

# Wide-Angle X-Ray Diffraction Studies of Nylon-Ionomer Blends

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## Synopsis

Blends of nylon 6 with poly(acrylic acid) polyacrylamide, poly(ethylene-co-acrylic acid), poly(ethylene-co-vinyl alcohol), poly(acrylamide-co-acrylic acid), and polypropylene were prepared by melt blending. Annealing treatments included treatments in vacuum, in water, and in 20% formic acid at various temperatures. WAXS (wide-angle X-ray scattering) patterns of melt chips and of undrawn, drawn, and textured yarns were obtained. The melt chips of 100% nylon 6 crystallize in the  $\alpha$  form while the chips of all the blends exhibit a single diffraction ring. All the blends behave similarly during different annealing treatments. When annealed in 20% formic acid at 102°C, the  $\alpha$  structure results. The as-spun fibers of nylon 6 and of the blends with poly(acrylamide-co-acrylic acid) and poly(ethylene-co-vinyl alcohol) exhibit a broad diffraction maximum in the region  $2\theta = 19\text{--}25^\circ$ . The  $\alpha$  content and its purity increase with increasing severity of the annealing treatment. The as-spun fibers of the blend with poly(acrylic acid), on the other hand, exhibit a highly oriented  $\gamma$  structure which is highly resistant to conversion to the  $\alpha$  form during the annealing treatments. Only when treated in 20% formic acid at 102° does the pure  $\alpha$  form result. The drawn textured yarns of nylon 6 exhibit both the  $\alpha$  and the  $\gamma$  forms. However, the  $\gamma$  content of the textured yarns from the blends varies with the type and concentration of the additives. The textured yarns from the blends with low levels (0.125%) of poly(acrylic acid) have a very high  $\alpha$  content. It is very unusual that the as-spun fibers with almost pure  $\gamma$  structure, when drawn, produce a structure with a high  $\alpha$  content.

## INTRODUCTION

Wide-angle X-ray scattering (WAXS) patterns of films and fibers of nylon 6 [poly( $\epsilon$ -caprolactam)] have shown that there are two principal crystalline modifications, namely, the monoclinic  $\alpha$  form and the pseudo hexagonal  $\gamma$  form.<sup>1-14</sup> Numerous intermediate structures have been observed depending upon fabricating conditions, chemical and thermal treatments.<sup>4,12</sup>

Rapidly quenched fibers produced by extruding with a low spinline tension exhibit a broad diffraction maximum in the region of 19–25° ( $2\theta$  value) with very little preferential crystallite orientation. When this as-spun material is annealed at high temperatures (above 150°C), the  $\alpha$  structure markedly increases at the expense of both the  $\gamma$  and the amorphous components. When annealed above 200°C in vacuum or in superheated steam (above 140°C) a highly perfected  $\alpha$  structure is obtained. The  $\alpha$  structure is characterized by two strong equatorial reflections at ca.  $2\theta = 20^\circ$  and  $24^\circ$ . Hot- or cold-drawn fibers exhibit WAXS patterns characteristic of both polymorphs. WAXS patterns of the pure  $\gamma$  form exhibit a single equatorial reflection at ca.  $2\theta = 22^\circ$  and a meridional reflection at ca.  $11^\circ$  and are observed for fibers produced by extruding with a high spinline

tension and a rapid wind-up rate or for fibers treated with a solution of iodine in potassium iodide.

Conversion of the  $\gamma$  structure to  $\alpha$  involves breaking and relocating of the hydrogen bonds, for which strong treatments such as superheated steam (155°C) or dilute solutions of formic acid or phenol are required. The  $\gamma$  form, produced by the iodine solution treatment, has been found to be very resistant to conversion to  $\alpha$  by annealing.<sup>2</sup>

We have examined the effects of small amounts of several different ionomers on the crystal structure of nylon 6. Polymer chips and as-spun, drawn, and textured yarns were employed.

## EXPERIMENTAL

Nylon 6 and the ionomers employed in the present study are described in Table I. The spinning conditions were optimized for nylon 6, and the various blends were spun, drawn, and textured under identical conditions. Nylon 6 was tumble blended with each of the ionomers at various concentrations, reextruded, pelletized, and dried. Trilobe multifilament (16 denier, 70 filaments) yarns were spun with a takeup speed of 300 m/min, ply drawn to a draw ratio of 3.2, and jet textured. The samples were prepared in a commercial laboratory.

Annealing of the polymer chips and the undrawn filaments was carried out at various temperatures for 1 h either in vacuum, in water, or in 20% (v/v) aqueous formic acid. The undrawn filaments were wound parallel to one another on X-ray sample holders and annealed at constant length.

WAXS patterns were obtained using nickle filtered  $\text{CuK}\alpha$  radiation and a Siemens X-ray spectrometer (30 kV, 20 mA). Diffractometer traces were obtained along the equator and the meridian. Typical diffraction scans are shown in Figures 1-14.

