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Following studies of the ferroelectric behavior of the odd-numbered nylons, the ferroelectric switching mechanisms have been investigated in terms of the crystal orientation or reorientation using wide angle X-ray diffraction method. It has been found that the degree of double crystallite orientation resulting from uniaxial stretching below T_g for the odd-numbered nylon films decreases with increasing amide content. The electric field poling results in a reorientation of unit cells without changing the crystal structure or chain packing in the nylon films. Moisture absorbed by the nylon samples can strongly affect the resultant reorientation of the crystal unit cell. With the presence of some level of moisture, a 90° reorientation of the unit cells is observed for all the nylons studied. A 72° unit cell reorientation is observed for nylon 11 samples when poled using a dry-air purge. This difference may be attributed to the increase in electric field applied to the crystalline phase when moisture is present in the amorphous region during poling.

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by B.Z. Mei, J.I. Scheinbeim and B.A. Newman

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FERROELECTRIC POLARIZATION MECHANISM OF

THE ODD-NUMBERED NYLONS

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Abstract

Following studies of the ferroelectric behavior of the odd-numbered nylons, the ferroelectric switching mechanisms have been investigated in terms of the crystal orientation or reorientation using wide angle X-ray diffraction method. It has been found that the degree of double crystallite orientation resulting from uniaxial stretching below T_g for the odd-numbered nylon films decreases with increasing amide content. The electric field poling results in a reorientation of unit cells without changing the crystal structure or chain packing in the nylon films. Moisture absorbed by the nylon samples can strongly affect the resultant reorientation of the crystal unit cell. With the presence of some level of moisture, a 90° reorientation of the unit cells is observed for all the nylons studied. A 72° unit cell reorientation is observed for nylon 11 samples when poled using a dry-air purge. This difference may be attributed to the increase in electric field applied to the crystalline phase when moisture is present in the amorphous regions during poling.

Introduction

Following studies[1-3] of Nylon 11 and Nylon 7 in our laboratory, the ferroelectric nature of the series of odd-numbered nylon polymers was further established by a demonstration of the hysteresis behavior between the electric displacement, D, and the applied electric field, E, for Nylon 5 and Nylon 9[4]. It was shown that with increasing dipole density, both the remanent polarization and the apparent coercive field of the odd-numbered nylons increase linearly. In the present study, in order to obtain additional insights into the ferroelectric switching behavior of the odd-numbered nylons, an investigation of the crystal orientation or reorientation resulting from both uniaxial stretching and electric field poling was carried out using wide angle X-ray diffraction methods. In addition, a major factor that influences the ferroelectric switching behavior of the nylons, moisture absorption, was also investigated.

Experimental

As-stretched and as-poled odd nylon films were prepared as described previously[4]. After evaporating gold electrodes on opposing sides of the films, the odd-numbered nylon samples were poled both with and without using a dry-air purge. When films were poled using a dry-air purge, a higher electric field with E_{max} = 250~300 MV/m was needed in order to obtain comparable remanent polarization to that obtained without using a dry-air purge. As-annealed and poled-annealed samples were prepared by annealing as-stretched and as-poled nylon films at 185°C for Nylon 11 and 200°C for both Nylon 7 and Nylon 5, for two hours in vacuum (~10^{-3} torr).

Flat-plate wide angle X-ray diffraction photographs were taken at room temperature using nickel-filtered Cu$k\alpha$ radiation. With CaF$_2$ as an internal standard, the d-spacings were measured and then indexed according to the unit cell proposed by

Hasegawa[5]. In these experiments, diffraction patterns in three modes, namely; end mode (incident X-ray beam along the draw direction), edge mode (incident beam perpendicular to the draw direction and parallel to the plane of the film), and transmission mode (incident beam perpendicular to the plane of the film) were taken to obtain information about crystallite orientation in the nylon samples, both before and after poling. Figure 1 shows the orientation of the samples with respect to the incident X-ray beam in these three modes.

Results

Figures 2-8 show the flat-plate wide angle X-ray diffraction photographs taken in the three diffraction modes along with schematic representations of the observed reflections indexed according to Hasegawa's proposed unit cells[5] for as-annealed nylon films, as well as poled-annealed films which were poled with or without using a dry-air purge. In these figures, (a), (b), and (c) represent end mode, edge mode and transmission mode respectively. Reflections that may be thought of as characterizing the crystal structures of the odd-numbered nylons, such as the (020) reflection, whose d-spacing corresponds to the spacing between hydrogen-bonded sheets; the (200) reflection, whose d-spacing corresponds to the spacing between hydrogen-bond chains, and the (001) reflection, whose d-spacing corresponds to the spacing between basal planes, are indexed and summarized in Table 1 to Table 3.

(1) Nylon 11

Before poling, as-annealed Nylon 11 films show clear double orientation which is evident on the diffraction patterns shown in Figures 2(a), 2(b), and 2(c). First, with the X-ray beam parallel to the chain axis (c-axis), the diffraction pattern shows a very sharp and unambiguous set of arcs of circles with an angular spread $\sim\pm15°$, as

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illustrated in Figure 2(a). A very strong (020) reflection is seen at 3.88Å on the equator, which confirms the fact that the hydrogen-bonded sheets are parallel to the plane of the film. Second, as shown in Figures 2(b) and 2(c), when the X-ray beam is perpendicular to the chain axis, the diffraction pattern is observed to be different if the beam is parallel or perpendicular to the film: The (020) reflection is only seen in the edge mode while the (200) reflection is only seen in the transmission mode. Also, comparing Figures 2(b) and 2(c), (00*l*) reflections appear on the meridian in the transmission mode pattern but off-meridian in the edge pattern. The explanation of this observation lies in the special morphology of the drawn nylon films, and can be accounted for by a "stacking fault disorder" which is the topic of a separate publication.

Figures 3(a), 3(b) and 3(c) provide information about the crystal orientation in poled-annealed nylon 11 films which were poled without using a dry-air purge. It is found that after poling, the (020) reflection is switched by 90° about the *c*-axis as shown in Figure 3(a). Meanwhile, the diffraction patterns shown in Figures 3(b) and 3(c) are again observed to be distinct and now indicate that after poling, a three dimensional orientation texture of the crystallites of the film occurs; however, the reorientation of the crystallites occurs by a 90° reorientation (rotation) of chains about the *c*-axis (the long axis) with respect to the initial orientation. This phenomenon is consistent with what was reported in our earlier work[3].

On the other hand, when samples are poled using a dry-air purge, as shown in Figures 4(a), 4(b) and 4(c), the poled-annealed films show a different reorientation from that discussed above. The most striking feature observed is that the (020) reflection shown in the X-ray diffraction pattern taken in end mode, as shown in Figure 4(a), rotates ~ 72° about the *c*-axis compared to the 90° rotation shown in Figure 2(a). This indicates that in the absence of water, or, at least, the presence of

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less water, a 72° reorientation of the hydrogen-bonded sheets occurs under the influence of the applied electric field and subsequent annealing. The X-ray diffraction patterns shown in Figures 4(b) and 4(c) are observed to be similar to that observed previously.

