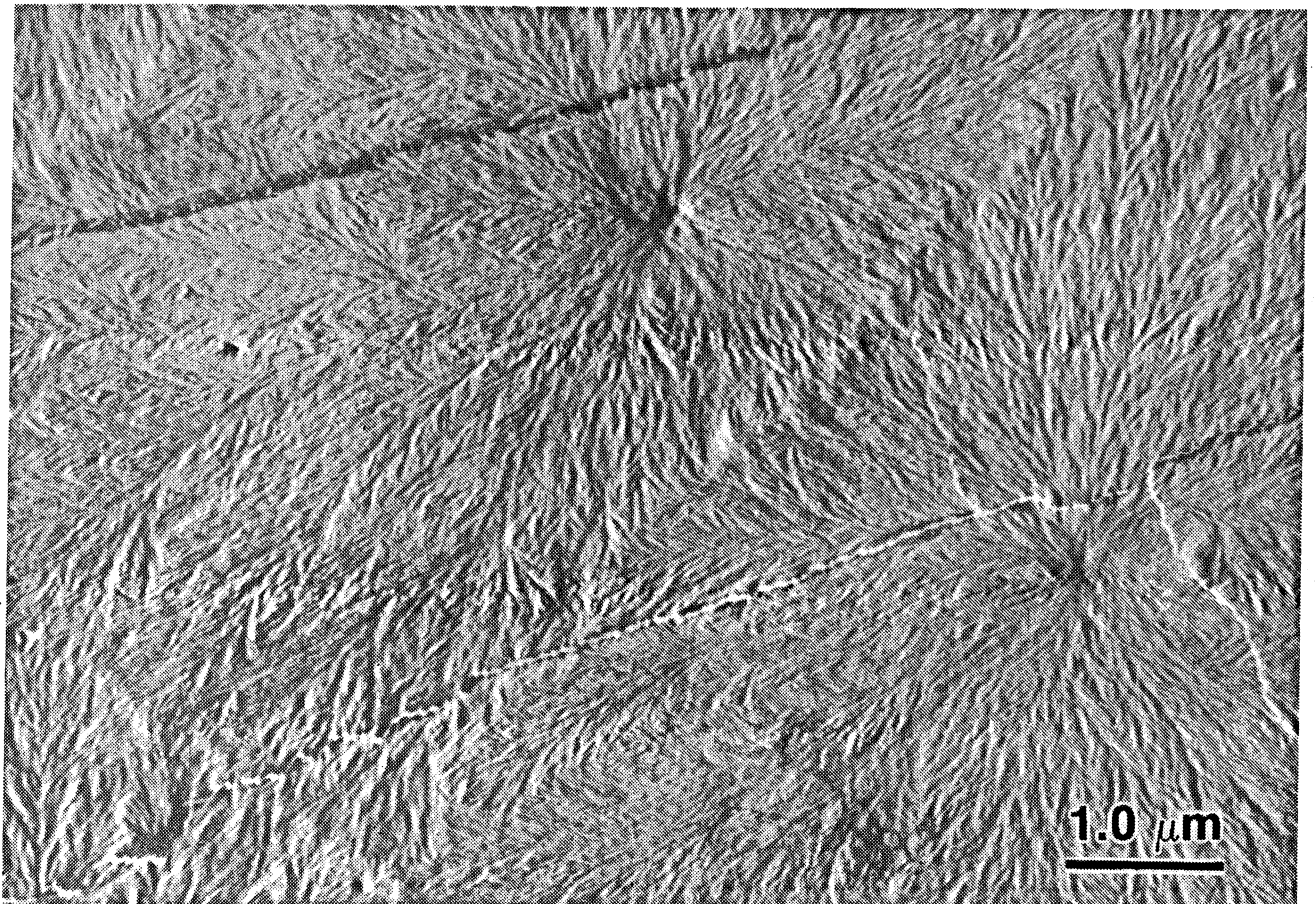
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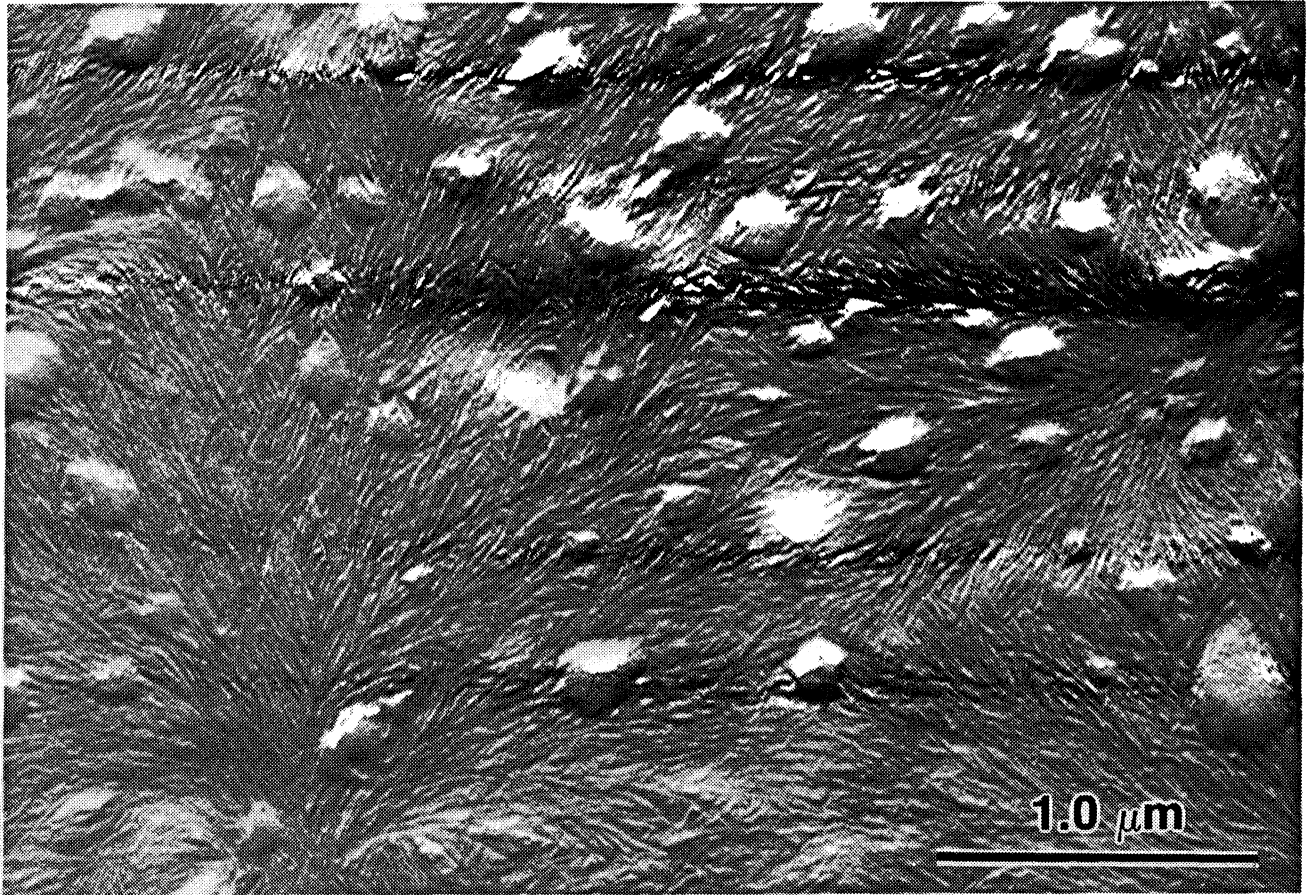