## RESULTS AND DISCUSSION

The additives used to prepare the blends with nylon 6 include highly polar poly(acrylic acid), weakly polar poly(acrylamide-co-acrylic acid) with high acid content and low acid content, poly(ethylene-co-acrylic acid), polyacrylamide, and poly(ethylene-co-vinyl alcohol), and nonpolar polypropylene. Concentrations of the additives in the blends varied from 0.125% to 6%. The notations used to denote the various blend systems are given in Table I.

TABLE I  
Polymer Samples

Polymer type	Source	$\bar{M}_n$	Acid content	Blend designation
Nylon 6	Allied Corp.	20,000	—	—
Poly(acrylic acid)	Polysciences	450,000	100%	NAA
Poly(acrylamide-co-acrylic acid)	Polysciences	200,000	80%	NCAH
Poly(acrylamide-co-acrylic acid)	Polysciences	200,000	20%	NCAL
Poly(ethylene-co-acrylic acid)	Polysciences	—	8%	NEAA
Polyacrylamide	Polysciences	$5 \times 10^6$	—	NAM
Polypropylene	Hercules	325,000	—	NPP
Poly(ethylene-co-vinyl alcohol)	Kuraway, Japan	—	—	NEVOH

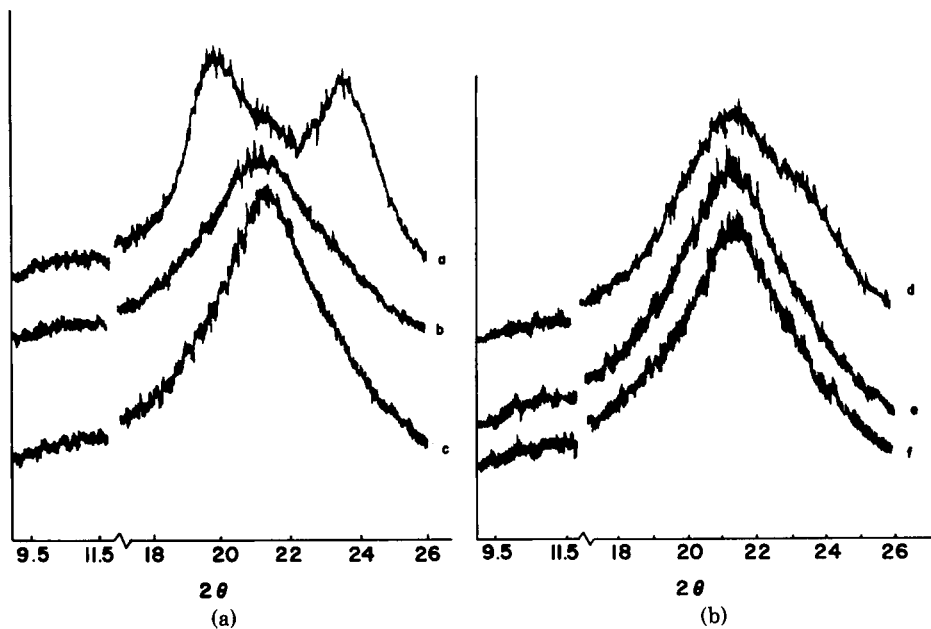


Fig. 1. WAXS patterns of polymer chips: (a) nylon 6; (b) NAA 0.125%, (c) NEAA 98/02; (d) NAM 99/01; (e) NEVOH 99/01; (f) NPP 96/04.

**Structure of Melt Chips**

The WAXS pattern of the nylon 6 chips shows two peaks characteristic of the  $\alpha$  structure; but those of all the blends exhibit only a single diffraction peak (Fig. 1). However, annealing of these blend chips in vacuum resulted in some de-

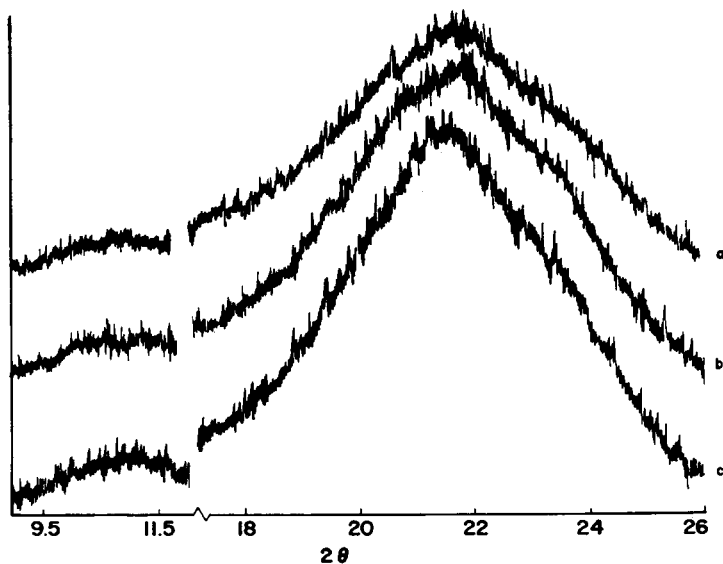


Fig. 2. X-ray diffraction scans of the chips of nylon blends vacuum annealed at 170°C for 1 h: (a) NAA 0.125%; (b) NEVOH 99/01; (c) NCAH 0.125%.

