AD-A252 269

TATION PAGE

Form Approved
OMB No. 0704-0188

to average 1 hour per response, including the time for reviewing instructions, searching existing data sources
wing the collection of information. Send comments regarding this burden estimate or any other aspect of this
len to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson
ce of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

2

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
June 1992

3. REPORT TYPE AND DATES COVERED
Technical (6/1/91-5/31/92)

4. TITLE AND SUBTITLE
Ferroelectric Polarization Mechanisms in Nylon 11

5. FUNDING NUMBERS
N00014-80-C-0795

6. AUTHOR(S)
B.A. Newman, J.W. Lee and J.I. Scheinbeim

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Mechanics and Materials Science
College of Engineering, Rutgers University
P.O. Box 909
Piscataway, NJ 08855-0909

8. PERFORMING ORGANIZATION REPORT NUMBER
#25

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Dr. JoAnn Milliken
Office of Naval Research
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

92-16784

11. SUPPLEMENTARY NOTES
In press, Macromolecules

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.
Reproduction in whole or in part is permitted for any
purpose of the United States Government.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The combined results of piezoelectric coefficient (d_{31}, e_{31}) measurements, FTIR spectroscopy and x-ray diffraction studies of three dimensionally oriented Nylon 11 films reveal that the polarization occurs in the crystalline regions. In addition, the orientation of dipoles in a poled Nylon 11 film is not altered by a high temperature annealing treatment (185°C). This unique high temperature stability of dipole orientation in the crystalline regions provides a method to investigate the polarization mechanism for poled Nylon 11 films. Our results indicate that the difference in observed x-ray diffraction patterns from unpoled and poled films results from an initial 90° field induced dipole reorientation mechanism. Further dipole orientation appears to result from a 180°C switching mechanism.

DTIC
ELECTE
JUN 2 9 1992
S A D

14. SUBJECT TERMS

15. NUMBER OF PAGES
25

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE

19. SECURITY CLASSIFICATION OF ABSTRACT

20. LIMITATION OF ABSTRACT

OFFICE OF NAVAL RESEARCH

Contract N00014-80-C-0795

Technical Report No. 25

Ferroelectric Polarization Mechanisms in Nylon 11

by

B.A. Newman, J.W. Lee and J.I. Scheinbeim

Prepared for Publication in

Macromolecules

Department of Mechanics and Materials Science
College of Engineering
Rutgers University
Piscataway, NJ 08855-0909

June 1992

FERROELECTRIC POLARIZATION MECHANISMS IN NYLON 11

Brian A. Newman, Jar Wha Lee and Jerry I. Scheinbeim

Dept. of Mechanics and Materials Science
College of Engineering, Rutgers University
P.O. Box 909
Piscataway, NJ 08855-0909, USA

Abstract

The combined results of piezoelectric coefficient (d_{31}, e_{31}) measurements, FTIR spectroscopy and x-ray diffraction studies of three dimensionally oriented Nylon 11 films reveal that the polarization occurs in the crystalline regions. In addition, the orientation of dipoles in a poled Nylon 11 film is not altered by a high temperature annealing treatment (185°C). This unique high temperature stability of dipole orientation in the crystalline regions provides a method to investigate the polarization mechanism for poled Nylon 11 films. Our results indicate that the difference in observed x-ray diffraction patterns from unpoled and poled films results from an initial 90° field induced dipole reorientation mechanism. Further dipole reorientation appears to result from a 180° switching mechanism.

Introduction

A ferroelectric material is a material with a spontaneous polarization, which can be changed in direction by the application of an electric field (1). Until recently, poly(vinylidene fluoride) (PVF_2) and its copolymers were the only polymers shown conclusively to be ferroelectric. The bulk polarization of poled phase I PVF_2 films is now known to arise from dipole orientation in the crystalline regions towards the direction of the applied poling field (1-3). Following wide angle x-ray diffraction studies and infrared absorbance measurements, two different dipole reorientation models based on 60° and 180° rotations about the chain axis were proposed (4-7). Hysteresis loops between the electric displacement D and the applied electric field E have been observed for phase I PVF_2 using conventional ac techniques (8,9), and the switching times for polarization reversal have also been measured (10).

A number of studies of piezoelectricity in the odd-numbered nylons has culminated recently in the demonstration of clear hysteresis loops of electric displacement D and applied electric field E, typical of ferroelectric materials, for Nylon 11 and Nylon 7 films prepared by quenching from the melt, followed by cold drawing (11-13). This new class of ferroelectric polymer, the odd-numbered nylons, have a crystal structure based on the packing of hydrogen-bonded sheets (14, 15). From previous studies (12, 16), and the lack of observed ferroelectricity in the even-numbered nylons, it is apparent that the ferroelectric response originates in the crystalline regions. Both the hydrocarbon sections, as well as the amide groups play an important role in the ferroelectric behavior of these semicrystalline nylons.

