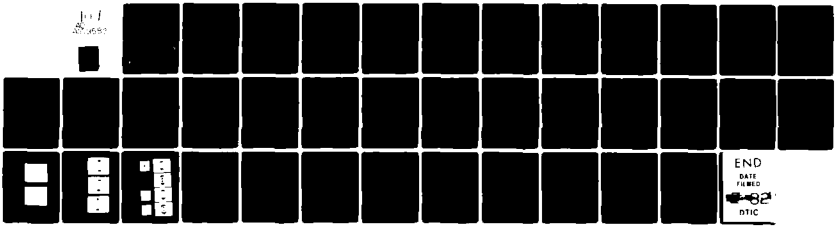
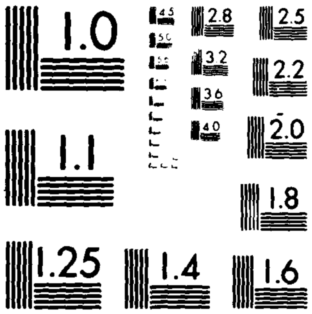
AD-A109 582 MASSACHUSETTS UNIV AMHERST DEPT OF POLYMER SCIENCE --ETC F/G 11/9
THE EFFECT OF ANHYDROUS AMMONIA ON THE CRYSTALLINE STATE DEFORM--ETC(U)
SEP 81 T KANAMOTO, A E ZACHARIADES N00014-75-C-0686
UNCLASSIFIED TR-15 NL



END
DATE
FILMED
82
DTIC


1.0
4.5
5.0
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

6

OFFICE OF NAVAL RESEARCH

Contract No. N00014-75-C-0686

Project No. NR 356-584

TECHNICAL REPORT NO. 15

"THE EFFECT OF ANHYDROUS AMMONIA ON THE CRYSTALLINE STATE DEFORMATION OF NYLONS 6 AND 6,6"

by

Tetsuo Kanamoto, Anagnostis E. Zachariades and Roger S. Porter
Polymer Science and Engineering Department
Materials Research Laboratory
University of Massachusetts
Amherst, Massachusetts 01003

September 14, 1981

DTIC
SELECTE
JAN 1 2 1982
D
A

Reproduction in whole or in part is permitted for
any purpose of the United States Government

Approved for Public Release; Distribution Unlimited

THE EFFECT OF ANHYDROUS AMMONIA ON THE CRYSTALLINE STATE DEFORMATION OF NYLONS 6 AND 6,6

by

Tetsuo Kanamoto*, Anagnostis E. Zachariades† and Roger S. Porter°

*Science University of Tokyo, Tokyo, Japan

†IBM Research Division, San Jose, California

°Polymer Science & Engineering Department, Materials Research Laboratory,
University of Massachusetts, Amherst, Massachusetts

ABSTRACT

The aliphatic polyamides Nylon-6 and -6,6 have been cold drawn using the new concept of reversible plasticization NH_3. Two aspects were investigated: The effect of NH_3 plasticization on the stress-strain behavior of nylon 6,6 and the extent of NH_3 absorption studied by x-ray analysis and reported for the structurally simpler nylon 6. X-ray analysis shows that ammonia is absorbed preferentially by the amorphous phase and that the plasticization has a significant effect on the mode of crystal unit cell orientation, the small angle void scattering and the interplanar spacings between sheets of hydrogen bonded chains. The effect of plasticization was documented by the lower yield stress, the higher draw ratio (8x) and tensile modulus (10 GPa) not attainable with unplasticized specimens.

INTRODUCTION

Recently there has been a considerable interest in the development of polymers with high modulus and strength. Crystalline state deformation by the techniques of extrusion (1-3) and drawing (4) has been used successfully to obtain such highly oriented states. In the case of high density polyethylene, morphologies with tensile moduli up to 70 GPa have been produced in several laboratories. The deformation of thermoplastics with strong intermolecular bonds is of particular interest because polymers with such bonding have higher crystalline melting points. However, their deformation is difficult and ordinarily can be achieved only at temperatures approaching the polymer melting point.

In a recent study we investigated the reversible plasticization of nylons 6 and 11 with anhydrous ammonia (5). According to this new concept, ammonia plasticizes the polymer by a temporary disruption of hydrogen bonding interactions between adjacent amidic groups in the chains. In the original study the nylon samples were exposed to anhydrous ammonia vapor and subsequently were deformed by the solid (crystalline) state extrusion technique. During the deformation process, the ammonia was retained in the sample by compression in the extruder and volatilized from the sample after exiting the die, i.e., after the deformation was completed.

Ammonia neither dissolves nor swells polyamides but is absorbed selectively by polyamides to an extent that depends on a) the vapor pressure of the ammonia atmosphere, b) treatment duration depending on sample thickness, and c) the number of hydrogen bonds in the polymer, i.e. the polyamide number. Thus, for nylons 6 and 11 the amount of ammonia absorbed was 18% and 10% of the weight of dry samples, respectively. The subject of this report is to examine the effect of reversible NH_3 plasticization on the stress-strain behavior of nylon 6,6 and to determine by x-ray analysis the extent of ammonia absorption and its effects on the deformation morphology of the structurally more simple nylon 6. The x-ray results of nylon 6,6 are not included since nylon 6,6 behavior is comparable to nylon 6.

EXPERIMENTAL

Nylon 6 and 6,6 (Mw=16,000) samples were prepared for drawing from commercial grades, Liquid Nitrogen Products Company. The 2 mm thick and ~5 mm wide samples were exposed to anhydrous NH_3 at ambient temperature in a pressure vessel as described earlier (5). The plasticized films were chilled by submerging the pressure vessel in liquid nitrogen and they were removed and mounted on an Instron tensile testing instrument. Drawing experiments were performed isothermally at ambient temperature and at a rate of 10 cm/min. Based on previous results, the amount of NH_3 absorbed by nylon 6 is about 20 wt % and the rate of NH_3 desorption is low at room temperature for 2 mm thick samples. Consequently, the amount of NH_3 that desorbed during sample handling and drawing was small and does not significantly affect the results. Some drawing tests at elevated temperatures were performed in an Instron environmental chamber. To prevent ammonia desorption from the sample in these higher temperature drawing experiments, the samples were surrounded with surgical rubber tubing which was gripped with the sample in the clamps. The rubber tube would stretch and act as a pressure vessel in which a saturated NH_3 atmosphere could be maintained during the short duration experiment. The stress-strain data for hot drawing were corrected for gripping and stretching the surgical rubber tubing with the nylon.

The modulus was determined at room temperature using a strain gauge extensometer at a strain rate of 8×10^{-4} sec^{-1}. The tensile modulus was determined from the tangent to the stress-strain curve at 0.1% strain.

Thermal analysis of the samples before and after ammoniation and deformation was performed using a Perkin-Elmer DSC Model 1B calibrated by the melt transition of Indium at a heating rate of 10°C/min. The fractional crystallinity was determined from transition heats, assuming 52.8 kj/kg for nylon crystals (6).

In addition, independent shrinkage tests were performed with drawn fibers by exposing them to ammonia under a vapor pressure of 10 MPa at room temperature for 5 hours.

Wide- and small-angle x-ray photographs of the variously treated nylon 6 samples were obtained with a flat plate and small angle camera, respectively, using Ni-filtered Cu-K_α radiation. All other diffraction patterns were recorded by transmission techniques with Cu-K_α radiation monochromatized with a Ni-filter and a pulse-height discriminator on a Rigaku RD-3A diffractometer. A Rigaku specimen holder which allowed the sample to be rotated around two independent axes was used for measuring the orientation relative to the drawing direction and the wide surface of the film (reference plane). Figure 1-a shows the sample rotation used. The degree of chain orientation along the draw direction was evaluated by the Hermans-Stein orientation function calculated from the azimuthal scan of the (0140) reflection which was possible to measure only with the highly-oriented specimens. Orientation functions were also determined for the (200) and (002+202) equatorial reflections for uniaxially oriented samples.

Wide angle x-ray photographs of nylon 6 samples plasticized with ammonia were taken before and after the desorption of ammonia. The samples were ammoniated either by submerging and keeping them in liquid NH_3 at -75°C for 100 hrs or by exposing them to a saturated NH_3 atmosphere at 21°C and ~9 Atm for 50 hrs in a pressure vessel. In the latter experiments, the samples were also cooled to -75°C on removal from the pressure vessel. To reduce the desorption of NH_3 during x-ray exposure, a number of precautions were taken. The diffraction patterns were recorded at -70 ±1°C, i.e., just above the freezing point of ammonia (-77.7°C). The goniometer head was precooled by liquid nitrogen gas flow to -70 ±1°C using a specially designed apparatus. The ammoniated nylon sample was transferred to the goniometer head in less than 10 seconds. The sample was allowed to equilibrate at -70°C for 3 minutes. X-ray was irradiated for 2.5 minutes for the oriented and 3.5 minutes for the unoriented nylon samples.