(2) Nylon 7

With similar sample preparation and thermal history, the as-annealed Nylon 7 films shows a decrease in double orientation compared to Nylon 11. The diffraction pattern of Figure 5(a), which is a c-axis projection, shows a series of rather broad arcs with an angular spread of ~±25°. The reflection indexed as (020) at 3.84Å is observed on the equator, and two reflections indexed as (200) at 4.37Å are seen on both side of the meridian. Figures 5(b) and 5(c) show the diffraction patterns taken with the X-ray beam perpendicular to the chain axis. As observed for Nylon 11, (00l) reflections are observed on the meridian for the transmission mode pattern but in an off-meridian direction for the edge mode pattern. Both (020) and (200) are seen at 3.80Å and 4.38Å in the edge mode and transmission mode. But the relative intensity between the (020) and (200) reflections observed is very different in the two cases: The (020) reflection is much stronger in the edge mode and weaker in the transmission mode than the (200) reflection. From these diffraction patterns taken in the three different modes, it is suggested that some double orientation is present in the film, but the extent of this double orientation is less than that observed in Nylon 11 films.

When subjected to an electric field, with or without using a dry-air purge, poled-annealed Nylon 7 samples, in Figure 6(a), show the same crystal reorientation seen previously in Figure 3(a); i.e., a 90° reorientation about the c-axis occurs for the hydrogen-bonded sheets. Furthermore, when the X-ray beam is perpendicular to the

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chain axis, the results are similar to those obtained for Nylon 11: reversed diffraction patterns were observed for the edge mode and transmission mode as compared with patterns taken before poling (compare 5(b) and 5(c) with 6(b) and 6(c)). After poling, the relative intensity of the (020) and (200) reflections is still different, but now the (020) reflection is much stronger in transmission mode and weaker in edge mode than the (200) reflection. Therefore, the poled-annealed films still attain a three dimensional orientation texture after poling, but rotated by 90° with respect to the orientation before poling.

(3) Nylon 5

In the case of Nylon 5, with a higher amide content, the crystalline regions in the as-annealed samples show much more uniaxial orientation and less double orientation. This is illustrated by the very broad arcs, with angular spreads ~±35, in the c-axis projection X-ray diffraction pattern shown in Figure 7(a). Nevertheless, the (020) reflection still appears on the equator and is not observed on the meridian in Figure 7(a). Therefore, some double orientation still exists. The diffraction patterns obtained from edge mode and transmission mode, shown in Figures 7(b) and 7(c), respectively, are similar: both (200) and (020) reflections are observed on the equator, and the (00l) reflections appear on both sides of the meridian. But it is noticed that the relative intensity between the (200) and (020) reflections is observed different: the (020) reflection is observed to be stronger in edge mode and weaker in transmission mode than the (200) reflection. This indicates that after uniaxially stretching at room temperature, the as-annealed Nylon 5 films also possess a double orientation; however, the degree of this double orientation is much lower than that of both Nylon 11 and Nylon 7 films.

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After poling, similar to the case of Nylon 7, the hydrogen-bonded sheets in poled-annealed Nylon 5 films are found to rotate by 90° about the *c*-axis with respect to their initial orientation, whether or not the samples were poled with or without using a dry-air purge, see Figure 8(a) compared to Figure 7(a). The diffraction patterns taken in edge mode and transmission mode, respectively, are observed to be similar and resemble those taken before poling. It is important to point out that after poling, the (020) reflection is observed stronger in transmission mode, and weaker in the edge mode than the (200) reflection.

Discussion

(1) The orientation of the crystallites in the melt-quenched and cold-drawn odd-numbered nylon films

It was found[3] that initially melt-quenched and cold-drawn Nylon 11 films are doubly oriented, with the molecular chains aligned in the draw direction and the hydrogen-bonded sheets parallel to the plane of the films. In the present X-ray diffraction study, we have verified that the as-annealed Nylon 11 films are doubly oriented. In addition, as shown in the results, the degree of double orientation of the crystallites in the as-annealed odd-numbered nylon samples is observed to gradually decrease as the dipole density increases. The double orientation phenomenon for the uniaxially stretched Nylon 11 films was first reported by Northolt in 1972[6]. He explained this phenomenon based on Gordon's assumption[7] that below T_g, the hydrogen bonds and thus the hydrogen-bonded sheets were not broken up in the drawing process, and that the regular stacking of hydrogen-bonded sheets in Nylon 11 films resulted in two-dimensional sheets which were oriented parallel to the plane of the film. However, it has been shown[8] that the hydrogen-bonded sheets do not break until after sample melting. A similar phenomenon is also observed in the case of the

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lower-order odd-numbered nylon films, such as Nylon 7 and Nylon 5 films, but the degree of orientation is reduced. The reason why uniaxial stretching at temperatures below T_g can result in a double orientation for the melt-quenched odd-numbered nylon films is not clear. However, it is obvious that the higher-order odd-numbered nylon films, which are probably better quenched initially due to their lower melting points, acquire a high degree of double orientation during uniaxial stretching, while the lower-order odd-numbered nylon films with higher melting points exhibit a low degree of double orientation. In other words, the observed reduced degree of crystal orientation of the lower-order odd-numbered nylon films may be related to the initial molecular order of the films after quenching.

In the case of lower-order odd-numbered nylons, with their high amide content, the molecules probably exhibit a certain degree of order after quenching into the ice water from a temperature 20~30° higher than the melting point. Therefore, during uniaxial stretching, it may be more difficult for the chains to rearrange or move, because of their low mobility, to form very organized doubly oriented hydrogen-bonded sheets. In addition, the restrictions presented by the hydrogen bonding to the relative movement of chains is also considered as an important factor that results in a low degree of double crystal orientation in the films. On the other hand, in the case of higher-order odd-numbered nylons, with a lower hydrogen-bonding content, the long, flexible hydrocarbon chain segments are initially poorly registered after quenching, and therefore are easy to move or rearrange to reach a high degree of double orientation during the uniaxial stretching. As a result, high-order odd-numbered nylons, such as Nylon 11, show a very organized doubly oriented crystallite distribution.

(2) The mechanisms of the ferroelectric polarization switching

Based on wide angle X-ray diffraction studies and FTIR measurements, a 90°
dipole reorientation resulting from electric field poling followed by 180° dipole
reorientations was postulated[3] for Nylon 11 films. It is believed that during poling,
the hydrogen bond dipoles in the Nylon 11 samples break and rotate into the direction
of the field, which is the state of lowest dipole orientation energy, then reform new
hydrogen-bonded sheets with the neighboring chains. This also results in a similar
reorientation of the hydrocarbon chain segments. The hydrogen bond dipoles in both
Nylon 7 and Nylon 5 films are also expected to reorient along the field direction after
poling. Further, the X-ray diffraction patterns show that, although Nylon 7 and Nylon
5 films exhibit a reduced double orientation, a 90° rotation of crystallites about the *c*-
axis also occurs after poling. It is interesting to see that the field-induced crystal
reorientation barely changes the initial degree of double orientation of the crystallites
in the nylons studied. For example, after poling, Nylon 11 films are observed to
exhibit a three-dimensional texture, while Nylon 5 films still maintain the initial
reduced double orientation. This strongly indicates that under the application of an
electric field, the chains merely rotate about their long axes without changing the
crystal structure or its texture. Therefore, the electric field-induced reorientation of
the hydrogen bond dipoles is believed to be independent of the initial order of the
hydrocarbon chain segments.