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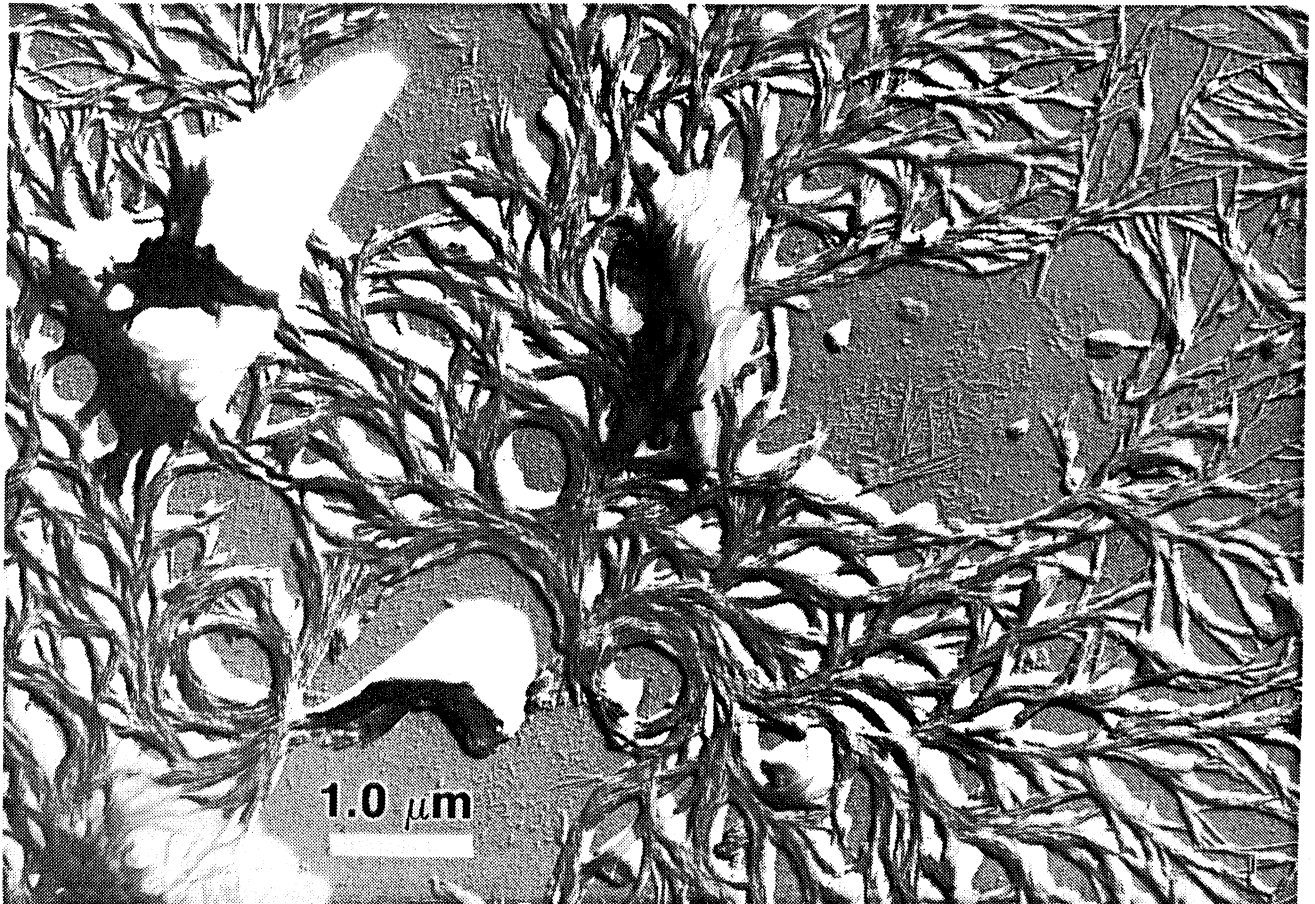
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