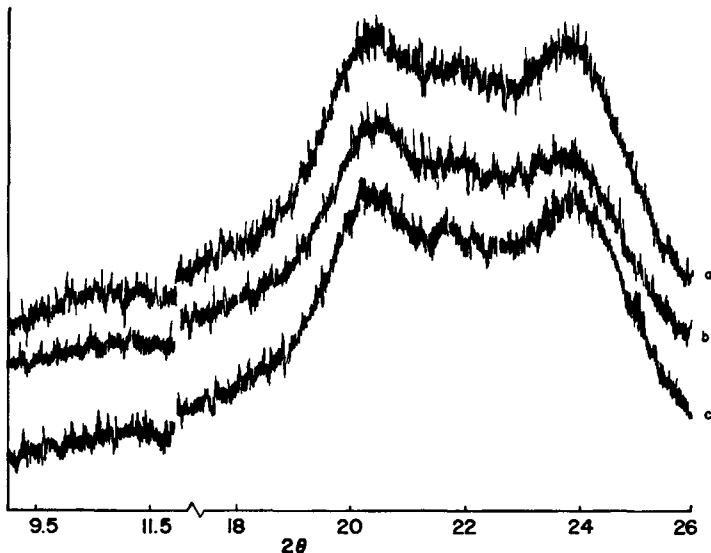


Fig. 3. X-ray diffraction scans of the chips of nylon blends treated in boiling water for 1 h: (a) NAA 0.125%; (b) NEVOH 99/01; (c) NCAH 0.25%.

velopment of the  $\alpha$  structure (Fig. 2). The  $\alpha$  content and its purity increased with the increasing severity of the treatment (Fig. 3). The chips treated with 20% formic acid at 102°C show the pure  $\alpha$  structure (Fig. 4). The angular separation between the two diffraction peaks is 4°, the maximum expected for the pure  $\alpha$  structure. Under given annealing conditions, all the blends studied, irrespective of the nature and the concentration of the additive, behave similarly.

The  $\alpha$  and the  $\gamma$  structures of nylon 6 have been well established. An  $\alpha$

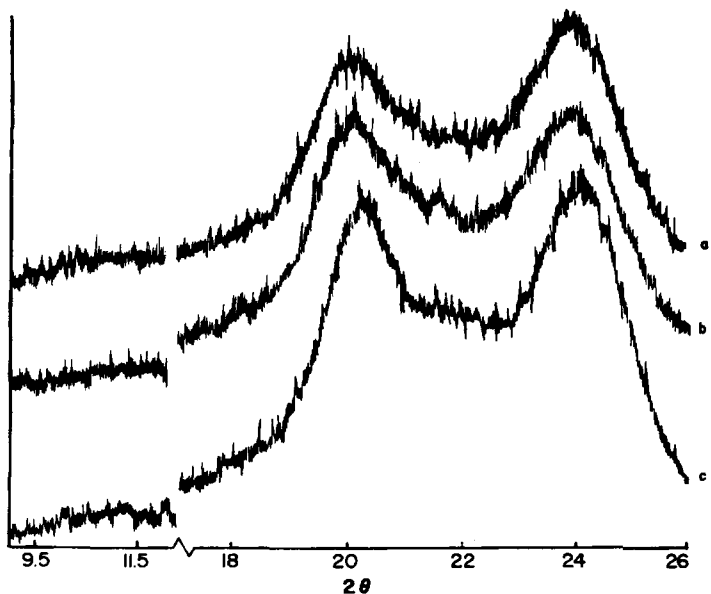


Fig. 4. X-ray diffraction scans of the chips of nylon blends with 20% formic acid at 102°C for 1 h: (a) NAA 0.125%; (b) NEVOH 99/01; (c) NEAA 98/02.

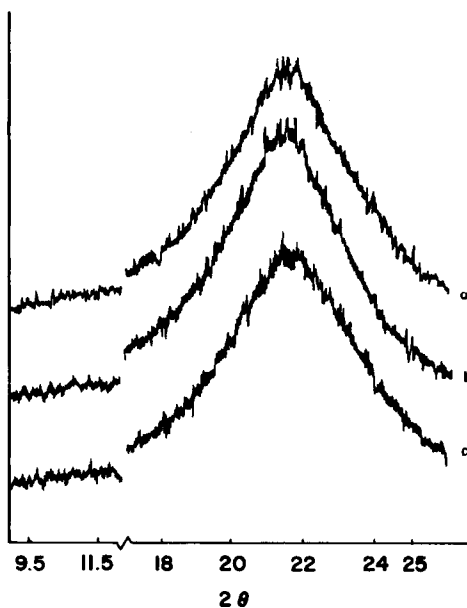


Fig. 5. Equatorial diffraction scans of the as-spun filaments: (a) nylon 6; (b) NCAH containing 0.125% poly(acrylamide-co-acrylic acid); (c) NEVOH containing 6% poly(ethylene-co-vinyl alcohol).