According to the crystal structures of the odd-numbered nylons proposed by
Hasegawa[5], which is shown in Figure 9, during poling, the original hydrogen bonds
(along the **a** direction) between the molecular chains are broken under the application
of an electric field. The broken dipoles would switch and form new hydrogen-bonded
sheets with the nearest neighboring chains in a direction closer to the external field
direction. In order to maintain the original crystal structure based on up-down chains

forming hydrogen-bonded sheets, there are only two possible neighboring chains, at the A or B positions, with which the hydrogen-bonded sheets can be reformed under the influence of the applied electric field. The angles between the original hydrogen-bonded sheets (a-axis) and A (ϕ_1) or B (ϕ_2) chains are estimated to be 58° and 84°, respectively.

One thing that must be borne in mind is that all the nylon films were poled before annealing when the hydrogen-bonded sheets were poorly stacked, and the d-spacing between them was actually larger than that calculated from the X-ray diffraction patterns. For example, in the case of Nylon 11, the d-spacing between the hydrogen-bonded sheets, d_{020}, is 4.22Å before annealing and reduces to 3.86Å after annealing[2]. Although accurate unit cell parameters for the unannealed odd-numbered nylons can not be obtained due to the diffuse X-ray diffraction patterns, the angles ϕ_1 and ϕ_2 can still be approximately calculated as 70° and 86°, respectively. If the switched dipoles form the new hydrogen-bonded sheets with chains at the A positions (the nearest neighboring chains), a 70 degree reorientation of the crystallites would be observed. While if the switched dipoles form the new hydrogen-bonded sheets with chains at the B positions, an 86 degree reorientation of the crystallites would be observed. It appears that, in fact, a 70° rotation for the crystallites may be more energetically favorable, because it does not require a large scale rearrangement of polymer chains.

It is noticed that when Nylon 11 films were poled using a dry-air purge, a 72° reorientation of the crystallites about the c-axis was observed, which is very close to the 70° crystallite reorientation. However, since the diffraction pattern, shown in Figure 4(a), was obtained from the poled-annealed samples, in other words, the new hydrogen-bonded sheets formed under the application of the external field would be closely packed during annealing, a 58° crystal reorientation would be observed. The

discrepancy may result from the rearrangement of the molecular chains during the reforming of the new hydrogen-bonded sheets. On the other hand, a 90° reorientation was found when the films were poled without using a dry-air purge. This indicates that under higher humidity, a large rearrangement of relative chain positions in the crystalline regions becomes possible for the melt-quenched and cold-drawn odd-numbered nylon films under the application of an external electric field. This may be attributed to a redistribution of the electric field within the nylon samples containing a certain amount of water.

It is believed that only the disordered portions of the polymer are accessible to water[9], and water molecules are considered to be in the intermolecular spaces of the amorphous and interfacial regions[10]. The moisture contained in nylon samples dramatically changes the dielectric constant of the amorphous regions, which changes the distribution of the electric field between the amorphous and crystalline phases. If a two-phase model (amorphous-crystalline in series) is assumed, the electric field applied to the crystalline phase increases as moisture in the amorphous regions increases. Therefore, the driving force for chain rotation and rearrangement increases. Further, water molecules trapped in the interfacial regions may make the molecular chains on the surface of the crystallites more mobile. In other words, when samples absorb water, a large rearrangement of chains, which usually starts from the crystal surface, becomes easier. Consequently, when Nylon 11 films are poled without using a dry-air purge, a 86° reorientation of the hydrogen-bonded sheets can be accomplished by reforming hydrogen bonds with the second nearest neighboring chains at the B positions. Since there is a certain degree of distribution of the (020) reflections, a pair of (020) reflections (resulting from the twinned or 180° rotated crystals) will be superimposed and observed as one reflection with an arc centered at 90° from the initial orientation.

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In the case of Nylon 7 and Nylon 5, the hydrogen-bonded sheets are observed to rotate 90° under the application of an electric field both with and without using a dry-air purge during poling. This may be attributed to their much higher amide concentration which binds much more water in the disordered regions and applies a larger torque to the dipoles and, therefore, to the hydrocarbon chain segments during electric field poling. In fact, for the lower order nylons, such as Nylon 5, it is extremely difficult to prevent water absorption from the surroundings even though a dry-air purge is used. So the effect of absorbed water is considered to be a very important factor in concentrating the field on the crystals which favors field-induced molecular chain rotation and rearrangement, even when the samples are poled using a dry-air purge. As a result, both Nylon 7 and Nylon 5 are observed to have a 90° field -induced crystallite rotation whether or not a dry-air purge is used during poling.

Conclusions

Based on the present study of the orientation changes of odd-numbered nylon chain segments during electric-field poling, the following conclusions can be drawn:

(1) The degree of double crystallite orientation resulting from uniaxial stretching below T_g for the melt-quenched odd-numbered nylon films is observed to decrease with increasing amide content.

(2) The electric field poling results in a reorientation of unit cells without changing the crystal structure or chain packing in the nylon films. The hydrogen-bonded sheets are formed primarily from up-down chains. Moisture absorbed by the odd-numbered nylon samples can strongly affect the resultant reorientation of the crystal unit cells. With the presence of some level of moisture, a 90° reorientation of the unit cells is observed for all the nylons studied. This reorientation occurs by rotation of the molecular chains about their long axes. A 73° unit cell reorientation is

observed for Nylon 11 samples when poled using a dry-air purge. This difference in the electric field-induced reorientation may be attributed to the increase in electric field applied to the crystalline phase when moisture is present in the amorphous regions during poling.

Table 1 Diffraction data of as-annealed and poled-annealed Nylon 11

As-annealed		Poled-annealed	
$d_{obs.}$(Å)	Index	$d_{obs.}$(Å)	Index
3.88	(020)	3.86	(020)
4.25	(200)	4.23	(200)
12.84	(001)	12.80	(001)

Table 2 Diffraction data of as-annealed and poled-annealed Nylon 7

As-annealed		Poled-annealed	
$d_{obs.}$(Å)	Index	$d_{obs.}$(Å)	Index
3.84	(020)	3.81	(020)
4.37	(200)	4.35	(200)
7.80	(001)	7.79	(001)

Table 3 Diffraction data of as-annealed and poled-annealed Nylon 5

As-annealed		Poled-annealed	
$d_{obs.}$(Å)	Index	$d_{obs.}$(Å)	Index
3.81	(020)	3.83	(020)
4.31	(200)	4.31	(200)
6.15	(001)	6.13	(001)