The following conditions were used to reduce x-ray exposure time; Ni-filtered Cu-K_α radiation generated at 40 KV and 40 mA, Kodak no-screen type film with a high sensitivity, pinhole collimator with ϕ=1 mm and sample to film distance of 5 cm. After taking the photograph of the ammoniated sample at -70°C, the temperature of the sample was raised to room temperature and kept for 4 hr to allow ammonia desorption. Then the sample was cooled again to -70°C and an x-ray photograph was taken under the same conditions as for the ammoniated sample. In all measurements, the sample size was about 0.8 x 0.8 x 20 mm. Silicon powder was used as an instrumental calibration standard. No correction for Lorentz, polarization, and absorption was made, because the quantities measured in this work are not influenced by such a correction.

RESULTS AND DISCUSSION

Anhydrous ammonia has been shown to act as a reversible platicizer for the solid state deformation of aliphatic polyamides. In the present study its effectiveness is demonstrated by the direct comparison of the stress-strain behavior of a plasticized (ammoniated) and a non-plasticized dry sample of nylon 6,6 at room temperature (Figure 2). Firstly, the untreated sample (A) was drawable only to a maximum draw ratio of 4 before tensile failure, whereas the plasticized samples (B) and (C) were extendable up to a draw ratio of 8. The draw ratio was determined from the ratio of the cross section areas of the undrawn to the drawn specimen. Secondly, the yield stress was reduced significantly as the amount of plasticizer in the sample was increased. The maximum reduction in yield stress, 45%, was obtained by exposing the 0.2 cm thick samples to ammonia for $\geq$12 hrs. The stress-strain behavior of a plasticized nylon sample was comparable to the behavior of a dry and untreated sample deformed at 120°C.

Strain hardening is a phenomenon associated with the solid state deformation of semicrystalline polymers. It imposes serious limitations to the achievement of high draw. Perkins (7) reports strain hardening at an early stage in the solid state extrusion as the reason for the low attainable draw ratio for nylons 11 and 12. Figure 2 indicates that NH_3 plasticization may extend effectively the solid state deformation well in to the strain hardening region of the unplasticized nylon. Figure 3 shows the effect of temperature on strain hardening for nylon 6,6 predrawn to ratio 7 which were treated with ammonia prior to drawing for 9 hrs. Thus by combinations of drawing temperature and NH_3 plasticization, the limitation of strain hardening can be largely overcome.

The effect of NH_3 plasticization on the modulus was also examined by ammoniating a nylon 6,6 film of draw ratio 8 and measuring the modulus as a function of time during the ammonia desorption. The variation in tensile modulus with time is shown in Figure 4. The modulus increased by 45% as ammonia was completley desorbed from the specimen after 4 hrs.

Thermal analysis shows that the original and a plasticized sample with ammonia at room temperature have the same peak melting point at 265°C. The plasticized sample has a higher crystallinity, 12%, (see Table 1) suggesting that ammonia facilitates molecular motion and reorganization. The thermogram differs for a cold and a hot drawn (120°C) sample to DR=4. The cold drawn sample has a higher crystallinity (7%) and a melting peak at 265°C with a shoulder at 267.5°C whereas the hot drawn sample has only one melting peak at 262°C. The thermograms of a plasticized cold drawn and a sample hot drawn at 120°C are similar. However, the crystallinity of the former (43.8%) is substantially higher than the hot drawn sample. X-ray diffraction patterns for ammoniated undrawn and drawn samples before ammoniation and after the NH_3 was desorbed from the samples are shown in Figures 5 and 6. An examination indicated that there is no detectable difference in the relative intensity of each reflection between the ammoniated and desorbed samples. The d-spacings of (200) and (002+202) planes also showed no meaningful change by ammoniation of both the unoriented and the oriented samples within a large experimental error, ±0.10 Å.

Figure 7 shows wide and small angle x-ray diffraction patterns of nylon 6 drawn under different conditions; (a) and (b), untreated and drawn at room temperature; (c), untreated and drawn at 120°C; and (d), plasticized with ammonia and drawn at room temperature. The wide angle photographs show high chain orientation for all samples. The two limiting stable crystal structures of nylon 6 are the α-form (monoclinic) with hydrogen bonds between anti-parallel chains and the γ-form (hexagonal) with hydrogen bonds between parallel chains (8,9). The α-form gives two strong equatorial reflections from (200) and (002+202) planes, while the γ-form is often characterized by a single strong equatorial reflection and a strong meridional (002) reflection. Although the diffraction patterns in Figure 7 exhibit streaks along the layer lines except on the equator suggesting the existence of crystal disorder along the chain direction, the α-modification is predominant for each sample in the sense of the above definition. However, Parker and Lindenmeyer (10) report that the above criteria for the α- and γ -structure are not enough. They state that a fiber period >17 Å is possible only for a crystal with hydrogen bonds between antiparallel chains (α-form), whereas bondings between parallel chains (γ-form) require the fiber period ≤16.8 Å.

The mode of hydrogen bond formation may be important in understanding the morphology of drawn nylon 6. Kaji and Sakurada (11) showed that an accurate value for the fiber period of nylon 6 α-form can be obtained only from the measurement of the (0140) reflection, when the crystallite size along the fiber axis is small. It is estimated that the number of repeat unit contained in the stem of a crystallite in the drawn samples is about 3, on the basis of the long period (~80 Å), crystallinity (~60%), and the fiber period (~17 Å). Thus, meridional scans were made around the (0140) region to determine the fiber period, and are shown in Figure 8 and Table II. Although the (0140) profiles have a tail at higher angles suggesting the coexistence of a small amount of γ-form, nevertheless, the patterns and fiber period confirm that the major crystal structure is the α-form with hydrogen bondings between antiparallel chains. This bonding may be easily formed for a folded-chain crystal morphology where a long chain molecule folds back and forth. However, for a crystallite with chain extended conformation, a large number of hydrogen bondings may be formed between parallel chains resulting in a fiber period $\leq$16.8 Å.

The wide angle x-ray fiber patterns recorded with incident beam parallel and perpendicular to the wide surface of drawn films were the same for both ammoniated and drawn samples at room temperature, and untreated and drawn samples at 120°C. However,for the film drawn at room temperature without ammoniating, the intensity of inner equatorial reflection (200) is stronger than that of the outer reflection (002+202) on the photograph taken with the beam perpendicular to the drawn film surface (Figure 7a). In contrast, the photograph obtained with the incident beam parallel to the film surface shows a reverse intensity distribution (Figure 7b). To analyze the specific orientations suggested by the fiber patterns, diffractometer scans were made for (200) and (002+202) reflections by rotating the sample around the fiber axis (Figure 1a). The intensity data were plotted in Figure 9 as a function of an angle ω which was defined as the angle between the normals to the film surface and to the reflecting plane (Figure 1b). The observed intensity at an angle ω is proportional to the number of the reflecting planes oriented as in Figure 1b. The two samples, ammoniated and drawn at room temperature, and untreated and drawn at 120°C, show no appreciable intensity variation with the angle ω for both (200) and (002+202) planes. In contrast, the sample drawn at room temperature without ammoniation, exhibited a specific orientation. The (200) and (002+202) reflections have intensity maxima at ω=0° and 67.5°, respectively. The characteristic orientations deduced from Figure 9 are schematically drawn in Figure 10. Figure 10a shows the uniaxial orientation of the former two samples, where the b-axis (chain direction) orients parallel to draw, and the a- and c-axes orient perpendicular to draw with no preferential orientation around the draw direction. Figure 10b illustrates the biaxial orientation characteristic for the film drawn at room temperature without ammoniation, where the b-axis orients along the draw direction, c-axis perpendicular to the wide surface, and a-axis at an angle of 67.5° from the normal to the wide surface of the film. These results show that the ammonia sorbed by nylon films has a similar effect on drawing as to increasing the temperature of drawing.

The chain orientation along the draw direction was directly evaluated by the orientation function, f_{0140}, calculated from the azimuthal scan of the (0140) reflection. The results are listed in Table II as well as the orientation functions determined from the two equatorial reflections of the (200) and (002+202) planes for uniaxial orientation. Independent of drawing condition and in orientation of a- and c-axis, all samples showed a similar degree of orientation.