The purpose of the present study is to present an analysis of the initial and subsequent polarization mechanisms of Nylon 11 films, based on measurements of the piezoelectric coefficients, FTIR absorbance studies, and wide angle x-ray diffraction measurements.

Experimental

As-stretched Nylon 11 films were produced by quenching the molten film (210°C) into an ice bath, cold drawing to a draw ratio of 3:1 at room temperature, and evaporating aluminum on opposing sides of the film as electrodes. As-poled Nylon 11 films were prepared using the same method as above, except that the films were polarized using a triangular electric pulse with a period of 640 sec and a maximum amplitude of 150 MV/m. As-annealed and poled-annealed samples were made by annealing the as-stretched and as-poled samples at 185°C under vacuum at a fixed length for two hours, respectively.

Piezoelectric coefficients for the as-poled and poled-annealed samples were measured at 3 Hz at room temperature using a Rheolograph Solid®, (Toyo Seiki, Japan).

Infrared spectra were obtained using a Perkin-Elmer Fourier Transform Infrared spectrometer (model 1720-X). The film samples used in this study were sufficiently thin to be within the absorbance range where the Beer-Lambert law is obeyed. Using a polarized infrared light source, the absorbed intensity of C=0 stretching and N-H stretching modes were examined to determine changes in dipole orientation after poling and annealing.

X-ray diffraction photographs were taken using Nickel-filtered Cu Kα radiation. Flat-plate camera photographs were used to record the wide angle x-ray diffraction patterns. In the flat-plate camera study, transmission mode (incident x-ray beam perpendicular to the plane of the film), edge-on mode (incident x-ray beam parallel to the plane of the film and perpendicular to the draw direction) and end-mode (incident x-ray beam along the draw direction) diffraction patterns were obtained.

Results and Discussion

The electric displacement D and applied field E hysteresis studies carried out previously clearly indicate that Nylon 11 films, prepared by quenching and cold-drawing, behave as a ferroelectric material (11,12). Further, previous studies also showed that annealing prior to poling significantly decreased the spacing between hydrogen bonded sheets and also that this annealed structure showed a reduced reorientation of dipoles with applied field. It was found that the coercive field increased from 62 MV/m to 115 MV/m and the remanent polarization decreased from 51 mC/m^2 to 17.3 mC/m^2 for films with increasing annealing temperature histories (25°C to 145°C). Films annealed at the melting temperature 185°C (before poling) did not show any hysteresis behavior at all, presumably because the coercive field values required exceeded the dielectric strength of the material (17).

These results clearly suggest that dipole reorientation in Nylon 11 films is inhibited by annealing. If this is true, then it suggests that the effect of increased temperatures (below the melting point) on Nylon 11 films which have been already poled to give a resultant dipole orientation, might not be the randomization of dipoles and subsequent depolarization, observed in PVF$_2$. In Table I the piezoelectric strain coefficients, d_{31}, and stress coefficients, e_{31}, measured at 3Hz at room temperature, are compared for as-poled and poled annealed films. The effect of annealing the poled films at 185°C under vacuum for two hours was to increase the measured values of d_{31} and e_{31} at room temperature slightly. This clearly supports the suggestion that the effect of annealing poled Nylon 11 films is not to randomize the dipoles. The implication of these results for the thermal stability of remanent polarization in poled odd-numbered nylons is clear and is the subject of a separate publication (13).

In Figure 1 the results of the FTIR measurements for the as-stretched, as-poled and poled annealed films are presented. Large differences in the absorbed intensities of the C=0 stretching modes at 1650 and the N-H stretching modes at 3300 between the as-stretched and the as-poled films strongly suggest that the hydrogen bonds break and the dipoles are rotated towards the field direction to reform bonds in a new direction, which remains when the applied field is removed. More importantly, comparing the absorbance spectrum obtained from the as-poled films with the spectrum obtained from the poled-annealed films, and in particular the absorbance intensities of the C=0 stretching modes and also the N-H stretching modes, very little difference is observed. This confirms the suggestion that annealing in vacuum at 185°C for two hours (under tension) does not cause any significant change in dipole orientation. Infrared band assignments were made on the basis of previous studies (18).