structure consists of hydrogen-bonded sheets with the hydrogen bonding between the adjacent antiparallel chains. It has an extended, almost planar chain conformation. The  $\gamma$  structure, on the other hand, consists of hydrogen-bonded sheets with hydrogen bonding between parallel chains. It requires tilting of the amide group out of its plane for complete hydrogen bonding. The type of structure that results in a given situation depends on the balance of different forces in a manner which minimizes the energy of the crystal. These forces include (1) the force required to twist a carbon-carbon bond needed to tilt the amide group, (2) the force required to break and remake the hydrogen bonds (i.e., the hydrogen bonded sheets), and (3) the van der Waal's forces between molecules. These forces vary depending upon the molecular chain length, the size of the crystal, the chain orientation, etc. It should be mentioned here that in nylons the number of methylene groups between the amide groups determines the balance between the van der Waal's forces and the hydrogen-bonding forces. When the number of methylene groups is greater than six, the dominance of the van der Waal's forces favors the  $\gamma$  structure. The opposite is true for nylons with shorter methylene sequence. Only in nylon 6 the  $\alpha$  and  $\gamma$  forms have nearly the same total energy such that they can exist under conditions near equilibrium. It is surprising that the additives with widely different functional groups produce the same type of structure. It is all the more surprising that the different blends behave similarly during different annealing treatments.

### Structure of As-Spun Fibers

The crystal structure of a rapidly quenched fiber, as would be produced by a commercial extrusion process, is poorly understood and the subject of some

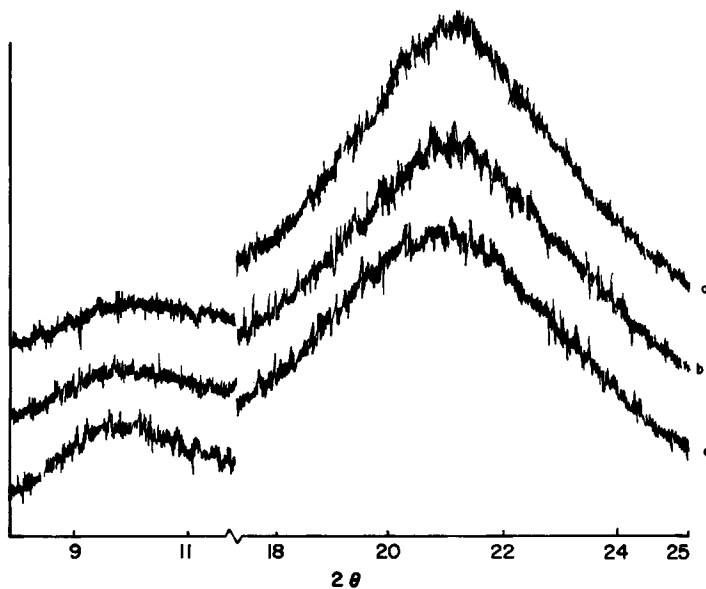


Fig. 6. Meridian diffraction scans of the as-spun filaments: (a) Nylon 6; (b) NCAH; (c) NEVOH.

controversy.<sup>1-4</sup> Both the equatorial and meridional diffraction scans of the as-spun nylon 6 fibers show a strong, broad peak at ca.  $21.5^\circ$  ( $2\theta$ ) [Figs. 5(a) and 6(a)], suggesting that nylon 6 crystallizes in the form of very small, very imperfect crystals with poor orientation about the fiber axis. The presence of the single diffraction peak led Parker and Lindenmeyer<sup>4</sup> to propose a hexagonal structure with bonding along two crystallographic axes, and Bankar et al.<sup>3</sup> to propose a structure closely related to the  $\gamma$  structure. The former model requires the adjacent chains to be all parallel or antiparallel, thus making subsequent transitions to the  $\alpha$  structure difficult. The latter model fails to account for the extremely low intensity of the meridional peak at  $10.8^\circ$  [see Fig. 6(a)]. According to Stepaniak et al.,<sup>2</sup> the as-spun fiber has the characteristics of a mixed conventional  $\alpha$ /pleated  $\alpha$  structure with only a small  $\gamma$  component. The pleated  $\alpha$  structure is derived from the  $\gamma$  structure of Arimoto<sup>8</sup> by slipping the hydrogen-bonded sheets past one another. Such a pleated  $\alpha$  structure has a single diffraction peak in the range  $2\theta = 19-25^\circ$ . However, these authors do not provide any evidence how this phase differs otherwise from a highly imperfect, poorly developed  $\alpha$  form. Furthermore, Gianchandani et al.<sup>1</sup> take a view which is not substantially different from that of Parker and Lindenmeyer,<sup>4</sup> although they believe the existence of both  $\alpha$  and  $\gamma$  type pseudo-hexagonal forms in the as-spun fibers. Both the NCAH and NEVOH blends exhibit a single diffraction peak [Figs. 5(b) and 5(c) and 6(b) and 6(c)], as in the case of the as-spun nylon. This behavior is in contrast to their behavior in the melt chip form. The intensity of the meridional peak at  $2\theta = 10.8^\circ$  suggests that the as-spun fibers of the blends contain a higher  $\gamma$  fraction than the nylon 6 fibers.