It is well known that nylon 6 can exist in several crystal forms that may vary continuously in crystal perfection, size, and unit cell parameters (12). As a measure of the lateral molecular packing, the d-spacings of (200) and (002+202) planes were carefully measured by diffractometer scan, as shown in Table I. The errors are estimated to be $< +0.01$ Å. The $d_{(200)}$, the distance between hydrogen-bonded chains, was not affected by sample treatment, being 4.38 A for all samples. However, the $d_{(002)}$, the distance between sheets of hydrogen-bonded chains, varied from 3.73 Å for original undrawn film to 3.85 Å for the film drawn at room temperature without ammoniation. It was also noticed that the ammoniated and cold-drawn or coextruded films have a shorter (002+202) spacing than the films drawn without ammoniation. The expansion of the spacing may be related to different crystal disorders. The increase of chain mobility by sorption of ammonia may help to reduce incorporation of crystal defects during drawing.

Small angle x-ray photographs of drawn nylon 6 are shown in Figure 7. All the samples gave meridional scatterings elongated perpendicular to the draw axis. The long periods in Table II were calculated by applying Bragg's law to the scattering angle measured along the meridional direction (draw axis).

The long period decreased by drawing from 95 Å for the original to ~80 Å for all drawn samples. A remarkable influence of drawing conditions was found in void scatterings centered around the direct beam and extended along the equator. The film drawn at room temperature without ammoniation gave commonly strong void scatterings, although the intensity varied from a part to part of the same sample (Figure 8a). The scatterings decreased for drawing of ammoniated film (Figure 8d) or drawing at higher temperature (Figure 8c).

It has been reported (5) that drawing of plasticized nylon samples with NH_3 may result in morphologies with an increased maximum attainable draw ratio, crystallinity and modulus, and high total birefringence. In the present x-ray study, it is also found that ammoniation of nylon prior to drawing indeed has important influences on cold-drawing and the resultant morphology; i.e., unit cell orientation, crystal perfection, and interfibrillar void. X-ray analysis with oriented and unoriented samples showed that under the conditions of ammoniation in this study, ammonia is absorbed selectively only by the amorphous phase, whereas the crystalline phase remains unplasticized. The preferential ammonia absorption by the amorphous phase results in a more deformable structure as is indicated by the higher attainable draw ratio. Thus, the plasticization had remarkable effects on drawing of nylons. Nevertheless, the resultant x-ray small-angle long period and the degree of chain orientation were not affected. These facts suggest that the plasticization does not appreciably facilitate the destruction and reorganization of the initial crystalline lamellae but it facilitates the deformation by intercrystallite shear slip or flow which proceeds primarily at the amorphous regions. A larger deformation may induce a greater amorphous chain orientation which induces further crystallization, as suggested by the larger increase in crystallinity (Table I). Such a deformation induced crystallization may also produce crystallite bridges which connect longitudinally the crystal blocks within a fibril resulting in a morphology showing a higher tensile modulus along the draw direction. The modulus achieved is still far from the theoretical value which may be reached by involving a massive crystalline deformation. There is a slow NH_3 desorption after the deformation which allows significant molecular reorganization. This is in accordance with shrinkage tests in which drawn samples of draw ratio 4 were exposed to NH_3 for 4-5 hrs. and shrunk by 6% similarly to wet shrinkage tests with boiling water (13).

CONCLUSIONS

We have investigated with two representative aliphatic polyamides (nylon 6 and 6,6) the effect of ammonia absorption on morphology and drawing. X-ray analysis was conducted with the structurally simpler nylon 6. The x-rays of ammoniated nylon 6 films at low temperature before and after desorption of ammonia suggested that ammonia does not go into crystalline regions and preferentially sorbed in amorphous regions. The plasticization with ammonia prior to drawing had significant influence on the mode of unit cell orientation relative to the wide surface of drawn films, small angle void scatterings, and interplanar spacings between sheets of hydrogen-bonded chains. Under the present experimental conditions there is no appreciable effect on the resultant degree of chain orientation and long period along the draw direction. The effect of plasticization was documented with nylon 6,6 by a) the ease of cold draw to a ratio of 8, not attainable with unplasticized specimens, b) the lowering of yield stress by 45%, and c) lowering tensile modulus by ~30%.

REFERENCES

1. J.H. Southern and R.S. Porter, J. Appl. Polym. Sci. 14, 2305 (1970).
2. A.G. Kohlbeck and D.R. Uhlmann, J. Polym. Sci., Polym. Phys. Ed. 15, 27 (1977).
3. W.T. Mead and R.S. Porter, J. Appl. Polym. Sci. 22, 3249 (1978).
4. G. Capaccio and I.M. Ward, J. Mater. Sci. 5, 219 (1975).
5. A.E. Zachariades and R.S. Porter, J. Appl. Polym. Sci. 24, 1371 (1979).
6. R. Greco and L. Nicolais, Polymer 17, 1049 (1976).
7. W. Perkins, Ph.D. Thesis, University of Massachusetts, 1978.
8. D.R. Holmes, C.W. Bunn and D.J. Smith, J. Polym. Sci. 17, 159 (1955).
9. Y. Kinoshita, Makromol. Chem. 33, 1 (1959).
10. J.P. Parker and P.H. Lindenmeyer, J. Appl. Polym. Sci. 21, 821 (1977).
11. K. Kaji and I. Sakurada, Macromol. Chem. 179, 209 (1978).
12. L.G. Roldan and H.S. Kaufman, J. Polym. Sci., Letters Ed. 1, 603 (1963).
13. K.L. DeVries, W.O. Statton and J.B. Park, J. Macromol. Sci., Phys. 409 (1978).

TABLE I

Thermal Characteristics of Nylon 6,6

Sample	Crystallinity (%)	Melting Peaks (°C)
Original, undrawn	24.8	265
Original, treated with NH_3, undrawn and removed	27.3	265
Untreated, drawn at room temp.	39.2	265, 267.5
Untreated drawn at 120°C	36.7	262
Treated with NH_3, drawn at room temp.	43.8	262

Table II. X-Ray Characterization of Drawn Nylon 6 Samples

Sample	Crystal system	d-Spacings (A)*				Long spacing (A)	Orientation Functions		
		$d_{(200)}$	$d_{(002+202)}$	$d_{(0140)}$	Fiber period		f_{200}	$f_{002+202}$	f_{0140}
Original, undrawn	α	4.38	3.724			95±4	0	0	0
Original, treated with NH_3 and removed, undrawn	α	4.377	3.725				0	0	0
Untreated, drawn at room temp.	α	4.38	3.85	1.232	17.25	78±3			0.901
Untreated drawn at 120·C	α	4.36	3.84	1.230	17.22	83±3	-0.410	-0.447	0.899
Treated with NH_3, drawn at room temp.	α	4.38	3.78	1.232	17.25	79±3	-0.400	-0.447	0.901
Treated with NH_3 coextruded	α	4.38	3.77						
Bunn's α-modification	α	4.42	3.70	1.231	17.24				

*Estimated errors are ±0.01 or ±0.005 A for $d_{(200)}$ and $d_{(002+202)}$, ±0.002 A for $d_{(0140)}$, and ±0.03 A for fiber period.