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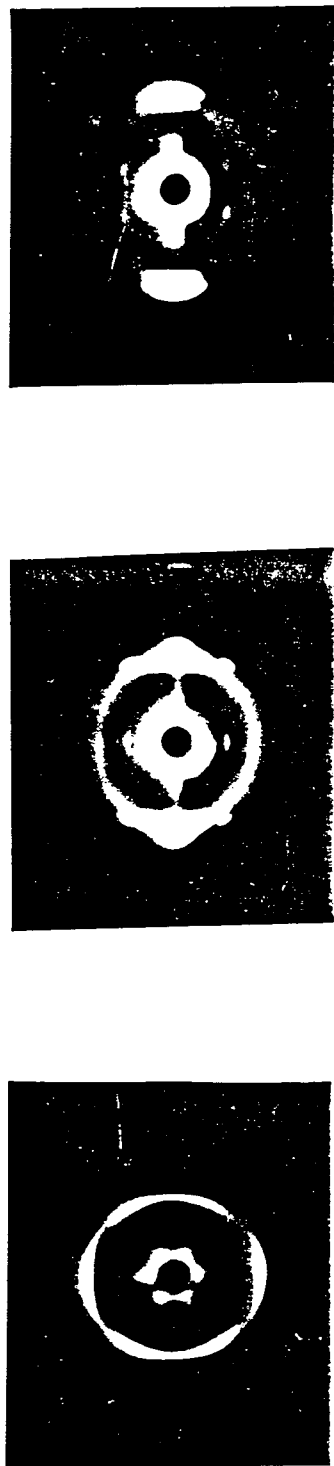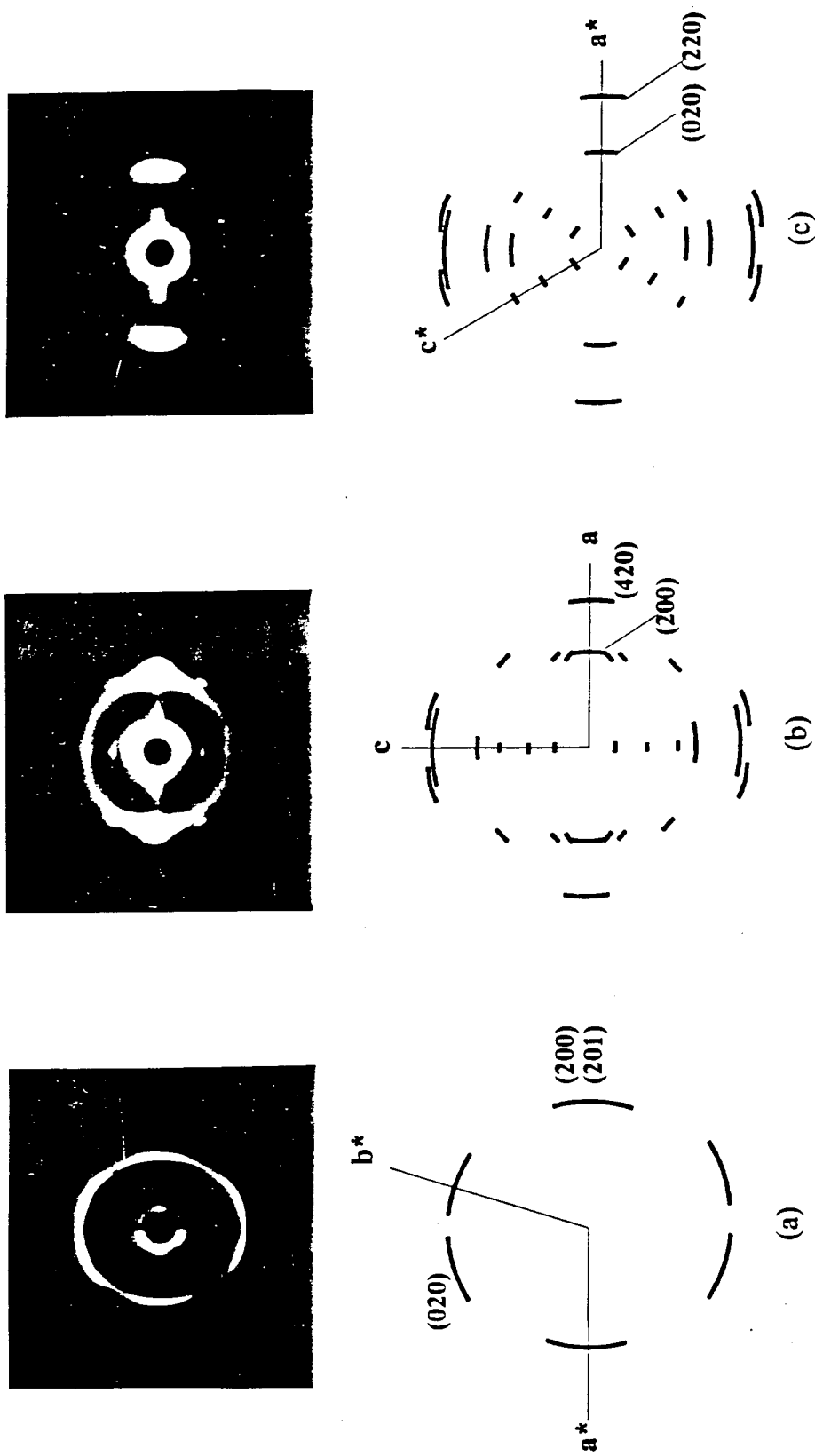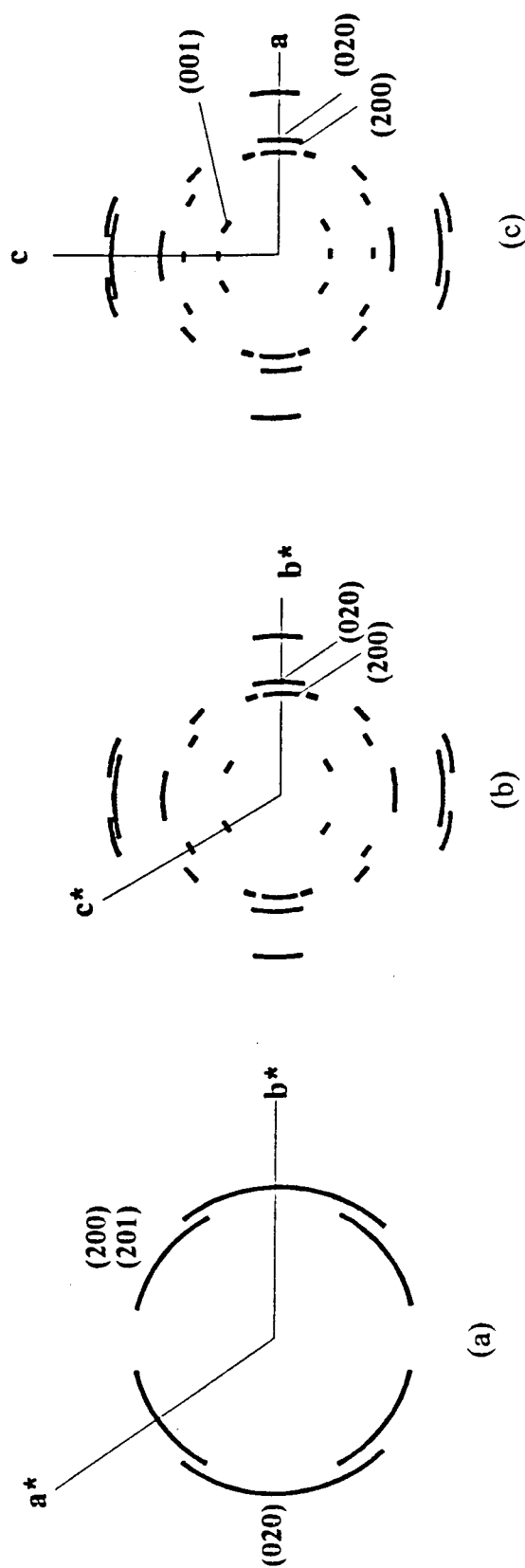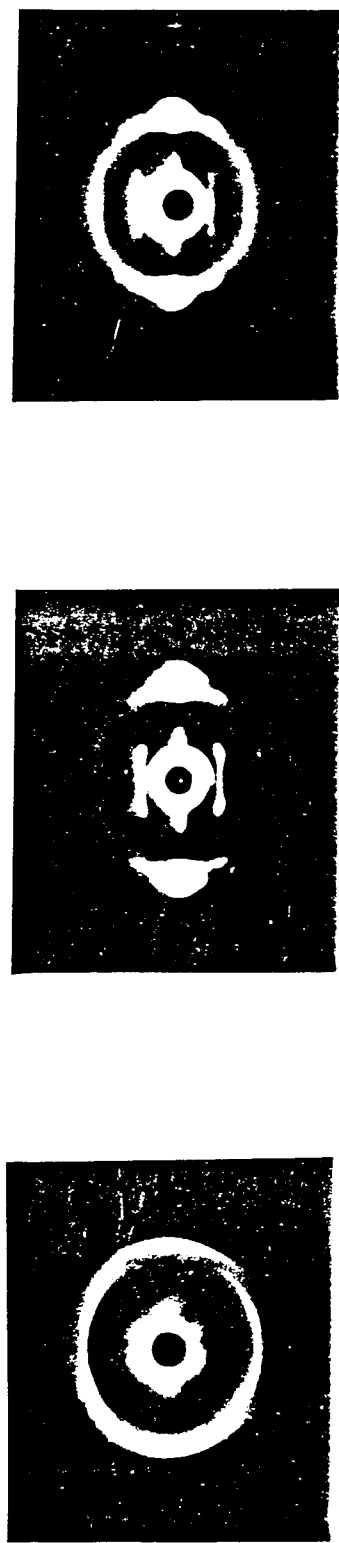10. A. D. McLaren and J W. Rowen, *J. Polym. Sci.*, **7**, 289, 1973.
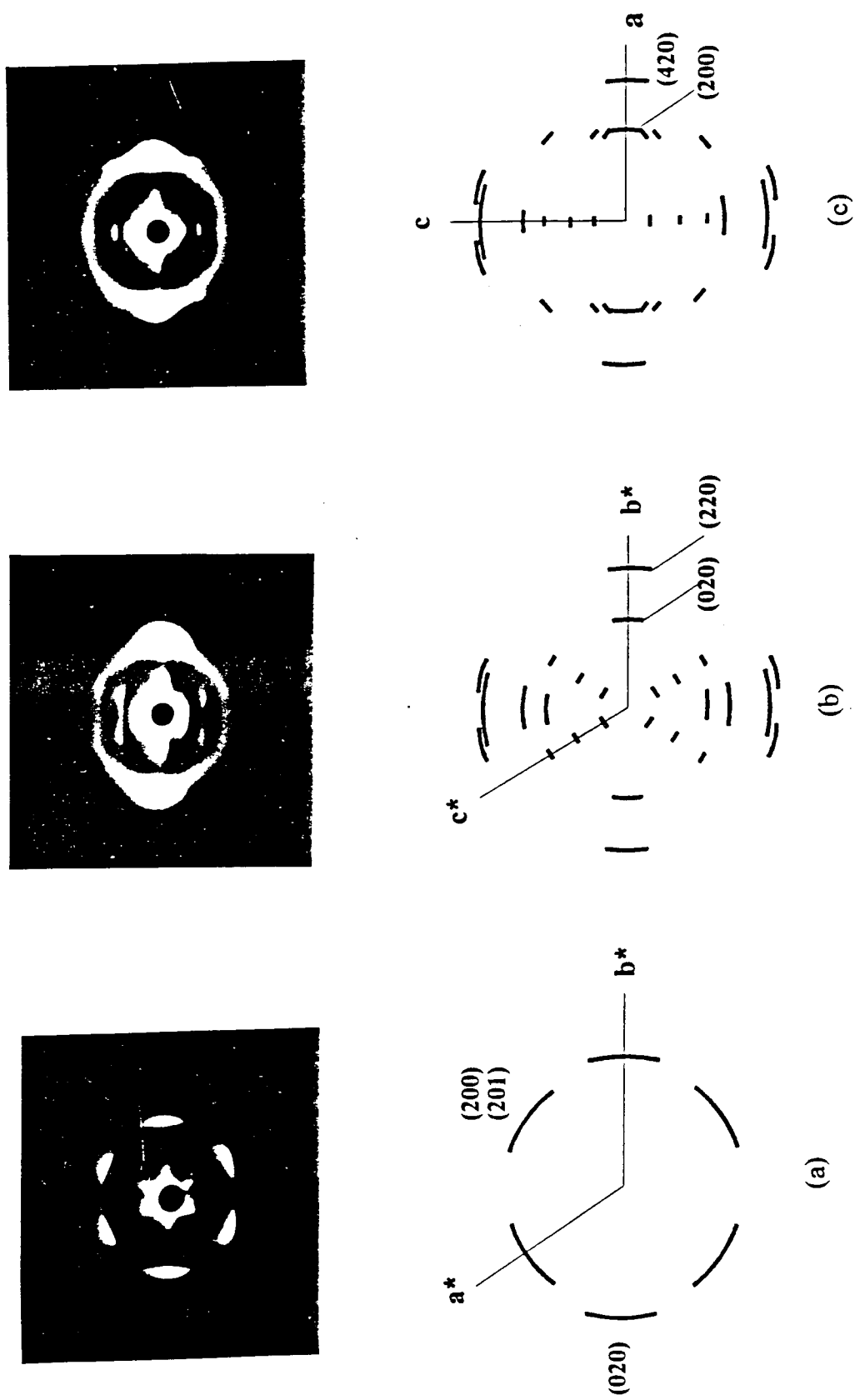
Figure 2 Flat plate wide X-ray diffraction patterns and corresponding schematic representations of as-annealed Nylon 11 films. (a) End mode. (b) Edge mode. (c) Transmission mode.