In contrast, the NAA blend exhibits a fairly well-developed  $\gamma$  crystalline structure [Figs. 11(a) and 12(a)]. The intensity ratio of the (020) meridional reflection, primarily caused by the pseudo-hexagonal  $\gamma$  form at  $10.8^\circ$ , to the (040)

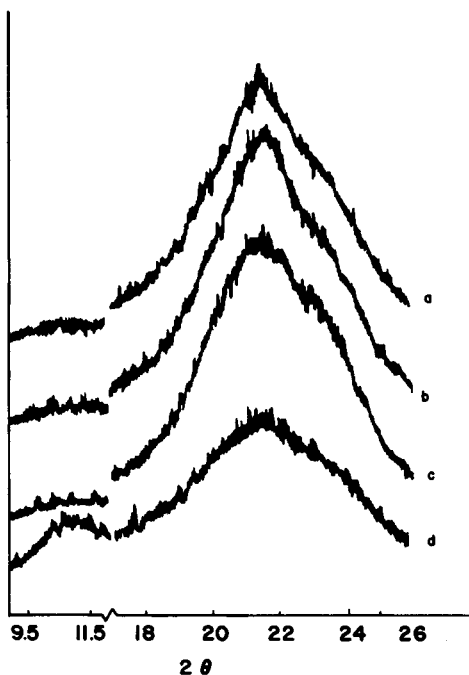


Fig. 7. Equatorial diffraction scans of the as-spun filaments vacuum annealed at 170°C for 1 h: (a) nylon 6; (b) NCAH; (c) NEVOH; (d) meridian scan of NCAH.

reflection at 20.9°, caused by the monoclinic  $\alpha$  form, is about 2.5, a value expected for the hexagonal  $\gamma$  form.<sup>7-9</sup> The intensity ratio of the meridional to the equatorial peaks for the as-spun nylon and NCAH and NEVOH blends is about 0.7,

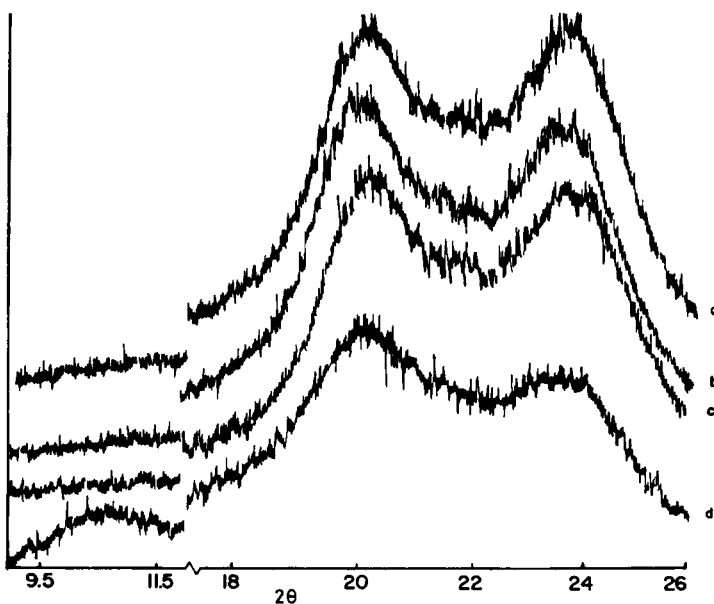


Fig. 8. Equatorial diffraction scans of the as-spun filaments boiled in water at 100°C for 1 h: (a) nylon 6; (b) NCAH; (c) NEVOH; (d) meridian scan of NEVOH.

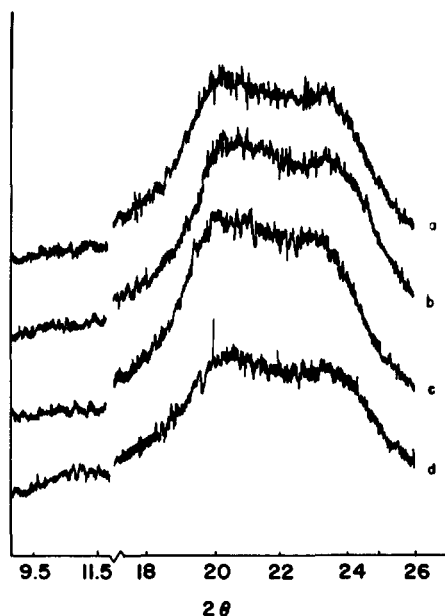


Fig. 9. Equatorial diffraction scans of the as-spun filaments treated with 20% formic acid at  $23^\circ\text{C}$  for 1 h: (a) nylon 6; (b) NCAH; (c) NEVOH; (d) meridian scan of NCAH.

suggesting that the molecules are not highly oriented. This ratio for the NAA blend is about 0.24, suggesting that the molecules of the as-spun NAA blend fibers are more highly oriented.