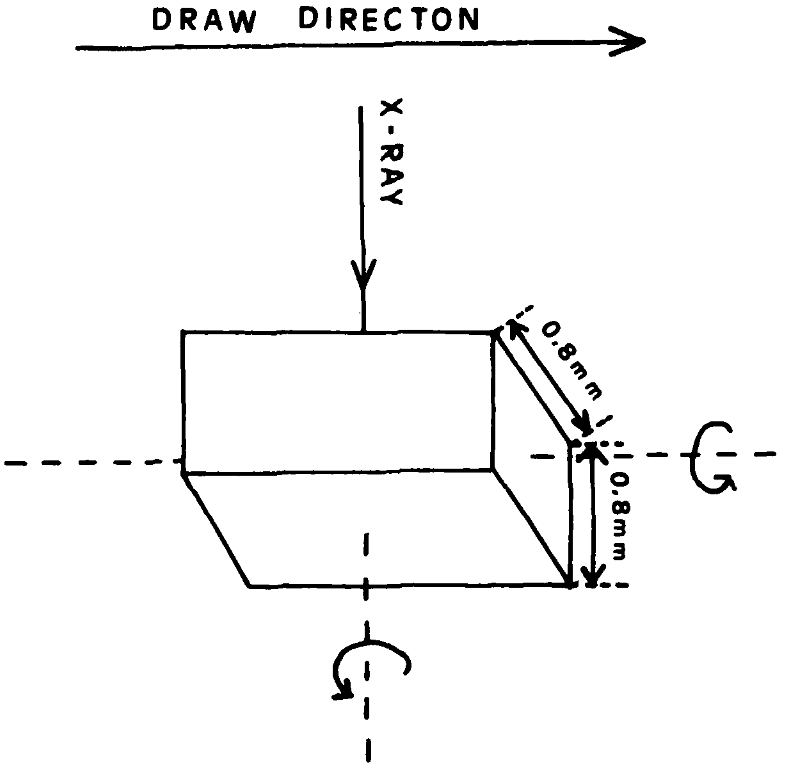
FIGURE CAPTIONS

Figure 1:	The sample rotations on the fiber specimen holder (a), and angle ω definition used to describe the orientation of a- and b-axes.
Figure 2:	Stress-strain behavior of nylon 6,6 nonplasticized (A) and plasticized with NH_3 for 9 hours (B) and 17 hours (C).
Figure 3:	Effect of temperature on the strain hardening region for pre-drawn ammonia plasticized nylon 6,6 films of DR=4.
Figure 4:	Effect on modulus of ammonia plasticization on drawn nylon 6,6 to DR=8.
Figure 5:	Wide angle x-ray photographs of the undrawn ammoniated film recorded at -70°C: (a), before desorption and (b), after desorption of ammonia.
Figure 6:	Wide angle x-ray fiber patterns of the drawn and then ammoniated film recorded at -70°C: (a) before treatment with ammonia, a photo taken at room temperature, (b) ammoniated, and (c) after desorption of ammonia.
Figure 7:	Wide angle (top) and small angle (bottom) x-ray photographs of nylon 6 films drawn under various conditions: (a) drawn at room temperature without ammoniating, the incident x-ray beam is perpendicular to the wide surface of the drawn film, (b) the sample as (a) but the incident beam is parallel to the wide surface, (c) a film drawn at 120°C without ammoniating, and (d) a film prepared by plasticizing with ammonia prior to drawing at room temperature.

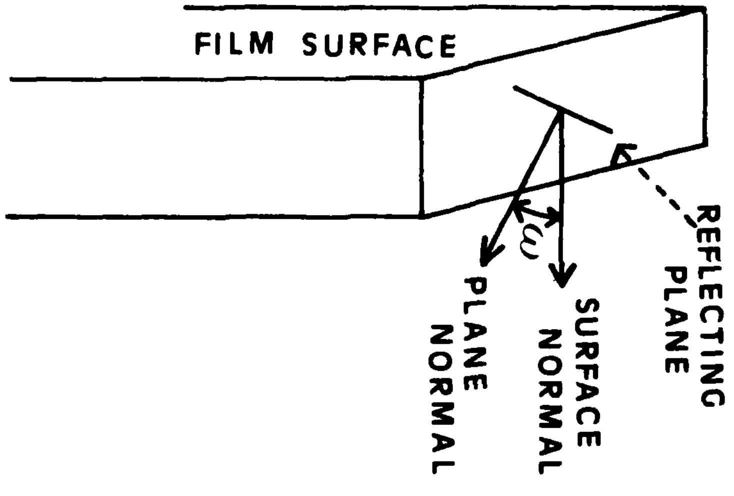
Figure 8: X-ray diffractometer scans of the (0140) region: (a) drawn at room temperature without ammoniation, (b) ammoniated and drawn at room temperature, and (c) drawn at 120°C without ammoniating.

Figure 9: Intensities of (200) and (002+202) reflections plotted as a function of an angle ω which is defined in Figure 1b. The (200) and (002+202) are represented by ● and o for the film drawn at room temperature without ammoniation, ▲ and ∧ for the film drawn at 120°C without ammoniating, and ■ and □ for the film ammoniated and drown at room temperature.

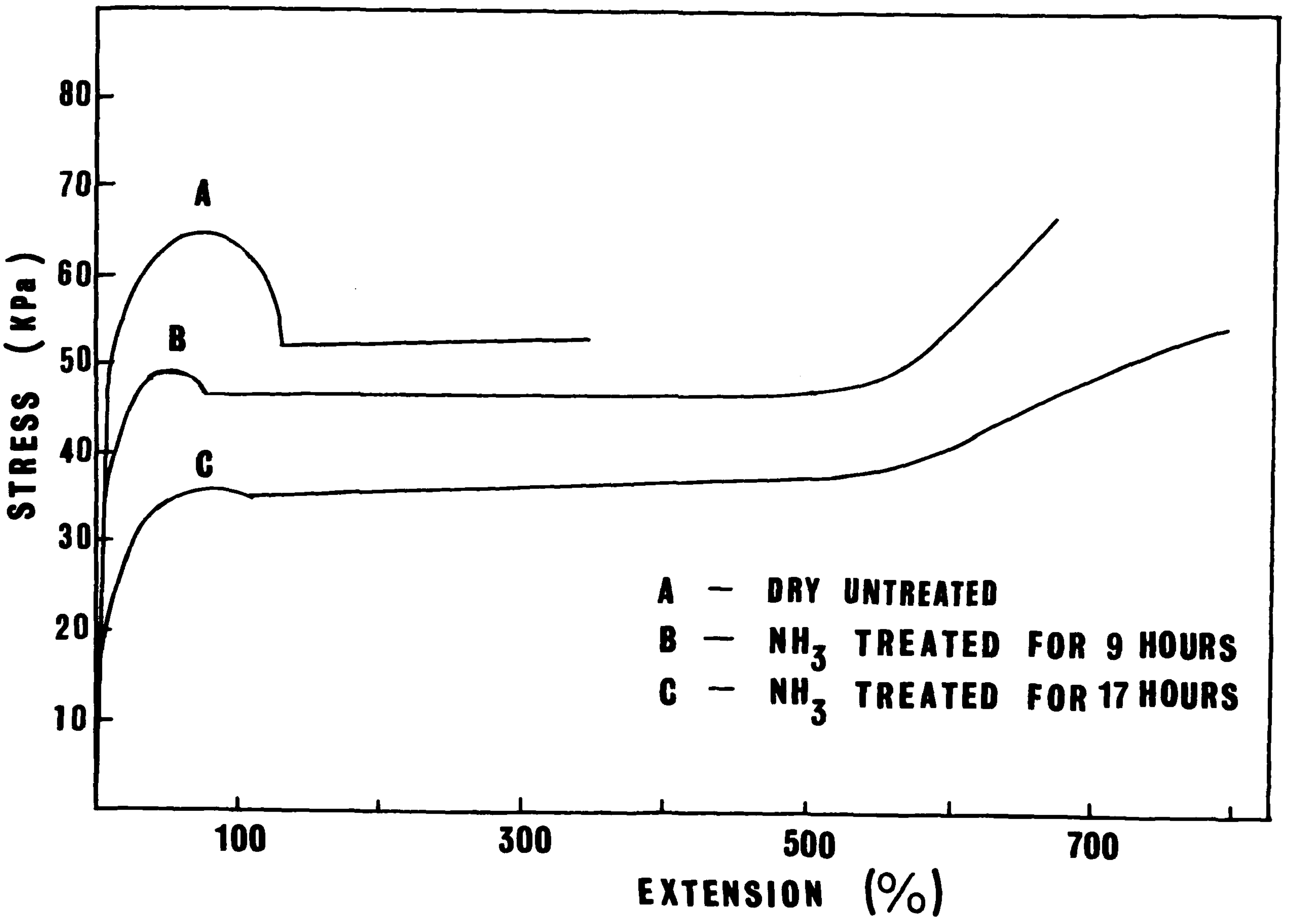
Figure 10: Schematic drawings of the orientation of the unit cell axes in the drawn films. (a) the uniaxial orientation observed in the samples drawn at 120°C and ammoniated prior to drawing at room temperature, and (b) the biaxial orientation observed in the sample drawn at room temperature without ammoniating.