Since the nylon films, as prepared, possess a three-dimensional texture (19), with the molecular chains oriented in the draw direction, and the hydrogen-bonded sheets in the plane of the film, it would be expected that the reorientation of dipoles caused by the application of high electric fields would lead to clear and unambiguous changes in the x-ray diffraction patterns confirming this. Although differences in the x-ray diffraction patterns obtained from as-stretched films and as-poled films were observed, the crystallites resulting from the preparation treatment were not sufficiently large and well-formed to give a diffraction pattern suitable to make an unambiguous confirmation.

However, the x-ray patterns obtained from films which had been subsequently annealed to increase crystallite perfection were, as expected, much improved. The combined results of the studies of the effect of annealing on FTIR absorbance and piezoelectric properties show that it is possible to investigate polarization mechanisms using wide angle x-ray diffraction studies of as-annealed and poled annealed films, since the hydrogen bonds do not break and the orientation of hydrogen-bonded sheets does not change during the high temperature annealing treatment.

Figures 2, 3a, 3b and Figures 4a and 4b show flat film photographs together with a schematic representation of the wide angle x-ray diffraction patterns of as-annealed and poled annealed Nylon 11 films. Most of the reflections observed could be indexed using the unit cell proposed by Hasegawa (20). On Figures 3a and 4b we notice streaks of diffracted intensity between certain important reflections which suggest either a large degree of structural disorder or a small crystal size in certain directions. It is well known that this phenomenon can give a number of anomalous reflections at incorrect d-spacing values and some reflections of this type can be observed on some of the photographs. They can be distinguished from normal reflections by their appearance, which is much more diffuse, as well as being of weak intensity. These reflections are not included on the schematic representations, and will be the subject of a separate publication. It should be further noted that the fact of a three-dimensional crystal texture does not entail an unique single crystal orientation with respect to the film axes. In fact, the unit cell proposed by Hasegawa is triclinic and four different orientations of this cell with respect to film axes are consistent with the texture proposed by Northolt. This further complicates the interpretation of the diffraction photographs, and a complete discussion of these issues will also be deferred to a later publication. Here we present those results relevant to the issues of the polarization mechanisms important to the ferroelectric behavior of Nylon 11 films.

Figure 2 shows the flat film photograph and the corresponding schematic representation for the as-annealed samples, when the incident x-ray beam is along the direction of draw (end-mode orientation). The meridional direction (vertical) on this photograph corresponds to the plane of the film. If the only orientation present in these films was uniaxial along the draw direction then the diffraction pattern anticipated for the geometry of this orientation would be a series of concentric rings. Figure 2 shows clearly that additional orientation is present, since all reflections are rather small arcs of circles with an angular spread of ~ ± 20°. The very strong equatorial reflection with d_{obs} = 3.89Å, indexed as (020), corresponding to the spacing between hydrogen-bonded sheets, confirms that the hydrogen-bonded sheets are parallel to the plane of the film.

The pattern is approximately hexagonal. The (200) and (220) reflections occurring on the first layer line in the 60° positions are consistent with the two different crystal orientations with a-axis in the plane of the film and perpendicular to the c-axis (the draw direction), as is also the position of the reflection on the first observed layer line, (~ 30° from the equator) and the meridional reflection, which are consistent with an assignment of ($2\bar{2}0$) and (420). Table 2 shows a list of index assignments and measured values of the d-spacings for the reflections observed. So, to summarize, Figure 2 clearly confirms that after annealing the Nylon 11 films are well crystallized, with crystal orientations consistent with the c-axis in the draw direction and hydrogen bonded sheets in the plane of the film.

Figure 3a shows the x-ray flat film photograph obtained and a schematic representation when the incident beam is perpendicular to the draw direction and in the plane of the film, (edge-on mode). Assuming the previous orientation assignment correct, the incident x-ray beam is parallel to the a-axis for Figure 3a. In the figure, the draw direction is vertical, while the normal to the plane of the sample is horizontal. Thus, the (020) reflection, corresponding to the spacing between hydrogen-bonded sheets, should be and is observed on the equatorial line. The second equatorial reflection can be indexed as $(2\bar{2}0)$. The meridional reflections, and reflections symmetrically disposed to either side of the meridian can be indexed (001), (002), (003), (126) and $(\bar{1}06)$. The complete indexing is summarized in Table 3 and is also consistent with the previous three-dimensional orientation proposed, two different crystal orientations being possible with the reciprocal lattice vector C^* symmetrically disposed to either side of the meridian.

Figure 3b shows the x-ray plot film photograph obtained and a schematic representation when the incident beam is perpendicular to the draw direction and perpendicular to the plane of the film (transition mode). The sample draw direction is again vertical, but the equatorial line is perpendicular both to the draw direction and the normal to the plane of the sample. Assuming the previously determined orientation, the equatorial line is parallel to the a-axis. The equatorial reflections observed are (200) and (420). The other reflections observed are (20ℓ), with the exception of several meridional reflections different in appearance from all others. The complete indexing is shown in Table 4 and is consistent with the crystal orientations already discussed. However, the subject of the special meridional reflections best seen in Fig. 3 will be discussed in a later publication.