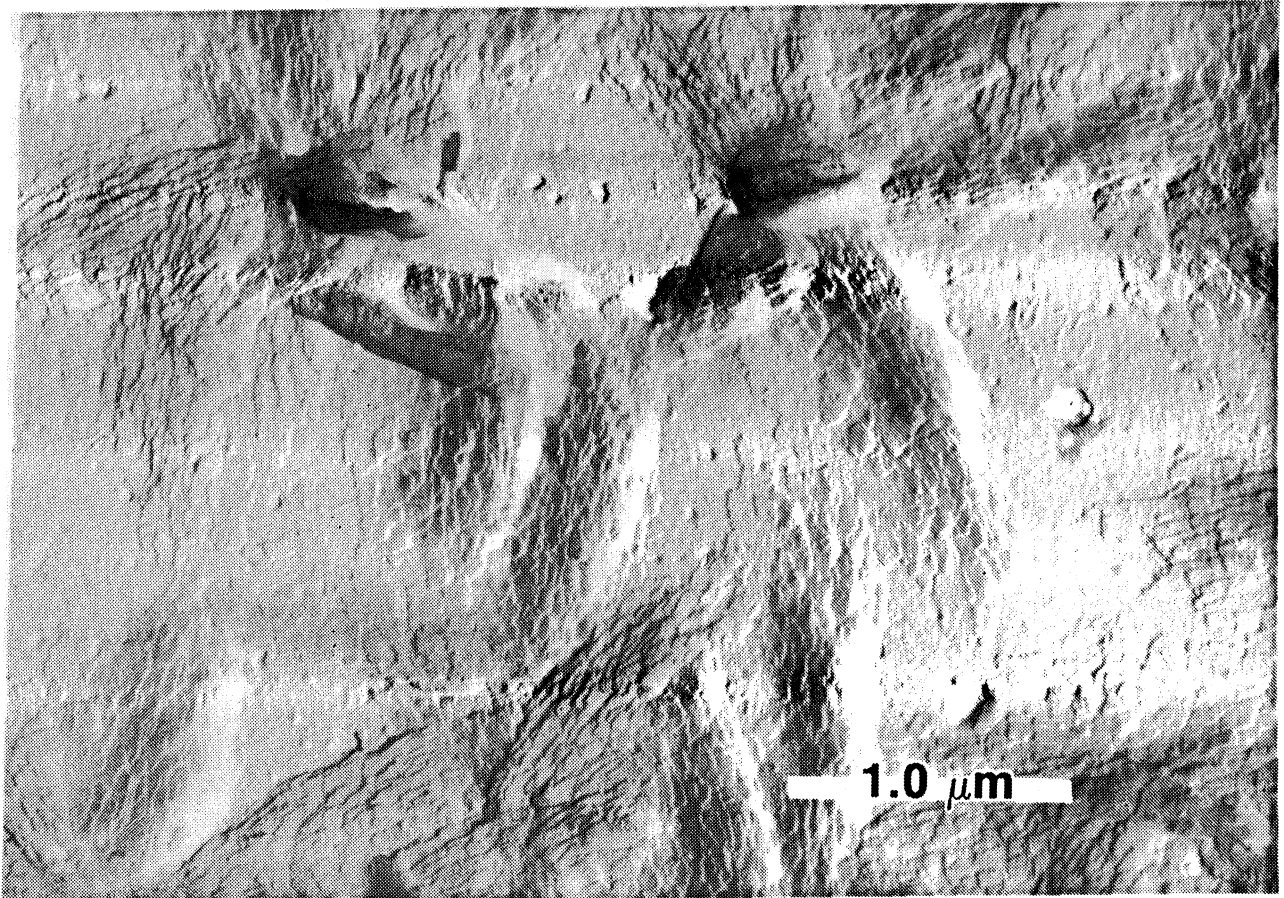
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