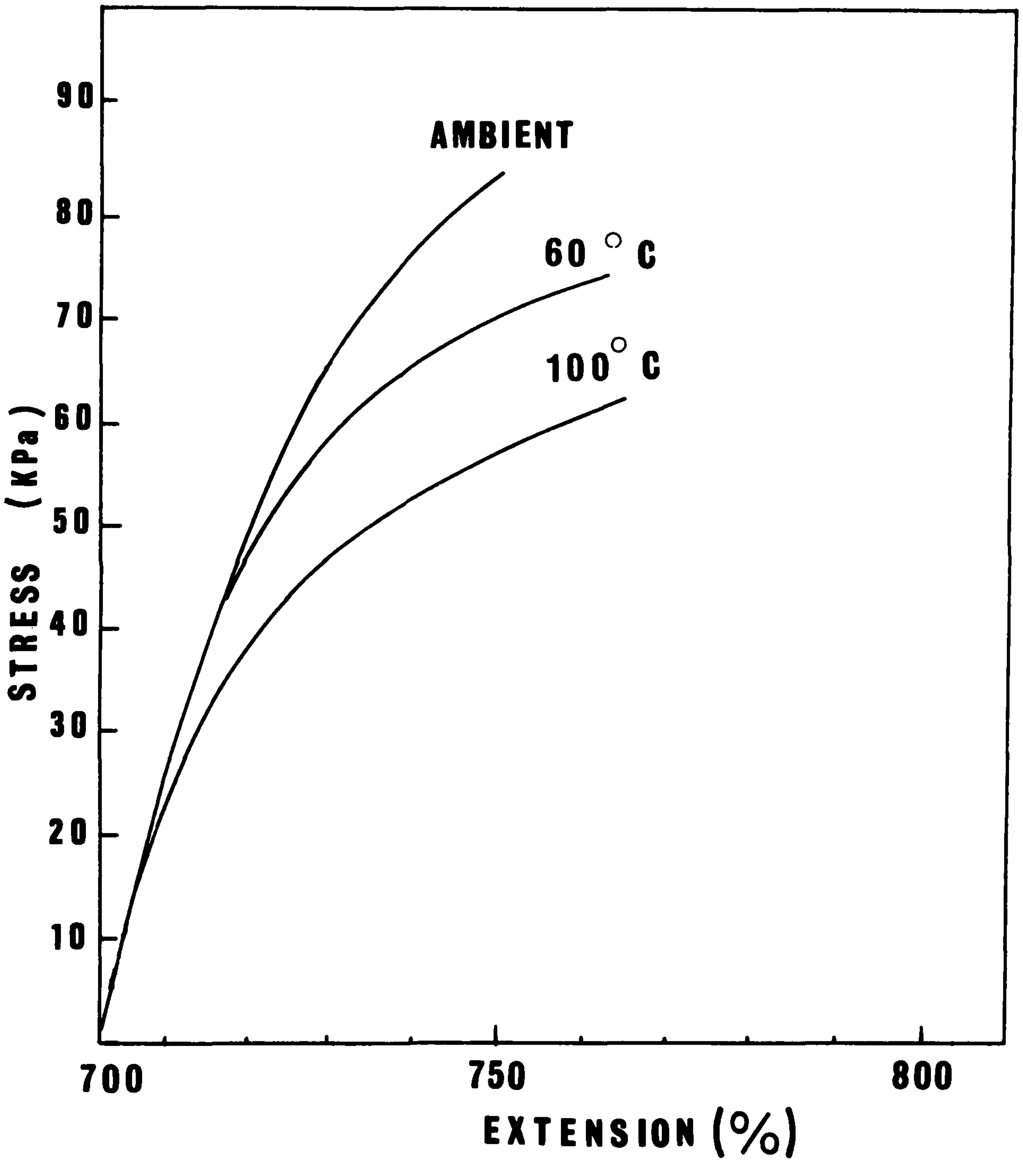

DRAW DIRECTON
X-RAY
0.8mm
0.8mm

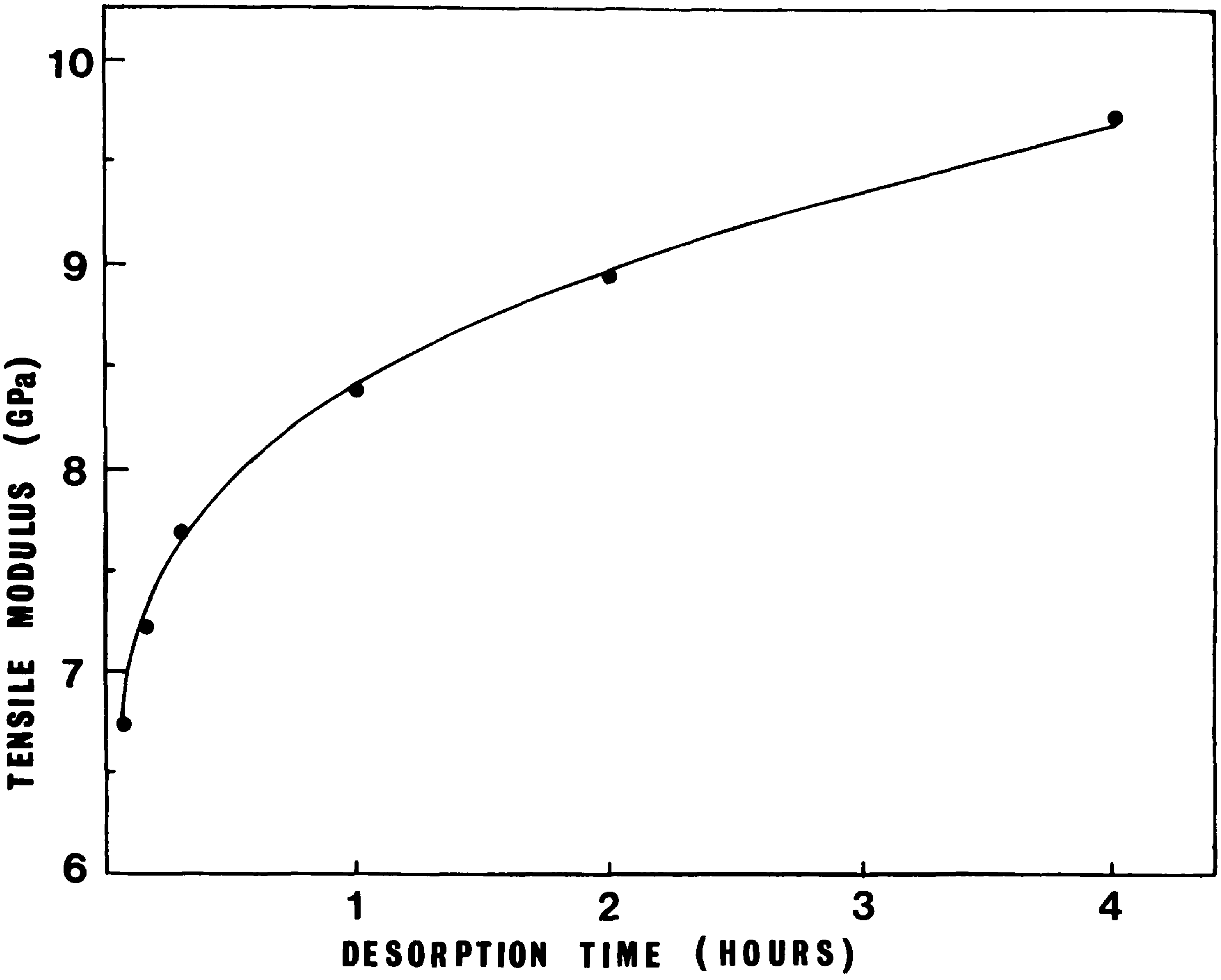
(a)


FILM SURFACE
REFLECTING PLANE
SURFACE NORMAL
PLANE NORMAL
ω

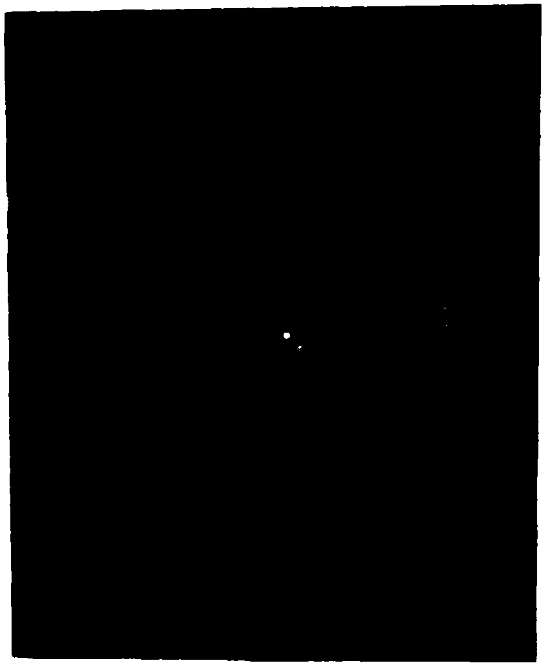
(b)


STRESS (KPa)
80
70
60
50
40
30
20
10
A
B
C
100
300
500
700
EXTENSION (%)
A — DRY UNTREATED
B — NH3 TREATED FOR 9 HOURS
C — NH3 TREATED FOR 17 HOURS