Figure 4a shows the flat film photograph and the corresponding schematic representation for the poled-annealed samples, when the incident x-ray beam is perpendicular to the draw direction, and in the plane of the film (edge-on mode), that is, the geometrical arrangement is similar to that used to obtain Figure 3a. The draw direction is vertical, while the normal to the plane of the sample is horizontal. Figure 4b shows the flat film photograph and the corresponding schematic representation for the poled-annealed samples, when the incident x-ray beam is perpendicular to the plane of the sample. The draw direction is vertical and the equatorial line is perpendicular both to the draw direction and to the normal to the plane of the sample, that is, the geometrical arrangement is similar to that used to obtain Figure 3b.

The most striking feature of Figures 4a and 4b is that, although the geometry used to obtain these photographs compares with that used to obtain Figure 3a and 3b for the unpoled samples, Figure 4a shows a similar diffraction pattern to Figure 3b, and Figure 4b shows a similar diffraction pattern to Figure 3a. Since the different diffraction patterns of Figure 3a and Figure 3b are obtained from geometrical arrangements which differ only by a rotation of 90° about the draw direction (c-axis), this fact is strong evidence for the claim that following poling and then annealing, the samples still show a three dimensional texture, but now rotated by 90° about the c-axis with respect to the initial orientation. Thus, following the poling procedure and annealing treatment, the hydrogen-bonded sheets are perpendicular to the plane of the poled films, having rotated 90° from their initial orientation in the plane of the films. This is easily understood when it is realized that the strong dipoles associated with the hydrogen bonds are, of course, in the plane of the hydrogen bonded sheets. Clearly, under the high electric fields used for poling, these dipoles rotated in the direction of the field, the state of lowest energy and after removal of the field this crystal orientation remained. This orientation continued to remain even during the annealing treatment, as evidenced by the FTIR data and the piezoelectric activity of the film measured after poling.

The observed hysteresis behavior during field reversal strongly suggests 180° switching of dipoles, and it is clear from Figure 5 that this can be accomplished without dramatic changes in crystal structure. It is evident, however, that the initial dipole reorientation must be a 90° switch, since it is known that the initial dipole orientation is in the plane of the film.

Conclusions

As a result of a study of crystal orientation in both poled and unpoled Nylon 11 films, which had been initially prepared by quenching from the melt and drawing, and finally annealing using both x-ray diffraction methods and FTIR, we conclude:

(1) The orientation of NH and C=O dipoles does not significantly change after annealing treatments, even annealing at temperatures close to the melting point.

(2) A dipole switching of 90° occurs with the initial application of electric field, to switch dipoles in the plane of the film into the field direction.

(3) Subsequent dipole switching of 180° occurs with electric field reversals.

(4) The piezoelectric coefficients are not decreased by annealing treatments, even at temperatures close to the melting points.

Acknowledgements

This work was supported by DARPA and the Office of Naval Research.

Figure Captions

Figure 1	Infrared spectra of as-stretched, as-poled, and poled-annealed Nylon 11 films.
Figure 2	Flat plate photograph, end mode, of 3-dimensionally oriented Nylon 11 film.
Figure 3a	Flat plate photograph, transmission mode, of 3-dimensionally oriented Nylon 11 film.
Figure 3b	Flat plate photograph, edge-on, mode of 3-dimensionally oriented Nylon 11 film.
Figure 4a	Flat plate photograph, transmission mode, of poled-annealed Nylon 11 film.
Figure 4b	Flat plate photograph, edge-on mode, of poled-annealed Nylon 11 film.
Figure 5	180° dipole switching (antiparallel packing) of chains in the hydrogen-bonded sheet structure.

Table Captions

Table 1	Piezoelectric coefficients of as-poled and poled-annealed Nylon 11 film.
Table 2	Diffraction data of end-mode flat plate photograph.
Table 3	Diffraction data of edge-on mode flat plate photograph.
Table 4	Diffraction data of transmission mode flat plate photograph.