Draw Direction

X-Ray

Sample

X-Ray
Film

(a) End mode

Draw Direction

X-Ray

Sample

X-Ray
Film

(b) Edge Mode

Draw Direction
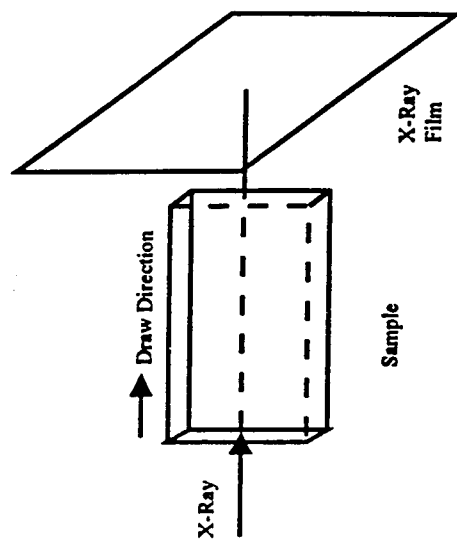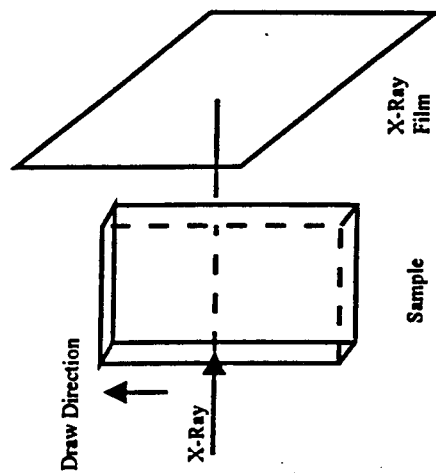
X-Ray
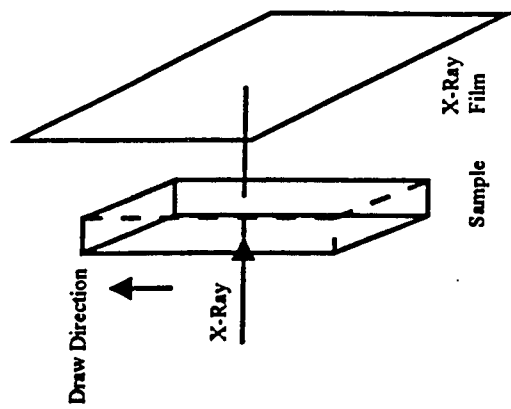
Sample