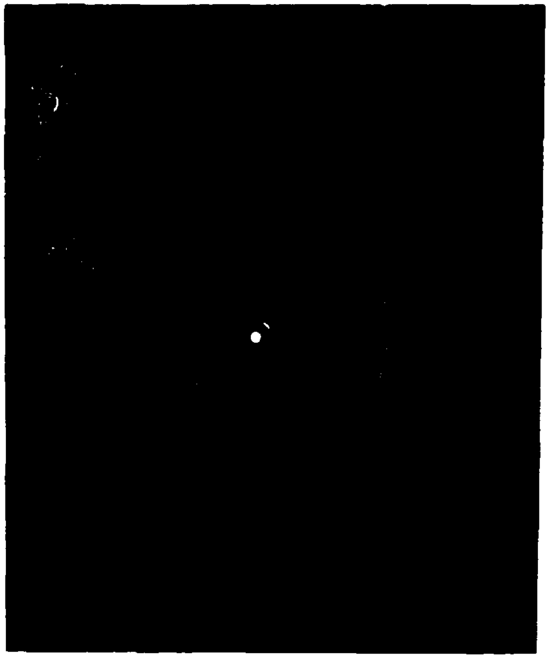

90
80
70
60
50
40
30
20
10
STRESS (KPa)
AMBIENT
60 ° C
100° C
700
750
800
EXTENSION (%)



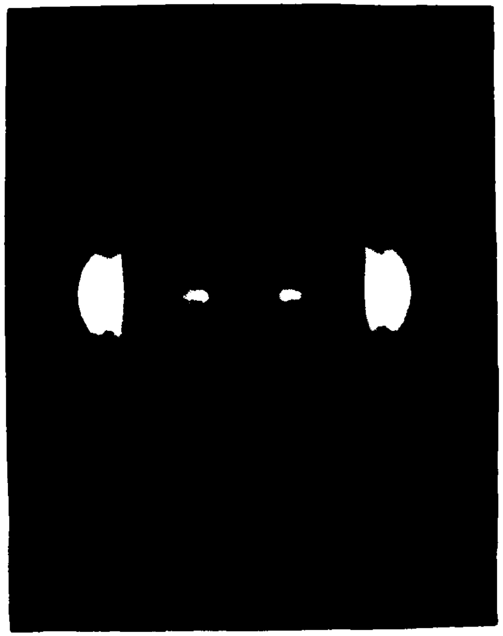
TENSILE MODULUS (GPa)
10
9
8
7
6
1
2
3
4
DESORPTION TIME (HOURS)



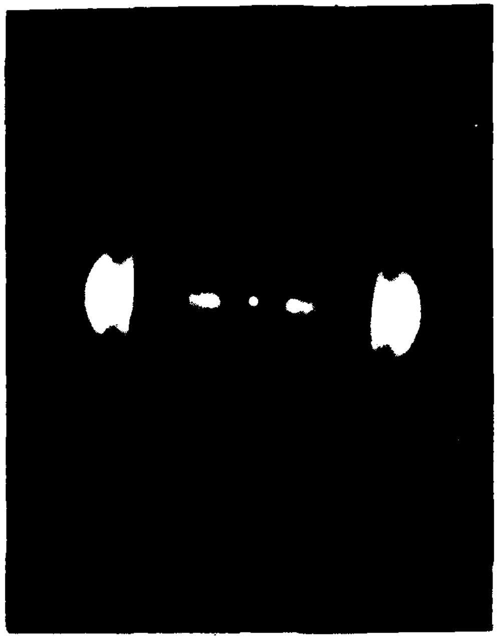
(a)



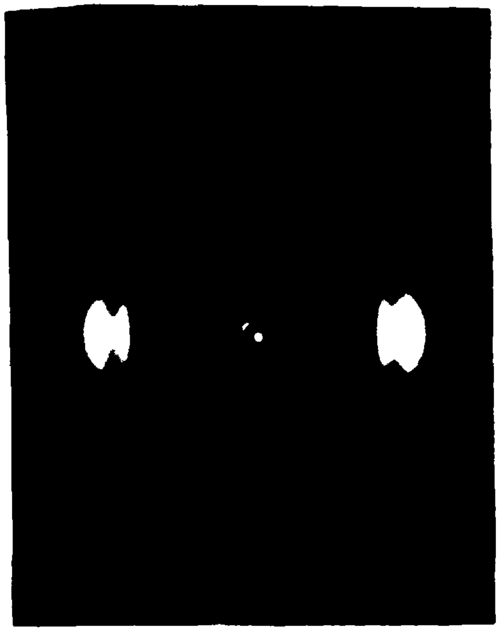
(b)



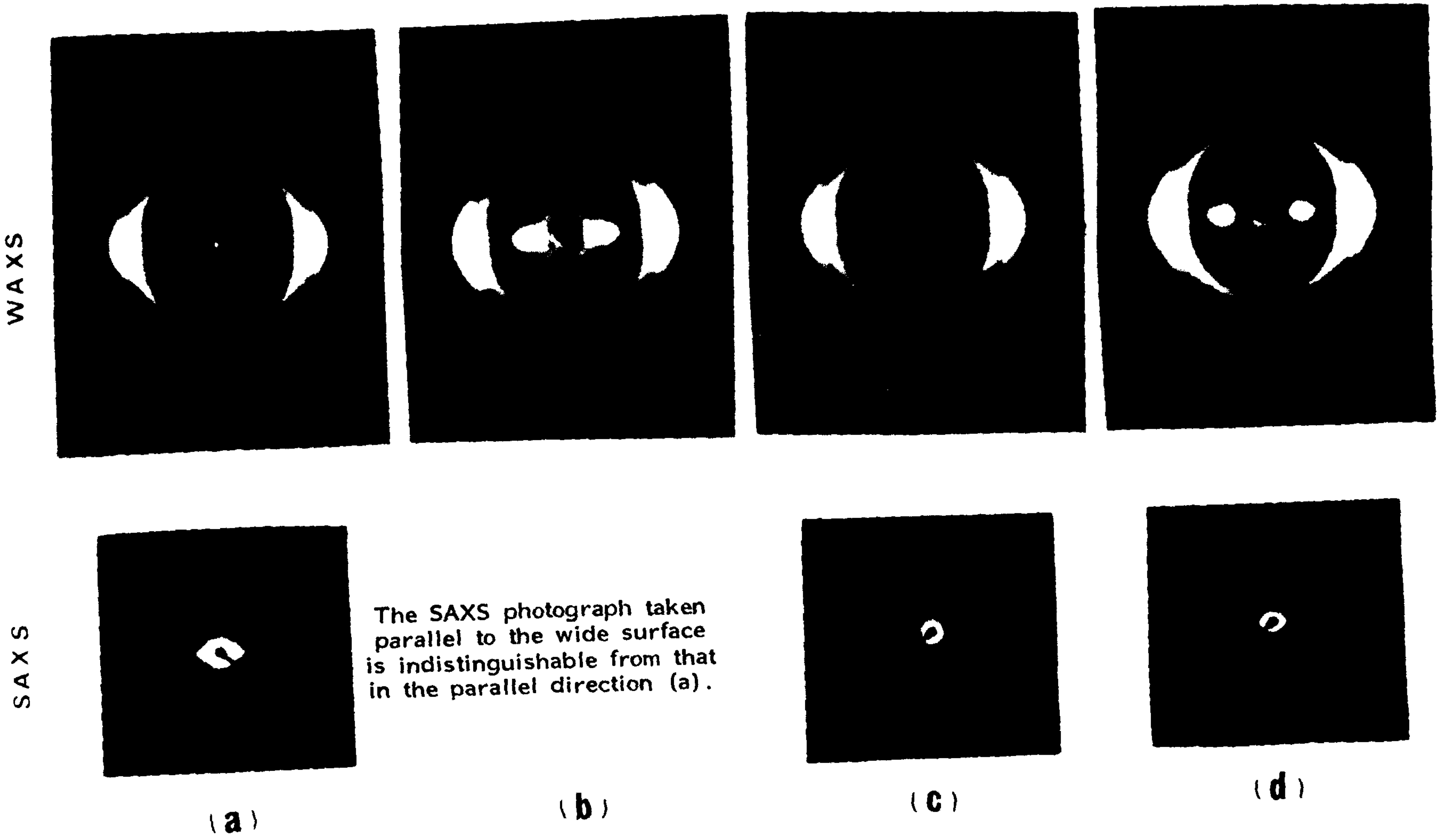
(a)