References and Notes

1. Naegele, D.; Yoon, D.Y., Appl. Phys. Lett. 1978, 33, 132.
2. Fukada, E.; Date, M.; Furukawa, T., Amer. Chem. Soc., Org. Coat. Plast. Chem. Prepr. 1978, 38, 262.
3. Tamura, M.; Hagiwara, S.; Matsumoto, S.; Ono, N., J. Appl. Phys. 1977, 48, 513.
4. Kepur, R.G.; Anderson, R.A., J. Appl. Phys. 1978, 49, 1232.
5. Aslaksen, E.W., J. Chem. Phys. 1972, 57, 2358.
6. Broadhurst, M.G.; Davis, G.T., Ann. Rep., Conf. Elec. Insul. Diel. Phen. 1979, 48, 447.
7. Devy-Aharon, H.; Sluckin, T.J.; Taylor, P.L.; Hopfinger, A.J., J. Phys. Rev. B. 1980, 21, 3700.
8. Tamura, M.; Ogasawara, K.; Ono, N.; Hagiwara, S., J. Appl. Phys. 1974, 45, 3768.
9. Furukawa, T.; Date, M.; Fukada, E.; Tajitsu, Y.; Chiba, A., Jpn. J. Appl. Phys. 1980, 19, 1109.
10. Furukawa, T.; Date, M.; Fukada, E., J. Appl. Phys. 1980, 51, 1135.
11. Lee, J.W.; Takase, Y.; Newman, B.A.; Scheinbeim, J.I., J. Polym. Sci., Part B. Polym. Phys. 1991, 29, 273.
12. Lee, J.W.; Takase, Y.; Newman, B.A.; Scheinbeim, J.I., J. Polym. Sci., Part B. Polym. Phys. 1991, 29, 279.
13. Takase, Y.; Lee, J.W.; Newman, B.A.; Scheinbeim, J.I., Macromolecules, accepted for publication.
14. Slichter, W.P., J. Polym. Sci. 1959, 36, 259.
15. Newman, B.A.; Sham, T.P.; Pae, K.D., J. Appl. Phys. 1977, 48, 4092.
16. Lee, J.W., Ph.D. Thesis, Rutgers University 1990.

17.

18. Skrovanek, D.J.; Painter, P.C.; Coleman, M.M., Macromolecules 1986, 19, 699.

19. Northolt, M.G., J. Polym. Sci., Part C. 1972, 38, 205.

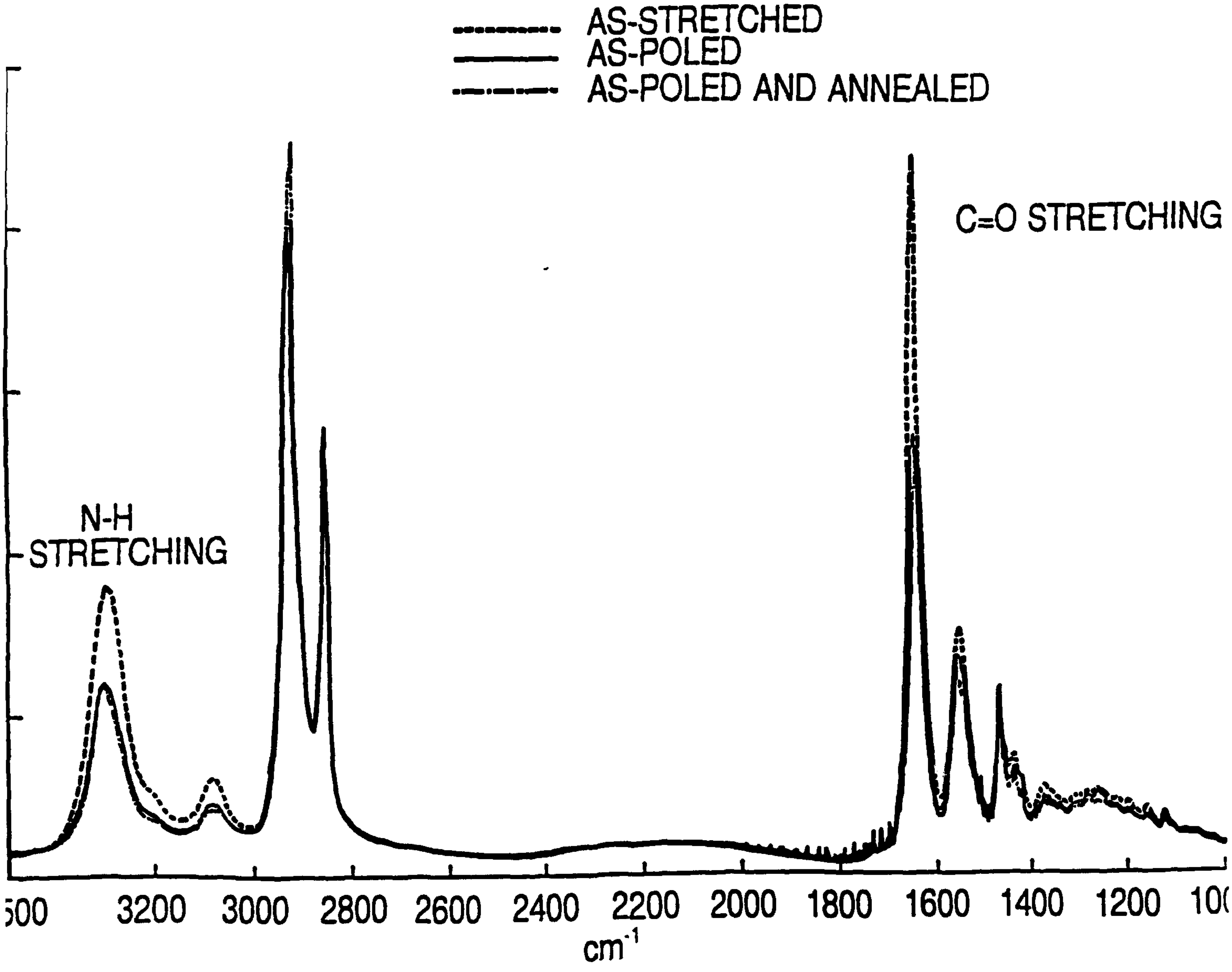
20. Hasegawa, R.H., private communication.