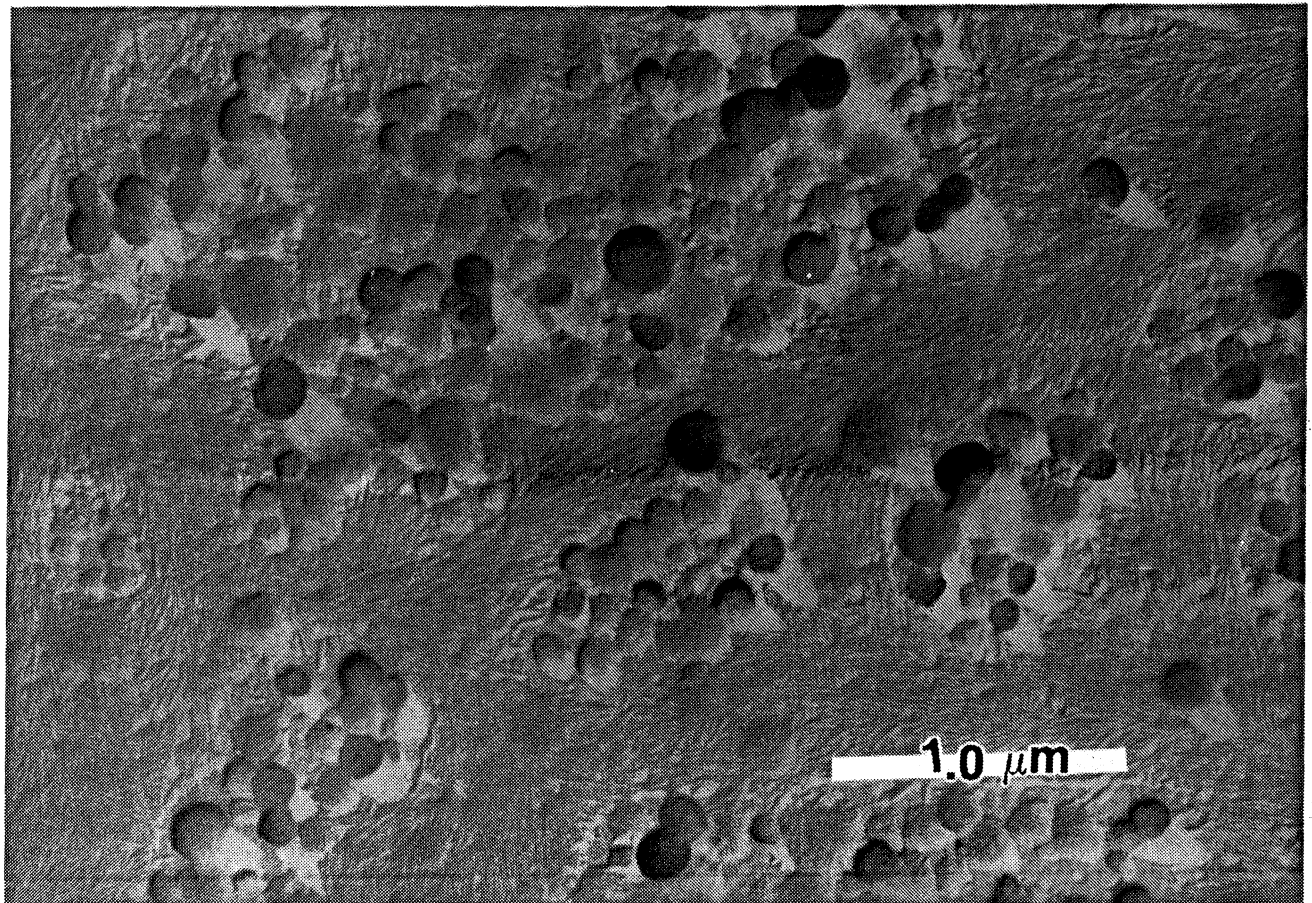
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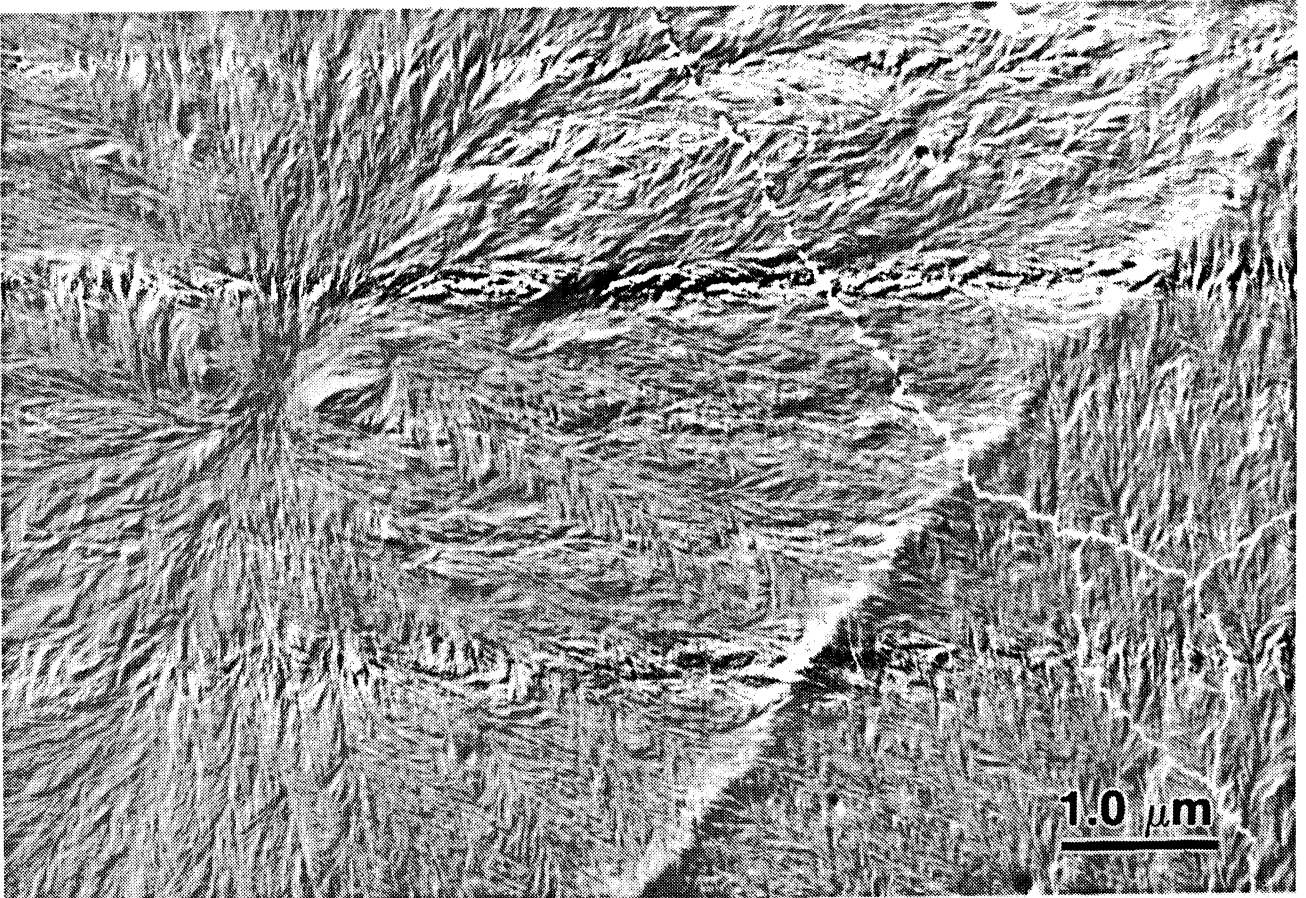