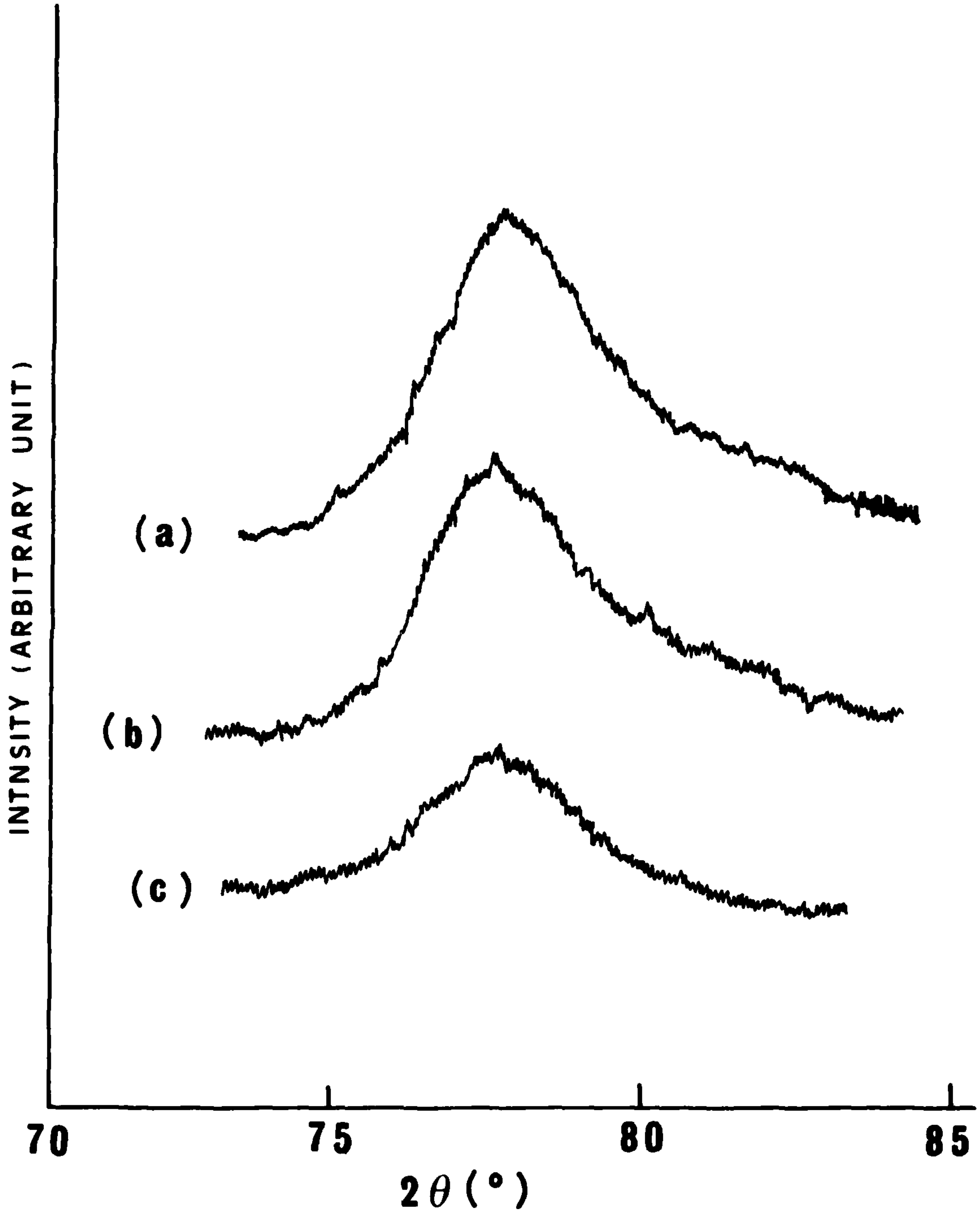
(b)