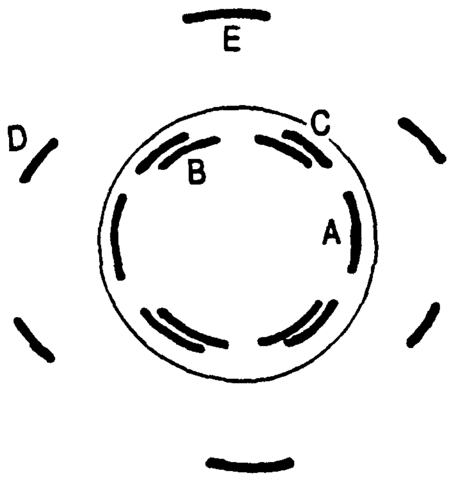
	d_{31} (pC/N)	e_{31} (mC/m^2)
as-poled	2.2	6.0
poled-annealed	2.3	7.5

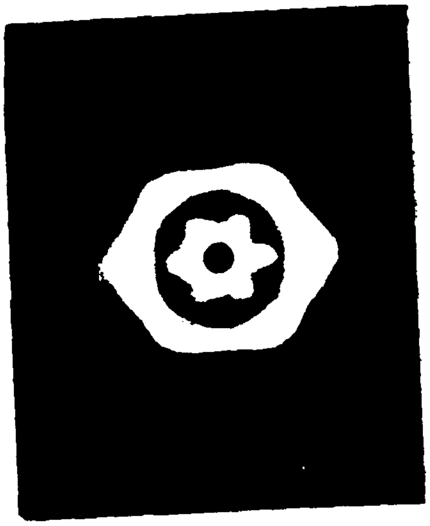
label	intensity	$d_{obs.}$ (Å)	index
A	vs	3.89	(020)
B	vs	4.27	(200)
C	m	3.87	(220)
D	vw	2.39	$(2\bar{2}0)$
E	vw	2.32	(420)

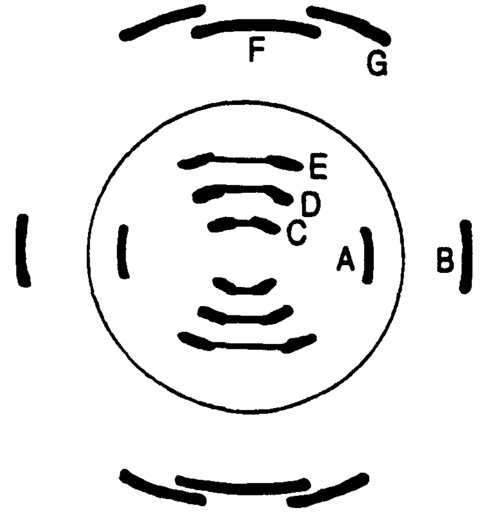
label	intensity	$d_{obs.}$ (Å)	index
A	vs	3.89	(020)
B	m	2.39	$(2\bar{2}0)$
C	vs	12.80	(001)
D	m	6.35	(002)
E	m	4.29	(003)
F	m	2.36	(126)
G	m	2.21	$(\bar{1}06)$