The vacuum annealed as-spun fibers of nylon and the NCAH and NEVOH blends exhibit a higher  $\alpha$  content developed at the expense of the pleated  $\alpha$

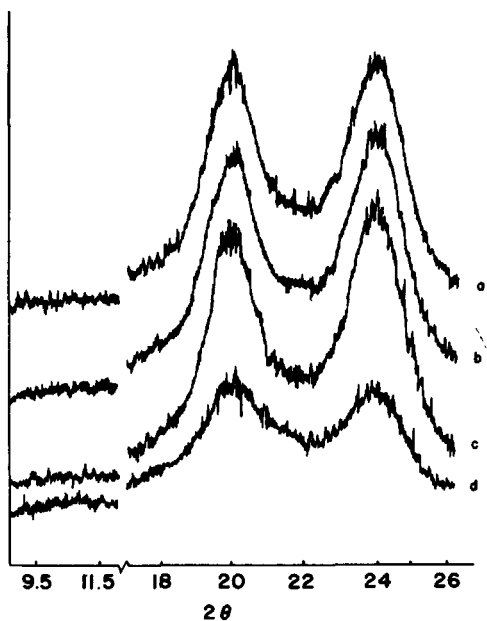


Fig. 10. Equatorial diffraction scans of the as-spun filaments treated with 20% formic acid at  $102^\circ\text{C}$  for 1 h: (a) nylon 6; (b) NCAH; (c) NEVOH; (d) meridian scan of NEVOH.



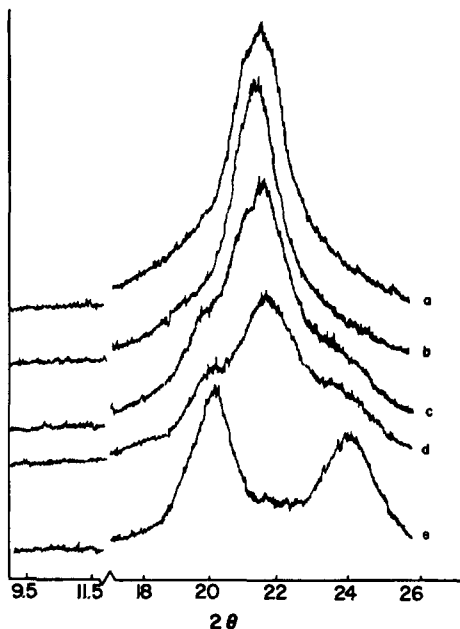


Fig. 11. Equatorial diffraction scans of the as-spun nylon poly(acrylic acid) blend filaments: (a) untreated; (b) vacuum annealed at 170°C; (c) boiled in water for 1 h; (d) treated with 20% formic acid at 85°C for 1 h; (e) treated with formic acid at 102°C for 1 h.

structure and the amorphous component. The  $\gamma$  content is hardly changed by vacuum annealing [compare Fig. 6(b) with Fig. 7(d)].

The treatment in boiling water, on the other hand, causes considerable increase in the  $\alpha$  content while the  $\gamma$  content decreases significantly (Fig. 8). The separation between the (200) and the (002,202) peak maxima is about 2.5°, indicating high purity for the  $\alpha$  structure.

The treatment in aqueous formic acid even at room temperature causes a significant increase in the  $\alpha$  content at the expense of both the  $\gamma$  and the pleated

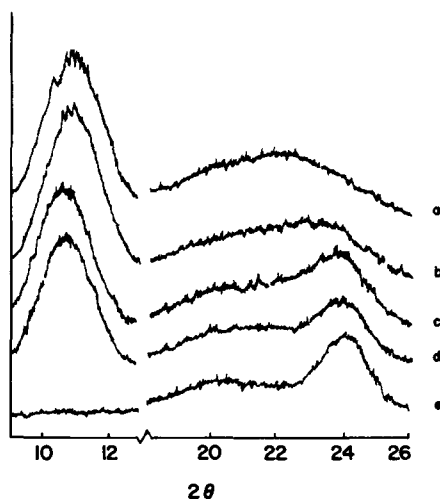


Fig. 12. Meridian X-ray scans of as-spun NAA blend yarns: (a) untreated; (b) vacuum annealed at 170°C; (c) water boiled for 1 h; (d) treated with 20% formic acid at 85°C for 1 h; (e) treated with formic acid at 102°C.

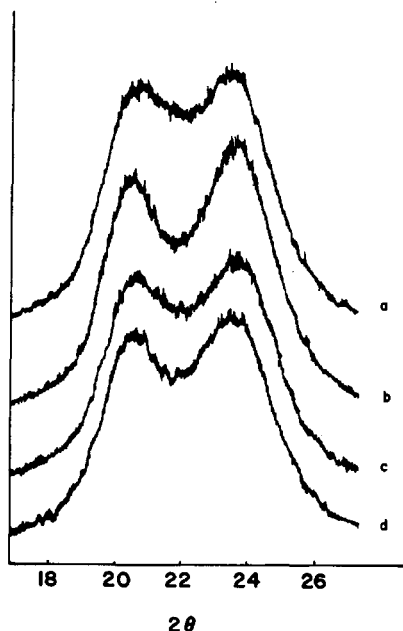


Fig. 13. Equatorial X-ray diffraction scattering of textured yarns: (a) nylon 6; (b) NEVOH 94/06; (c) NCAH 0.125%; (d) NAA 0.125%.