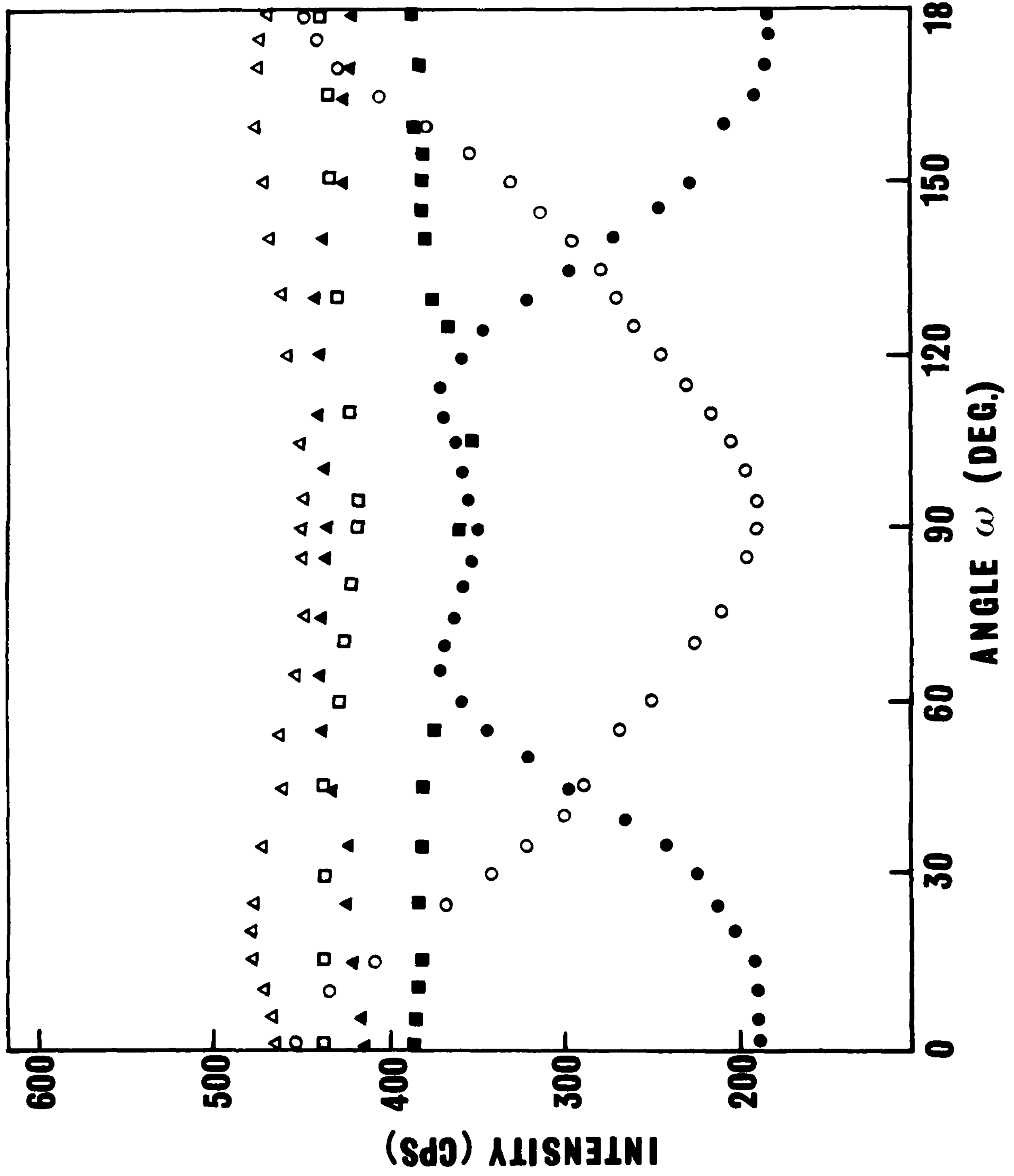


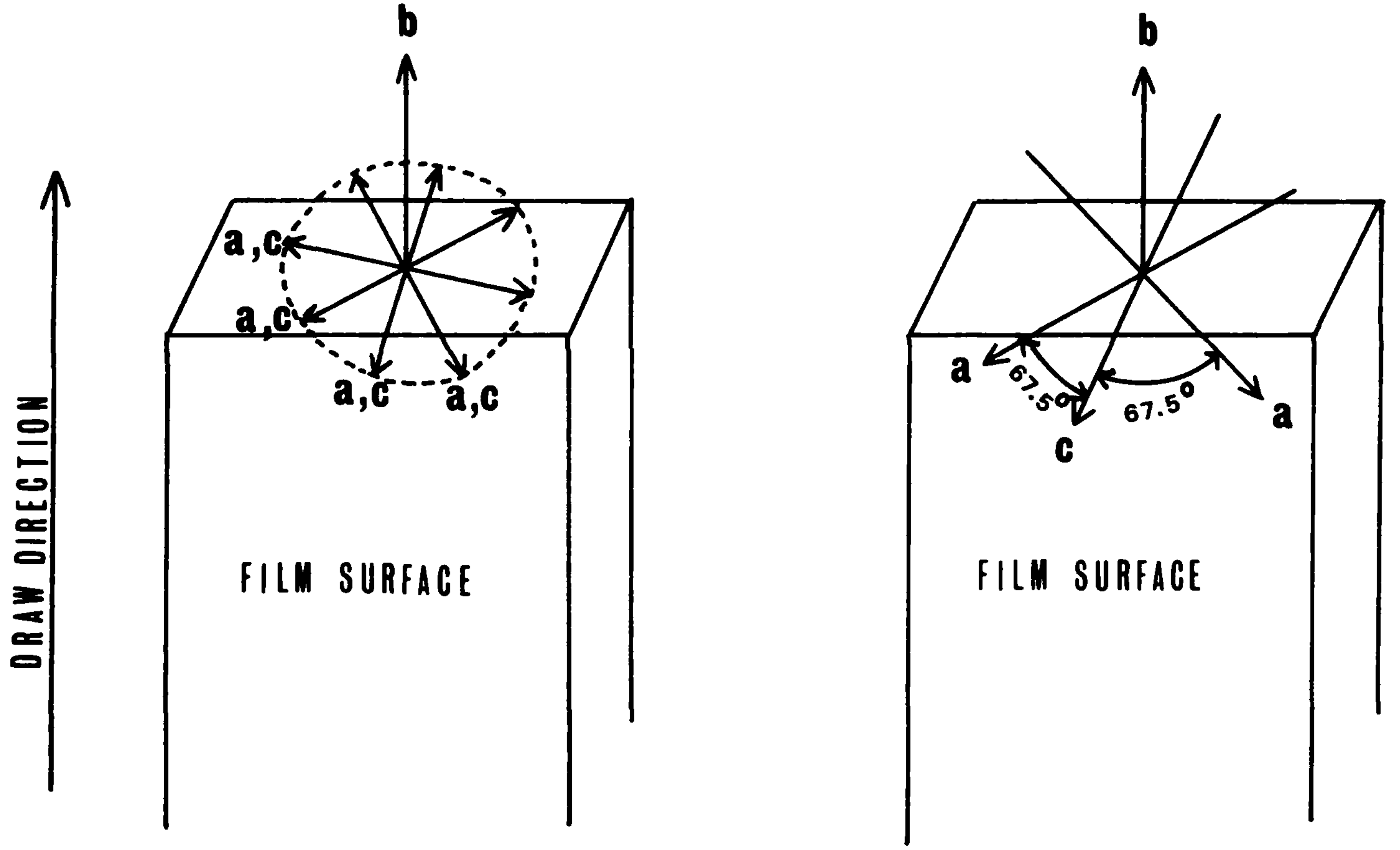
(c)



The SAXS photograph taken parallel to the wide surface is indistinguishable from that in the parallel direction (a).


INTNSITY (ARBITRARY UNIT)
(a)
(b)
(c)
70
75
80
85
2θ(°)


INTENSITY (CPS)
600
500
400
300
200
ANGLE ω (DEG.)
0
30
60
90
120
150
180



(a) UNIAXIAL

(b) BIAXIAL

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 15	2. GOVT ACCESSION NO. AD-A109552	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (*and Subtitle*) The Effect of Anhydrous Ammonia on the Crystalline State Deformation of Nylons 6 and 6,6		5. TYPE OF REPORT & PERIOD COVERED Interim 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(*s*) Tetsuo Kanamoto, Anagnostis E. Zachariades and Roger S. Porter		8. CONTRACT OR GRANT NUMBER(*s*) N00014-75-C-0686
9. PERFORMING ORGANIZATION NAME AND ADDRESS Polymer Science and Engineering University of Massachusetts Amherst, Massachusetts 01003		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 356-584
11. CONTROLLING OFFICE NAME AND ADDRESS ONR Branch Office 666 Summer Street Boston, Massachusetts 02210		12. REPORT DATE September 14, 1981 13. NUMBER OF PAGES 32 (incl. tables and figures)
14. MONITORING AGENCY NAME & ADDRESS(*if different from Controlling Office*)		15. SECURITY CLASS. (*of this report*) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (*of this Report*)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (*of the abstract entered in Block 20, if different from Report*)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*)

Ammonia, Nylon 6, Nylon 66, Drawing, Deformation, Crystallinity, Modulus, Plasticizer, X-Ray

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

The aliphatic polyamides nylon-6 and -6,6 have been cold drawn using the new concept of reversible plasticization NH_3. Two aspects were investigated: the effect of NH_3 plasticization on the stress-strain behavior of nylon 6,6 and the extent of NH_3 absorption studied by x-ray analysis and reported for the structurally simpler nylon 6. X-ray analysis shows that ammonia is absorbed preferentially by the amorphous phase and that the plasticization has a significant effect on the mode of crystal unit cell orientation, the small angle void

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*) scattering and the interplanar spacings between sheets of hydrogen bonded chains. The effect of plasticization was documented by the lower yield stress, the higher draw ratio (8X) and tensile modulus (10 GPa) not attainable with unplasticized specimens.

P4-2/A23

472:GAN:716:tam
78u472-608

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1
ONR Branch Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106	1
ONR Branch Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Dr. Fred Saalfeld Chemistry Division Naval Research Laboratory Washington, D.C. 20375	1

	No. Copies
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Dr. Rudolph J. Marcus Office of Naval Research Scientific Liaison Group American Embassy APO San Francisco 96503	1
Mr. James Kelley DTNSRDC Code 2803 Annapolis, Maryland 21402	1

TECHNICAL REPORT DISTRIBUTION LIST, 356A

No. Copies

Dr. Stephen H. Carr
Department of Materials Science
Northwestern University
Evanston, Illinois 60201 1

Dr. M. Broadhurst
Bulk Properties Section
National Bureau of Standards
U.S. Department of Commerce
Washington, D.C. 20234 2

Dr. T. A. Litovitz
Department of Physics
Catholic University of America
Washington, D.C. 20017 1

Professor G. Whitesides
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 1

Professor J. Wang
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112 1

Dr. V. Stannett
Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27607 1

Dr. D. R. Uhlmann
Department of Metallurgy and Material Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 1

Naval Surface Weapons Center
White Oak
Silver Spring, Maryland 20910
Attn: Dr. J. M. Augl
Dr. B. Hartman 1

Dr. G. Goodman
Globe Union Incorporated
5757 North Green Bay Avenue
Milwaukee, Wisconsin 53201 1

No. Copies

Picatinny Arsenal
SMUPA-FR-M-D
Dover, New Jersey 07801
Attn: A. M. Anzalone
Building 3401 1

Dr. J. K. Gillham
Princeton University
Department of Chemistry
Princeton, New Jersey 08540 1

Douglas Aircraft Co.
3855 Lakewood Boulevard
Long Beach, California 90846
Attn: Technical Library
C1 290/36-84
AUTO-Sutton 1

Dr. E. Baer
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106 1

Dr. K. D. Pae
Department of Mechanics and Materials Science
Rutgers University
New Brunswick, New Jersey 08903 1

NASA-Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attn: Dr. T. T. Serofini, MS-49-1 1

Dr. Charles H. Sherman, Code TD 121
Naval Underwater Systems Center
New London, Connecticut 1

Dr. William Risen
Department of Chemistry
Brown University
Providence, Rhode Island 02192 1

Dr. Alan Gent
Department of Physics
University of Akron
Akron, Ohio 44304 1

TECHNICAL REPORT DISTRIBUTION LIST, 356A

No.
Copies

Mr. Robert W. Jones
Advanced Projects Manager
Hughes Aircraft Company
Mail Station D 132
Culver City, California 90230 1

Dr. C. Giori
IIT Research Institute
10 West 35 Street
Chicago, Illinois 60616 1

Dr. M. Litt
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106 1

Dr. R. S. Roe
Department of of Materials Science
and Metallurgical Engineering
University of Cincinnati
Cincinnati, Ohio 45221 1

Dr. Robert E. Cohen
Chemical Engineering Department
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 1

Dr. David Roylance
Department of Materials Science and
Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02039 1

Dr. T. P. Conlon, Jr., Code 3622
Sandia Laboratories
Sandia Corporation
Albuquerque, New Mexico 1

Dr. Martin Kaufmann, Head
Materials Research Branch, Code 4542
Naval Weapons Center
China Lake, California 93555 1

Professor S. Senturia
Department of Electrical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 1

No.
Copi

Dr. T. J. Reinhart, Jr., Chief 1
Composite and Fibrous Materials Branch
Nonmetallic Materials Division
Department of the Air Force
Air Force Materials Laboratory (AFSC
Wright-Patterson Air Force Base, Ohio 45

Dr. J. Lando
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

Dr. J. White
Chemical and Metallurgical Engineering
University of Tennessee
Knoxville, Tennessee 37916

Dr. J. A. Manson
Materials Research Center
Lehigh University
Bethlehem, Pennsylvania 18015 1

Dr. R. F. Helmreich
Contract RD&E
Dow Chemical Co.
Midland, Michigan 48640 1

Professor Garth Wilkes
Department of Chemical Engineering
Virginia Polytechnic Institute and
State University
Blacksburg, Virginia 24061

Dr. Kurt Baum
Fluorochem Inc.
6233 North Irwindale Avenue
Azuza, California 91702

Professor C. S. Paik Sung
Department of Materials Sciences and
Engineering Room 8-109
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

DATE

FILMED

2-8