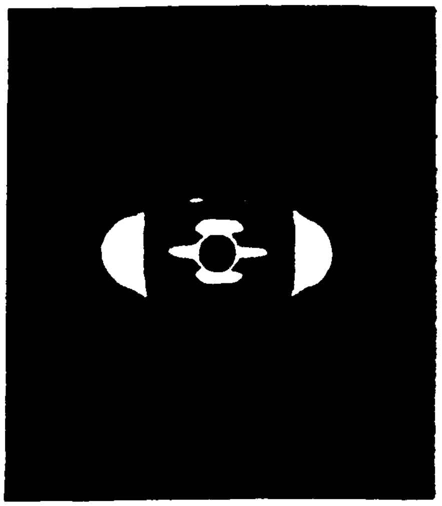
label	intensity	$d_{obs.}$ (Å)	index
A	vs	4.27	(200)
B	m	2.39	(420)
C	s	4.35	$(20\bar{1})$
D	m	3.95	$(20\bar{2})$
E	w	3.45	$(20\bar{3})$
F	w	2.36	(126)
G	m	2.21	$(\bar{1}06)$


AS-STRETCHED
AS-POLED
AS-POLED AND ANNEALED
N-H STRETCHING
C=O STRETCHING
500
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
10
cm^{-1}

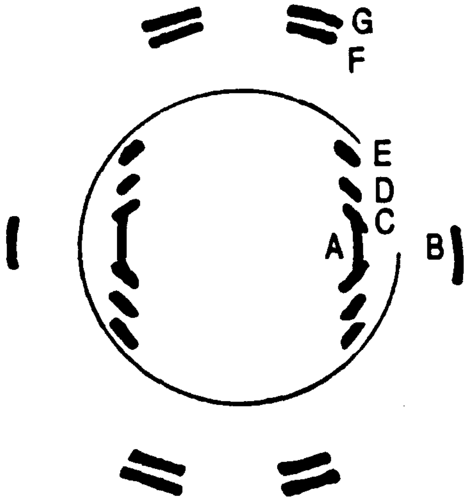

E
D
C
B
A

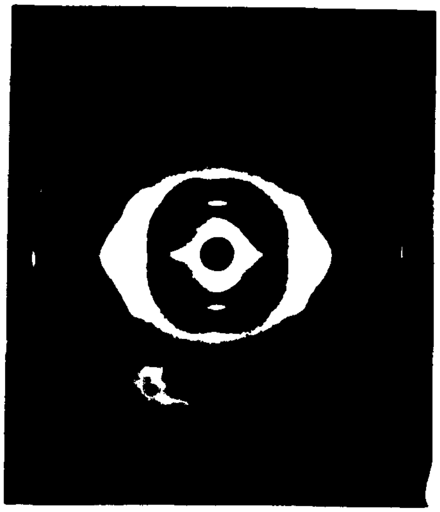




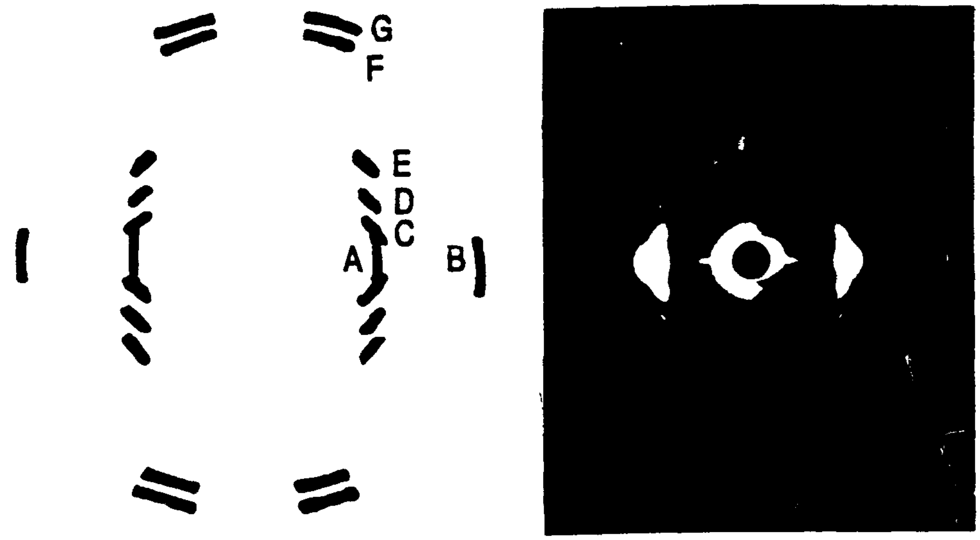


3a





3b


G
F
E
D
C
A
B

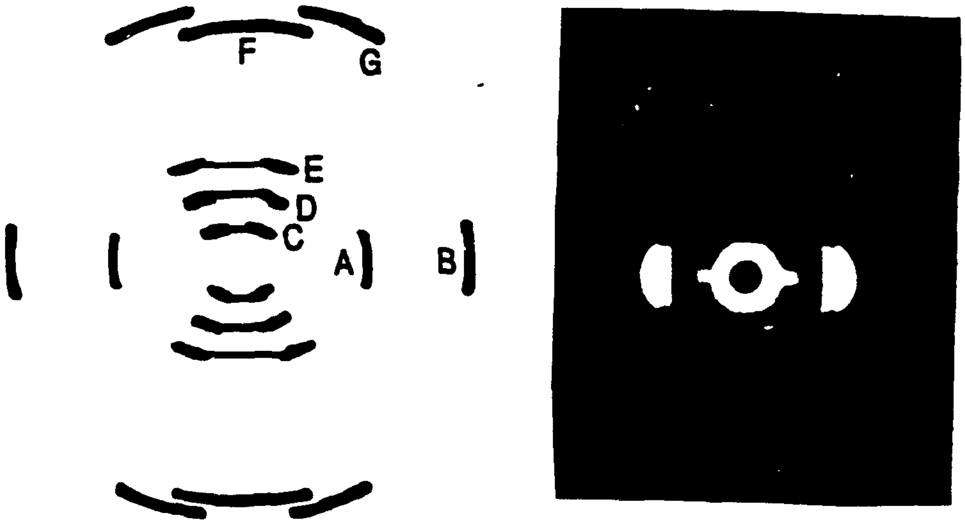


Figure 4b

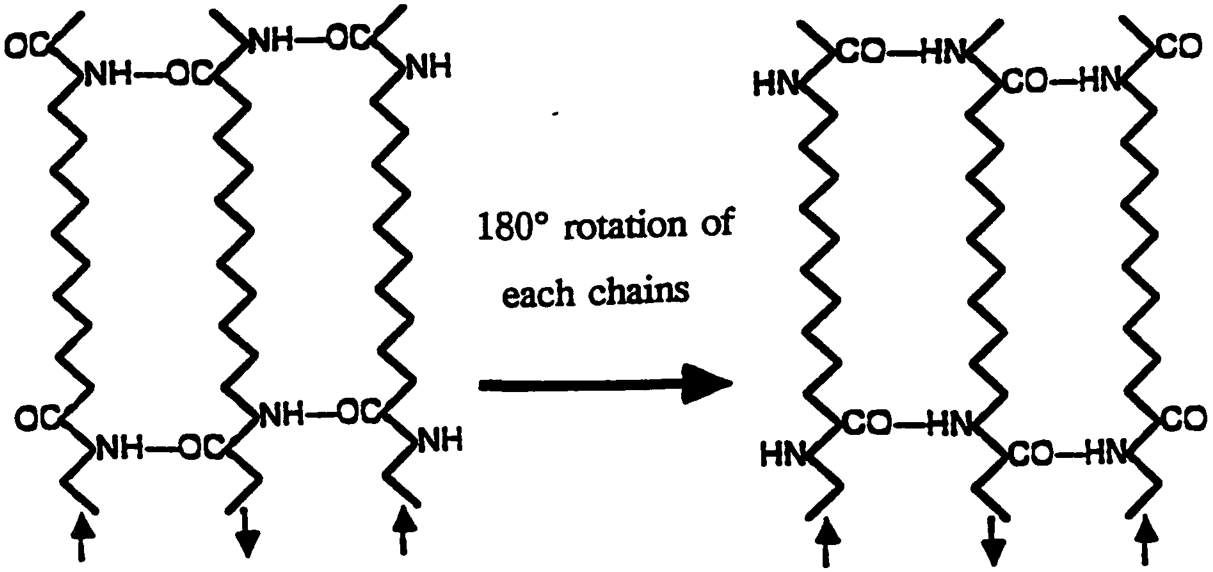

OC
NH—OC
NH—OC
NH
OC
NH—OC
NH—OC
NH
180° rotation of each chains
HN
CO—HN
CO—HN
CO
HN
CO—HN
CO—HN
CO

Figure 5

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)*
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Air Weapons Center
Weapons Division
China Lake, CA 93555-6001

Dr. Elek Lindner (1)
Naval Command, Control and Ocean
Surveillance Center
RDT&E Division
San Diego, CA 92152-5000

Dr. Bernard E. Douda (1)
Crane Division
Naval Surface Warfare Center
Crane, Indiana 47522-5000

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

Dr. Harold H. Singerman (1)
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Eugene C. Fischer (1)
Code 2840
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Defense Technical Information
Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

* Number of copies to forward