X-Ray
Film

(c) Transmission Mode

Figure 1 Orientation of the odd-numbered nylon film samples with respect to the incident X-ray beam in the flat plate wide angle X-ray diffraction study

(a)

(b)

(c)
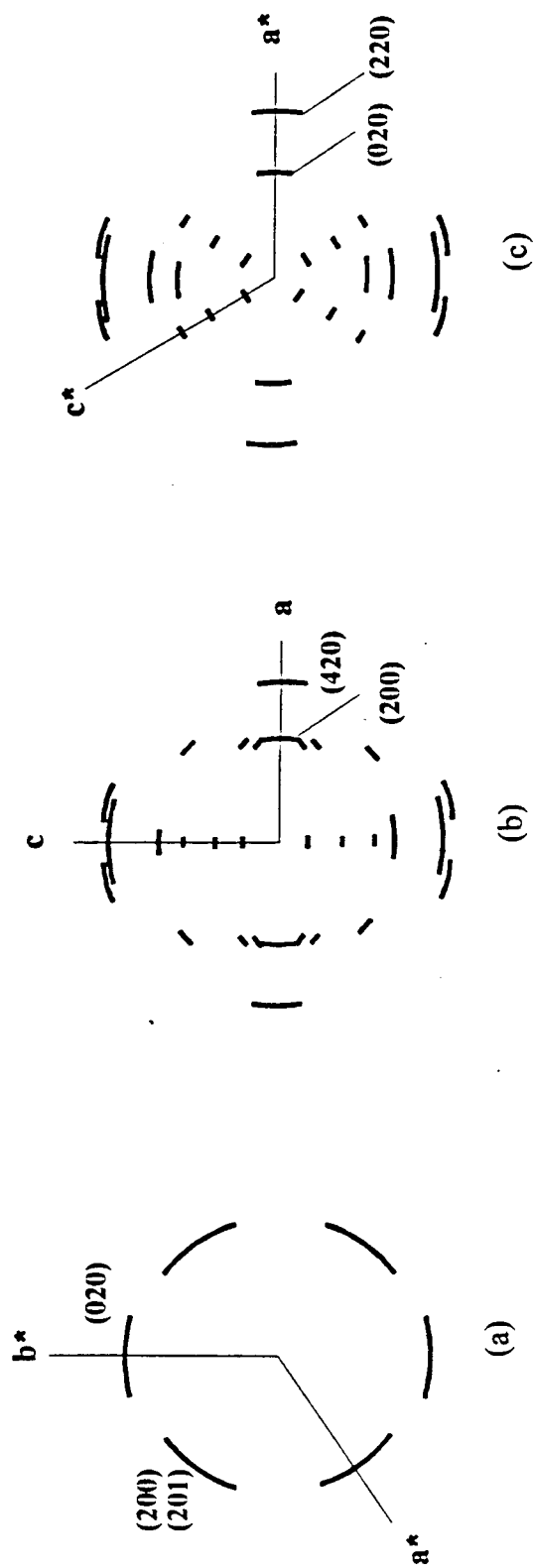
Figure 3 Flat plate wide X-ray diffraction patterns and corresponding schematic representations of poled-annealed Nylon 11 films. Samples were poled without using a dry-air purge.

(a) End mode. (b) Edge mode. (c) Transmission mode.

Figure 4   Flat plate wide X-ray diffraction patterns and correspondind schematic representations of poled-annealed Nylon 11 films. Samples were poled using a dry-air purge. (a) End mode. (b) Edge mode. (c) Transmission mode.
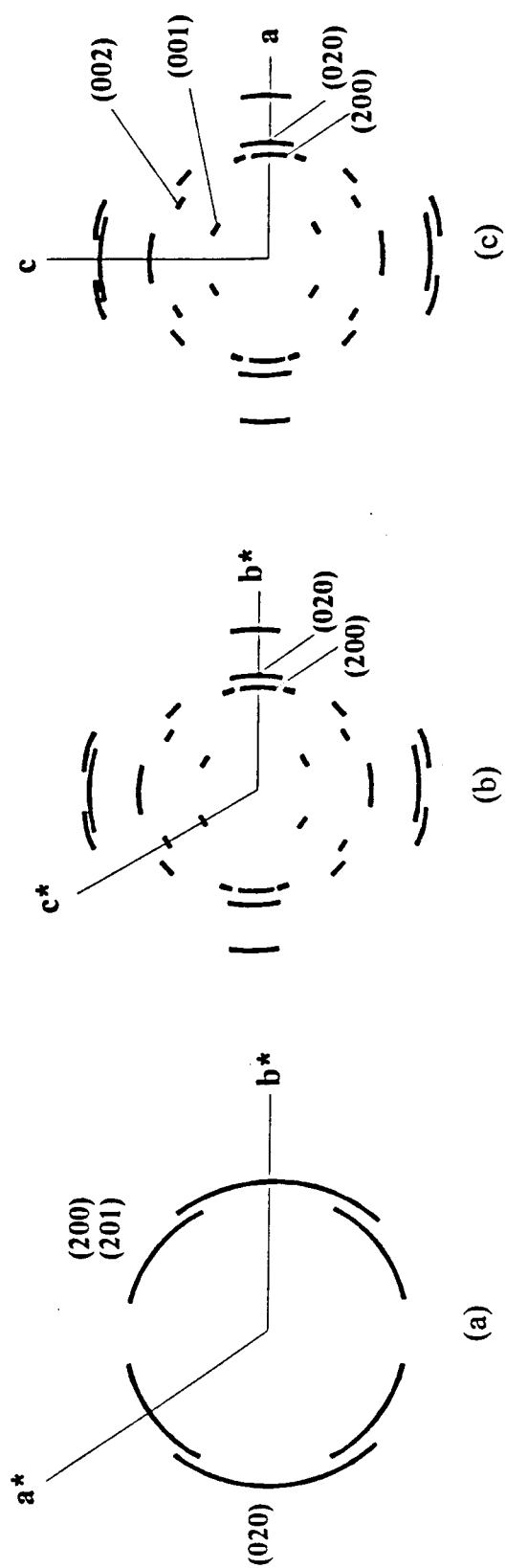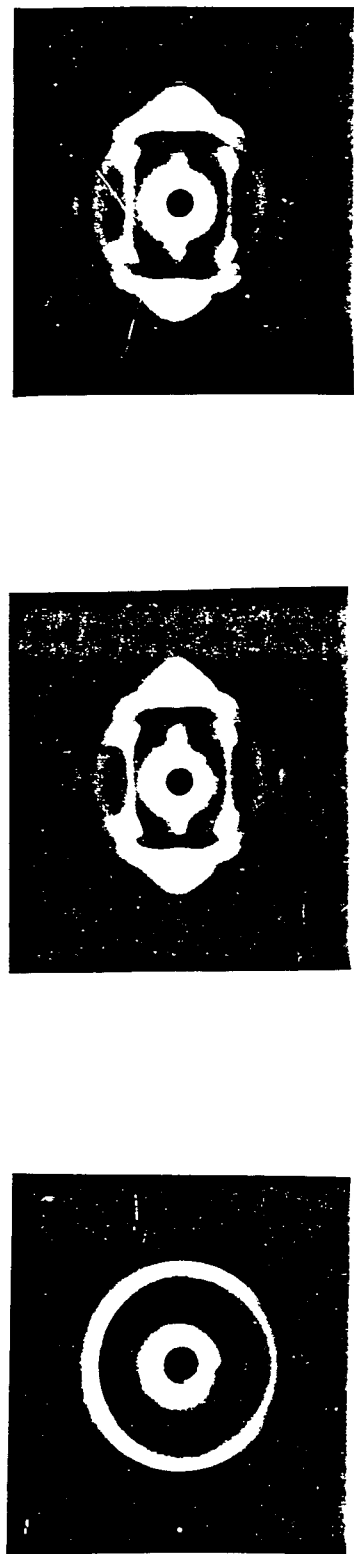
(a)