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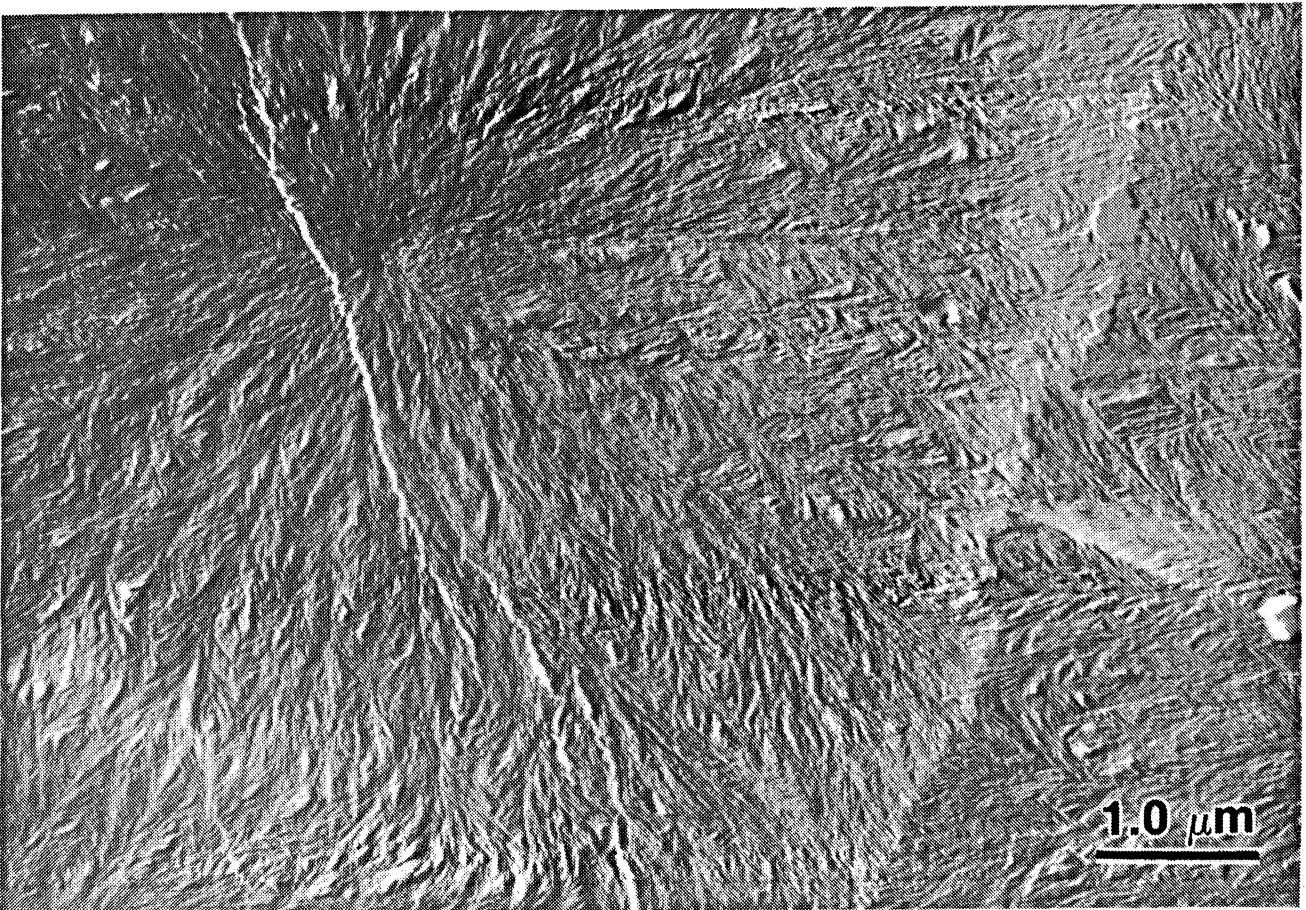


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