$\alpha$  structures and the amorphous content (Fig. 9). The content and purity of the  $\alpha$  structure increase the higher the temperature of the formic acid treatment. At 102°C pure  $\alpha$  structure is obtained (Fig. 10). There is no trace of the  $\gamma$  structure in the NCAH and NEVOH blends. The separation between the equatorial reflections is the maximum (4°). The as-spun fibers of nylon 6 and of the NCAH and NEVOH blends [the concentration of the additive ranging from 0.125% of poly(acrylamide-co-acrylic acid) in the NCAH blend to 6% (1-6) of poly(ethylene-co-vinyl alcohol) in the NEVOH series] behave similarly during the chemical and/or thermal treatments.

The as-spun fibers of the NAA blend, on the other hand, behave very differently. Vacuum annealing at temperatures up to 170°C causes only minor increases in the  $\alpha$  content at the expense of the amorphous content. Even severe treatments such as boiling water and 20% formic acid at temperatures up to 90°C do not cause significant increases in the  $\alpha$  content as in the case of the NCAH and NEVOH blends. Whatever increase is observed in the  $\alpha$  content is apparently caused by the crystallization of the amorphous phase and not by the conversion of the  $\gamma$  structure. The intensity ratio of the (020) to the (040) peaks for the treated NAA fibers (except those treated in formic acid at 102°C) is in the range of 2.5-3.0, suggesting that the  $\gamma$  content is almost unchanged by any of the above treatments. It is interesting to note that a new meridional peak at  $2\theta = 24^\circ$  grows in intensity and the severity of the treatment (Fig. 12). The treatment with formic acid at 102°C, however, converts fully the  $\gamma$  structure to the pure  $\alpha$  structure (the peak separation is 4°). It is seen from Fig. 11(e) that the equatorial peak at  $2\theta = 24^\circ$  is weaker than the (200) peak at  $2\theta = 20^\circ$  and that there is a corresponding increase in the intensity of the meridional peak at  $2\theta = 24^\circ$  (actually a new peak). These observations suggest that the population

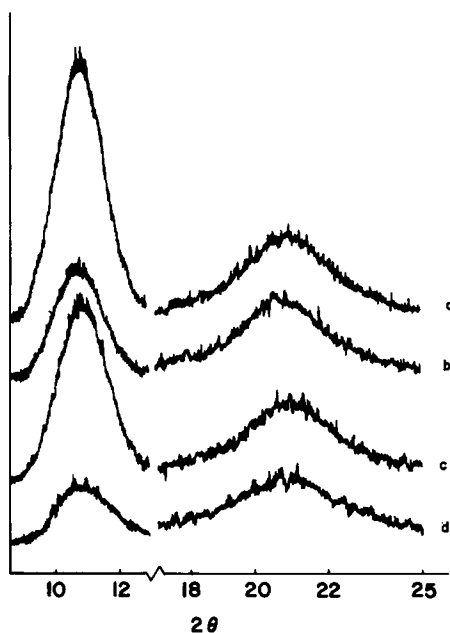


Fig. 14. Meridian X-ray diffraction scattering of textured yarns: (a) nylon 6; (b) NEVOH 94/06; (c) NCAH 0.125%; (d) NAA 0.125%.

of one or both the (002) and (202) planes which contribute to the intensity of the equatorial diffraction peak at  $2\theta = 24^\circ$  in the  $\alpha$  structure of nylon 6 is decreased in the NAA blend and that the population of a plane or planes which contribute at  $2\theta = 24^\circ$  in the meridional reflection is increased. A systematic investigation is needed to relate the intensity changes in the equatorial and meridional reflections of the NAA blend to the structural changes.

### Structure of Textured Filaments

The textured yarns of nylon 6 and the blends exhibit a crystalline structure which is a mixture of both the  $\alpha$  and the  $\gamma$  structures (Fig. 13). The relative amounts of these  $\gamma$  structures, however, vary significantly, depending upon the chemical structure and the concentration of the additive. No quantitative determination of the  $\alpha$  and the  $\gamma$  indices and the total crystallinity of these samples has been attempted. Instead, the fractional peak heights (i.e., the peak height above the base line drawn connecting the points at  $2\theta = 15^\circ$  and  $30^\circ$  on the equator to the total height) of the equatorial diffraction peaks at  $2\theta = 20.7^\circ$  and  $23.6^\circ$  are taken as an approximate measure of the relative total crystallinity of the sample.