(b)

(c)

Figure 5   Flat plate wide angle X-ray diffraction patterns and corresponding schematic representations of as-annealed Nylon 7 films. (a) End mode. (b) Edge mode. (c) Transmission mode.
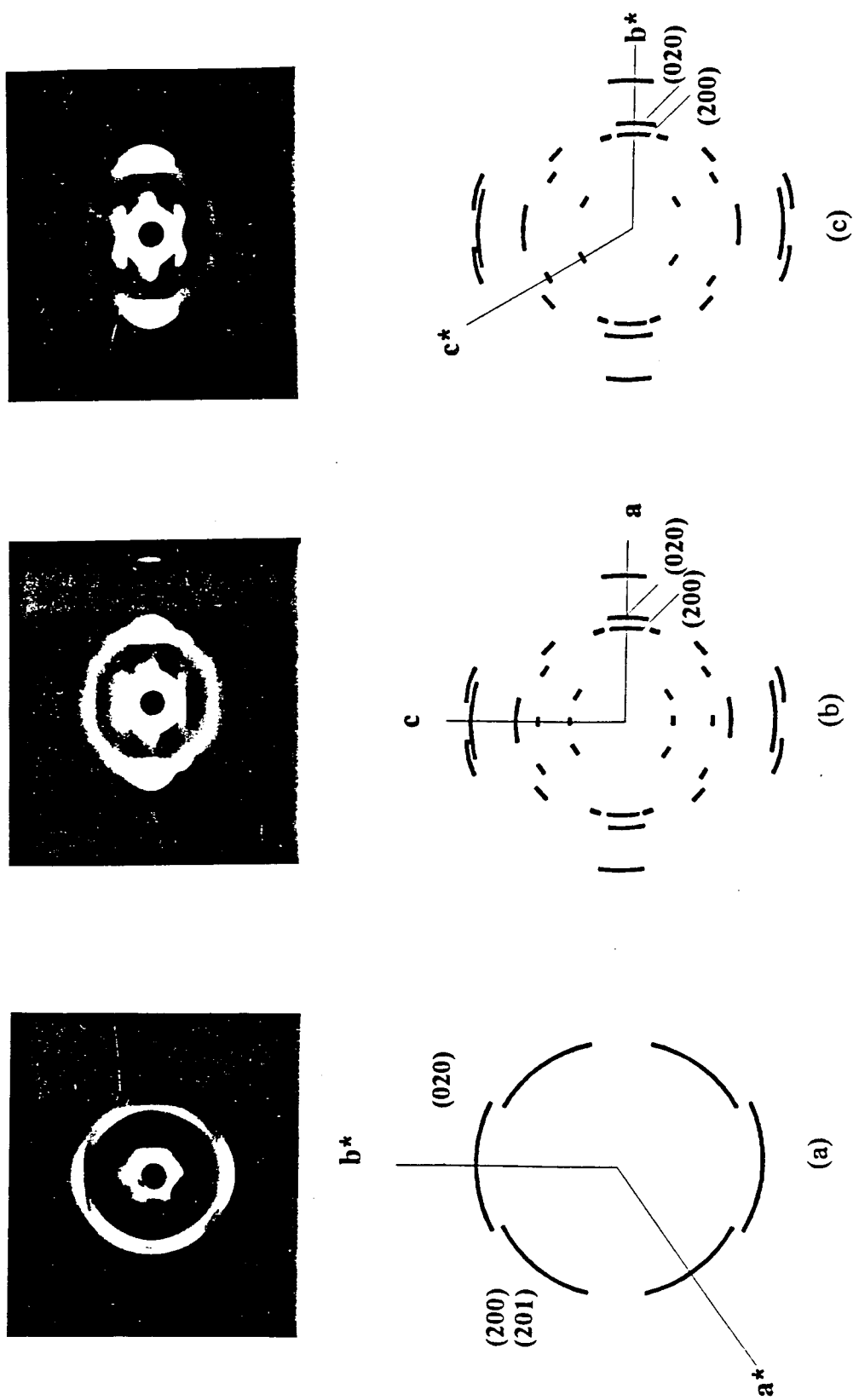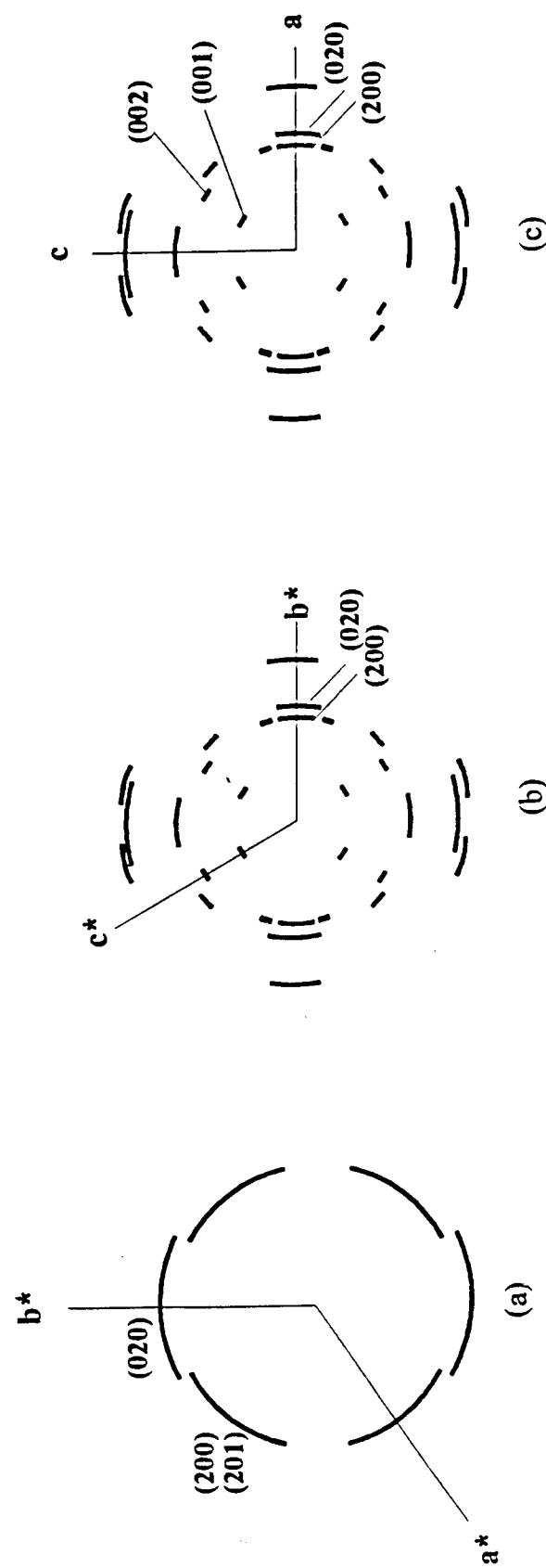
Figure 6   Flat plate wide angle X-ray diffraction patterns and corresponding schematic representations of poled-annealed Nylon 7 films.   (a) End mode.   (b) Edge mode.   (c) Transmission mode.