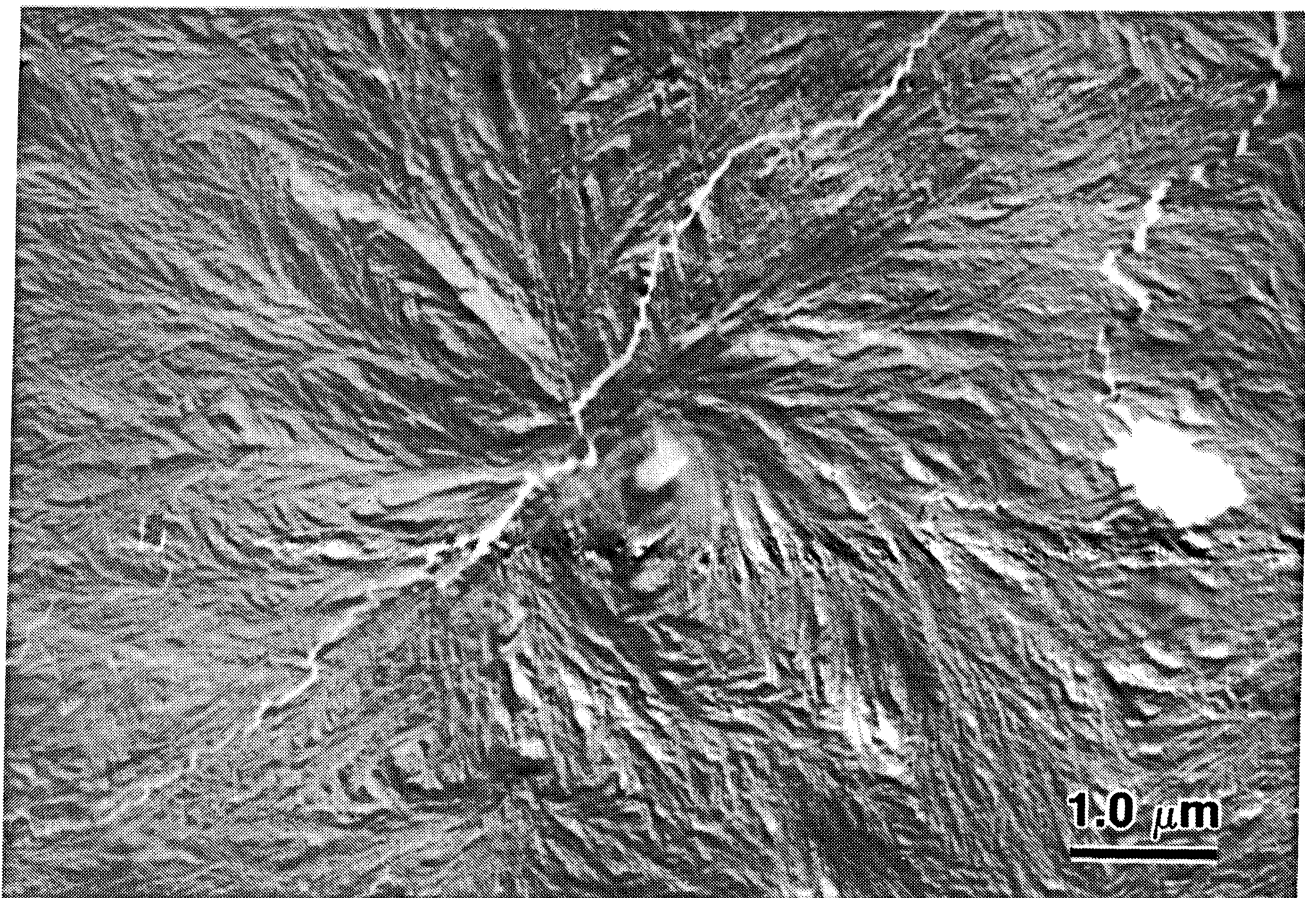
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