From Table II it is clear that all the samples have approximately the same relative crystallinity. The intensity ratio of the meridional peaks (Fig. 14) at  $10.8^\circ$  and  $20.9^\circ$  (the base line was drawn connecting the points at  $2\theta = 8^\circ$  and  $30^\circ$  on the meridian), which is a measure of the  $\gamma$  content, has been calculated to be 0.3 for the  $\alpha$  structure and 2.5 for the pure  $\gamma$  structure.<sup>7-9</sup> The  $\gamma$  content is lower in all the blends than in nylon 6 (Table III). For a given additive, the  $\gamma$  content decreases with increasing concentration of the additive. The most striking decrease in the  $\gamma$  content is observed for the NAA fibers. Though

TABLE II  
 Equatorial WAXS Data on Textured Nylon Blend Yarns

Sample	Minor component (%)	Background at 15°	Peak Heights at		Ratio $P/(P + B)$ at	
			20.7°	23.6°	20.7°	23.6°
Nylon 6	0	10.0	71	76	0.89	0.90
NEAA	2	7.5	45	47	0.87	0.88
NPP	4	9.0	52	57	0.87	0.90
NEVOH	1	7.0	50	56	0.88	0.90
NEVOH	2	8.0	54	60	0.87	0.89
NEVOH	4	9.0	66	75	0.89	0.90
NEVOH	6	9.0	69	78	0.93	0.90
NCAH	0.125	9.0	60	67	0.88	0.90
NAA	0.125	9.0	63	68	0.91	0.90

poly(acrylic acid) is presented at a very low level, the textured yarn has the lowest  $\gamma$  content compared with all other samples investigated here. Nylon 6 with 1/8% concentration of poly(acrylamide-co-acrylic acid) with an acid content of 80% or 2% concentration of poly(ethylene-co-acrylic acid) shows that the formation of the  $\gamma$  structure during drawing is about the same as for nylon 6. It should be noted here that the poly(acrylic acid) does not suppress the formation of the  $\gamma$  structure during drawing. The starting material, i.e., the as-spun filament itself, has the well-developed, highly oriented  $\gamma$  structure instead of the poorly developed structure found in the as-spun fibers of nylon 6 and other blends. The  $\gamma$  structure is converted to the  $\alpha$  structure during drawing.

One may be tempted to attribute the observed structural differences of the blends to differences in compatibility of the component polymers. The polyamides including nylon 6 are known to form incompatible blends with polyolefins.<sup>15</sup> From our studies of blends of nylon 6 with poly(acrylic acid), polyacrylamide and their copolymers and poly(ethylene-co-vinyl alcohol) cast from formic acid solutions at widely different component ratios, it is known that nylon 6 forms miscible blends with poly(ethylene-co-vinyl alcohol), at low levels (up to 30%)<sup>16</sup> and with the other polymers at all levels.<sup>17</sup> Since all the blends excepting NAA behave similarly structurally, it is apparent that the miscibility or otherwise is not the cause of the observed structural differences in these blends.

End group analysis of the NAA and NCAH blends indicates that some crosslinking takes place during melt blending. This is confirmed by insolubility measurements in formic acid. Undissolved fiber fragments were present in solutions of both the blends. Since the NCAH blend behaves like any other blend other than the NAA blend, the crosslinking is probably not the reason for the observed differences.

It is probable that poly(acrylic acid) breaks the hydrogen bonds between adjacent sheets, and a new hydrogen bond network is formed between poly(acrylic acid) and nylon 6, as discussed earlier. However, in the absence of any orientation, the NAA blend behaves like any other blend. It exhibits in the melt chip form a single diffraction peak, and the  $\alpha$  content increases with increasing severity of the annealing treatment, as in the case of the NCAH or NEVOH blends. Surprisingly, these molecules orient themselves during extrusion under the tension of winding (though the takeup speed is only 300 m/min) and crystallize with the  $\gamma$  structure. This structure is highly resistant to conversion to  $\alpha$  during

TABLE III  
Meridian WAXS Data on Textured Nylon Blend Yarns

Sample	Minor component (%)	Background at 8°	Peak Heights at		Ratio of peaks
			10.8°	20.9°	
Nylon 6		10.0	82.5	27	3.06
NEAA	2	8.5	48	18	2.67
NPP	4	9.0	56	25	2.27
NEVOH	1	8.5	39	17	2.26
NEVOH	2	9.5	44	23	1.96
NEVOH	4	9.5	41	25	1.67
NEVOH	6	9.5	35	25	1.41
NCAH	0.125	9.5	55	23	2.44
NAA	0.125	9.0	18	20	0.92

annealing just as the  $\gamma$  structure obtained by I/KI treatment.<sup>1</sup> Strong treatments such as treating with 20% formic acid at 102°C or drawing are required to convert to the  $\alpha$  structure. These fibers also exhibit superior mechanical properties. The mechanical and optical properties of the blends will be discussed elsewhere.

### CONCLUSIONS

1. Nylon 6 melt chips exhibit a diffraction pattern characteristic of the  $\alpha$  structure while the blends exhibit a single diffraction ring. The  $\alpha$  content increases with the severity of the annealing treatment.

2. The as-spun fibers of nylon 6 and the NCAH and NEVOH blends exhibit a single diffraction peak while the as-spun NAA fibers exhibit the highly oriented  $\gamma$  structure. This  $\gamma$  structure is highly resistant to conversion to  $\alpha$  during annealing.

3. The textured yarns of the blends of the NEAA, NCAH, NEVOH, NPP, and NAA series have lower  $\gamma$  content than nylon 6. Poly(acrylic acid) when melt-blended with nylon 6 even at a low level of 0.125% results in drawn fibers with very low  $\gamma$  content.

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