Figure 7 Flat plate wide angle X-ray diffraction patterns and corresponding schematic representations of as-annealed Nylon 5 films. (a) End mode. (b) Edge mode. (c) Transmission mode.
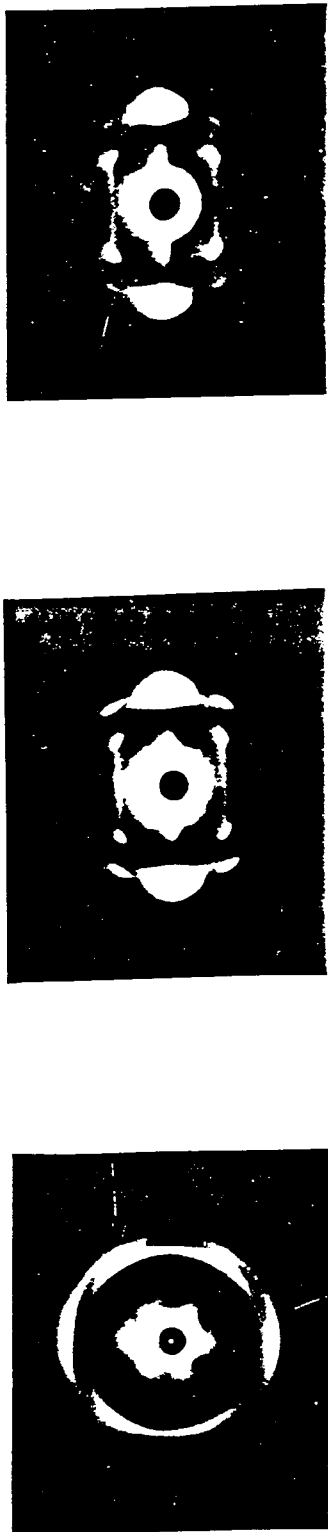
Figure 8 Flat plate wide angle X-ray diffraction patterns and corresponding schematic representations of poled-annealed Nylon 5 films. (a) End mode. (b) Edge mode. (c) Transmission mode.
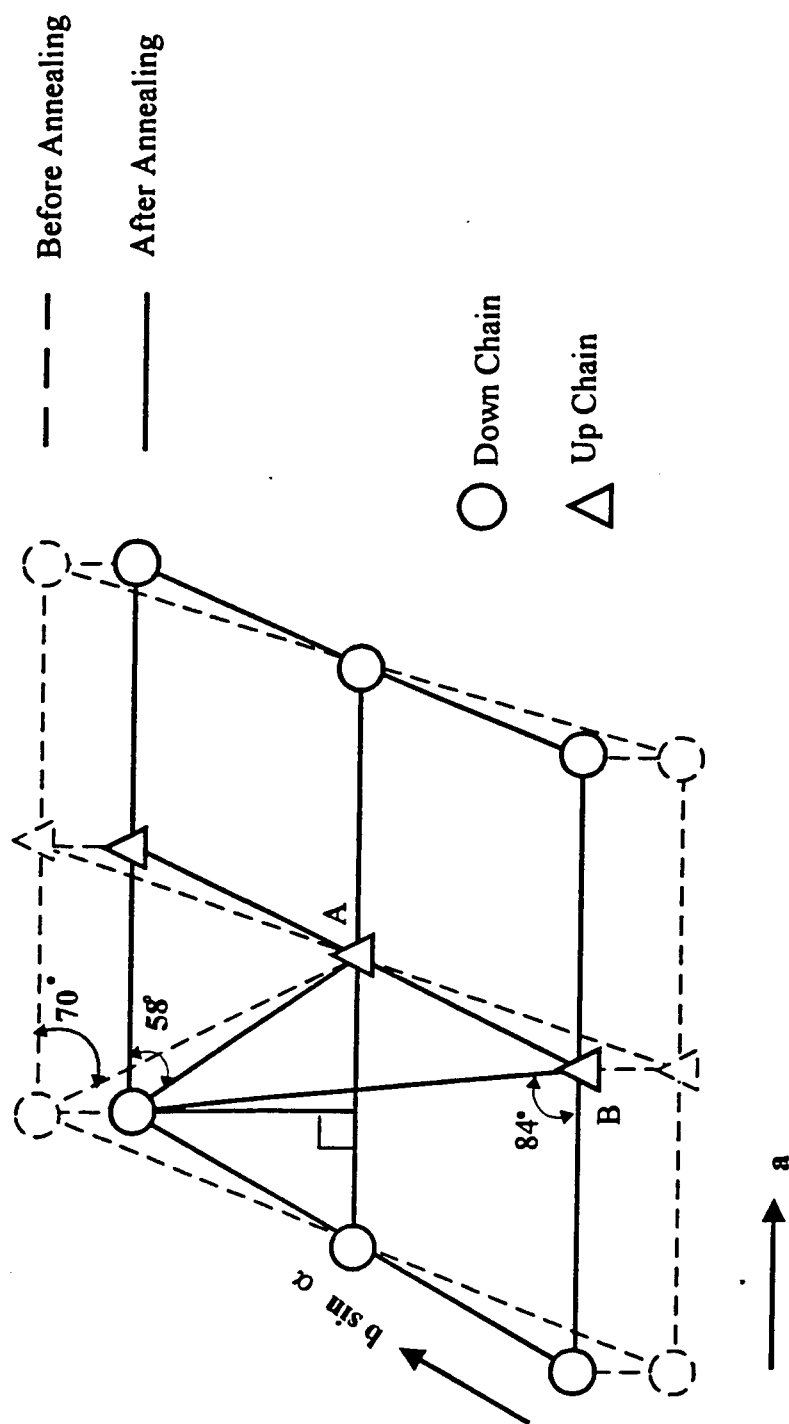
Figure 9 C-axis projection of a unit cell of doubly oriented Nylon 11 before and after annealing