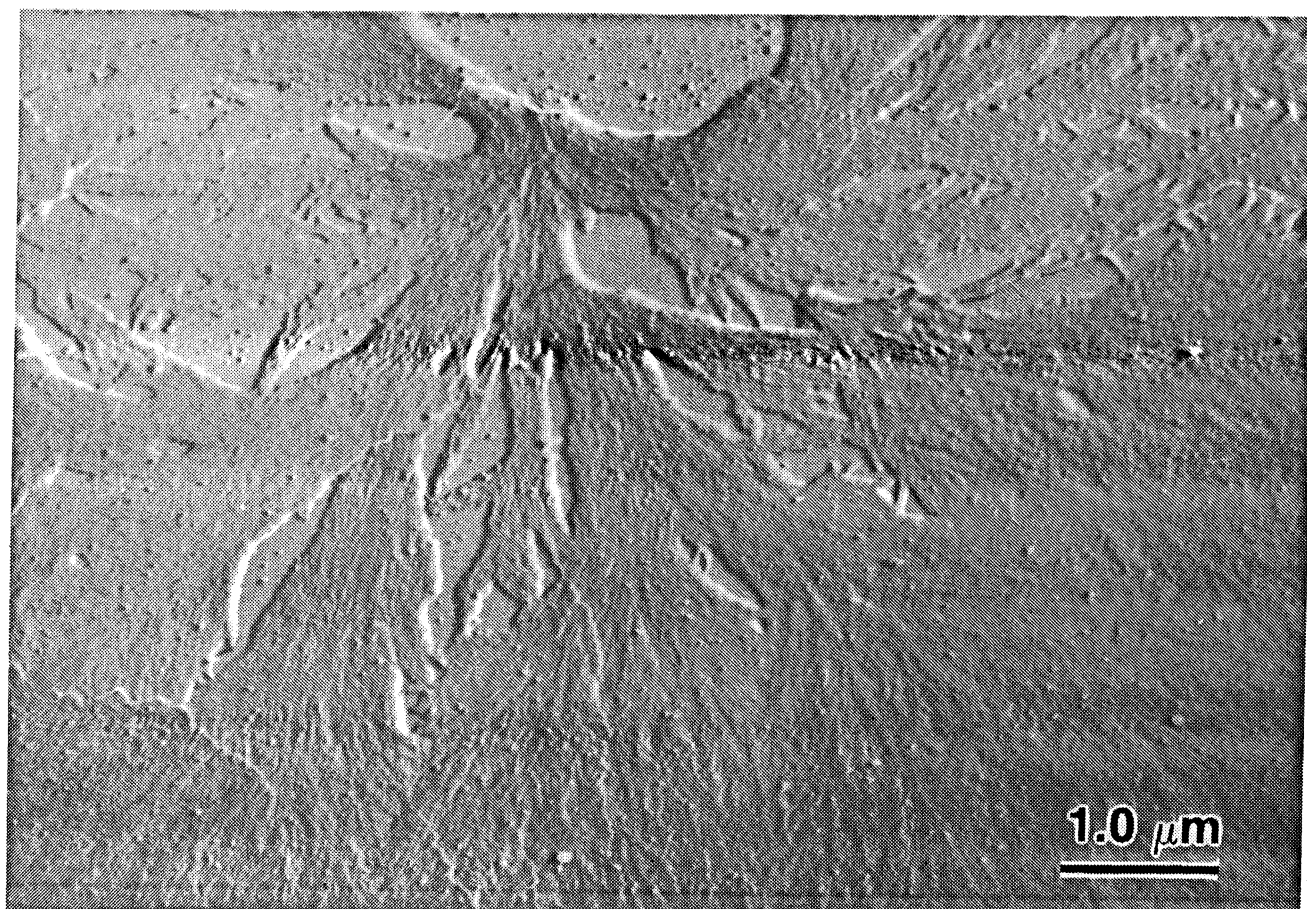
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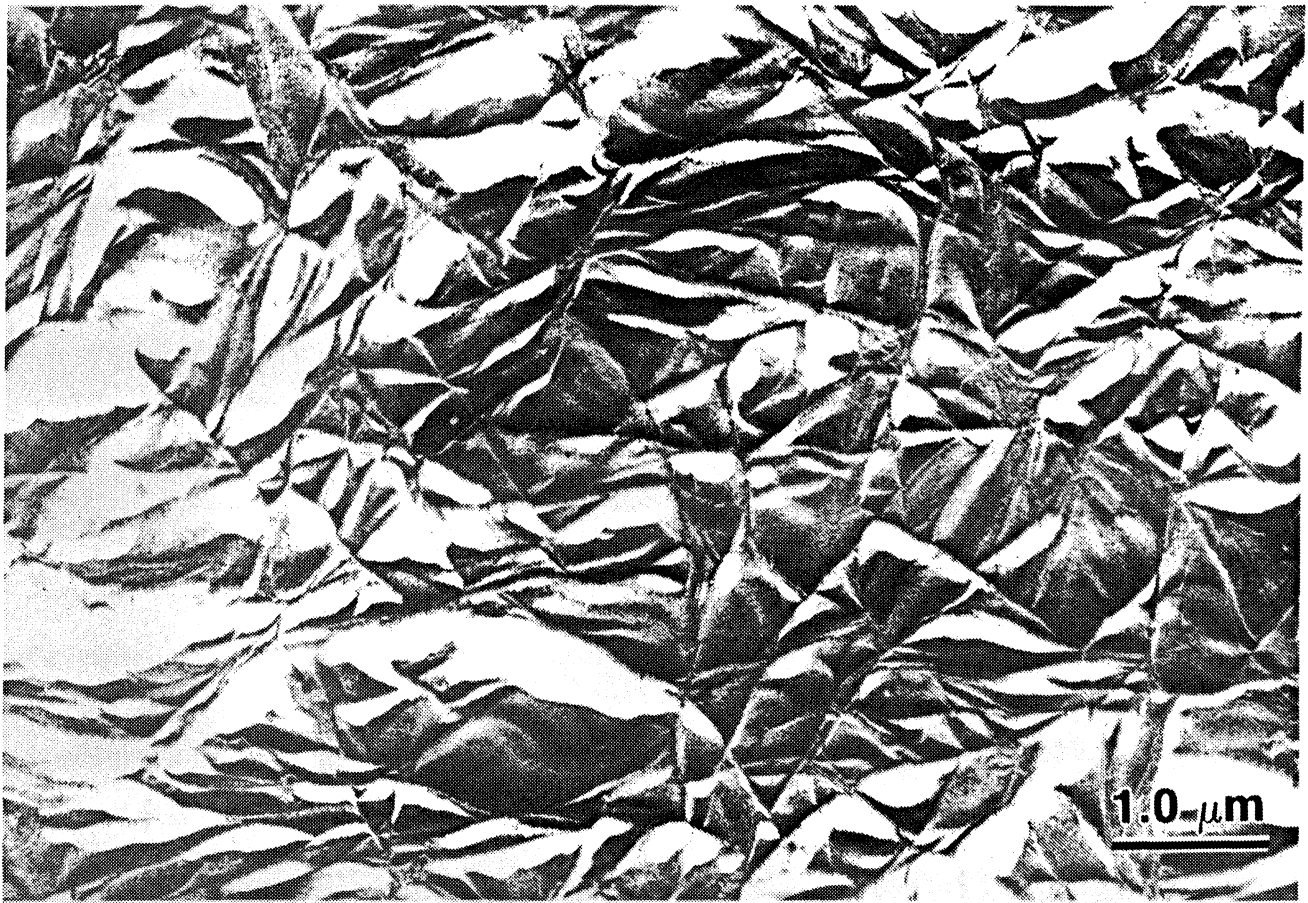
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10. Morphology of the melt prepared PA-6/66 1:1 blend shadowed at 225°C (438°F).