

AD-A054 615

NORTHWESTERN UNIV EVANSTON IL DEPT OF MATERIALS SCIENCE F/G 11/9
ELECTRIC FIELD-INDUCED STRUCTURE IN POLY(ACRYLONITRILE).(U)
MAY 78 S I STUPP, S H CARR

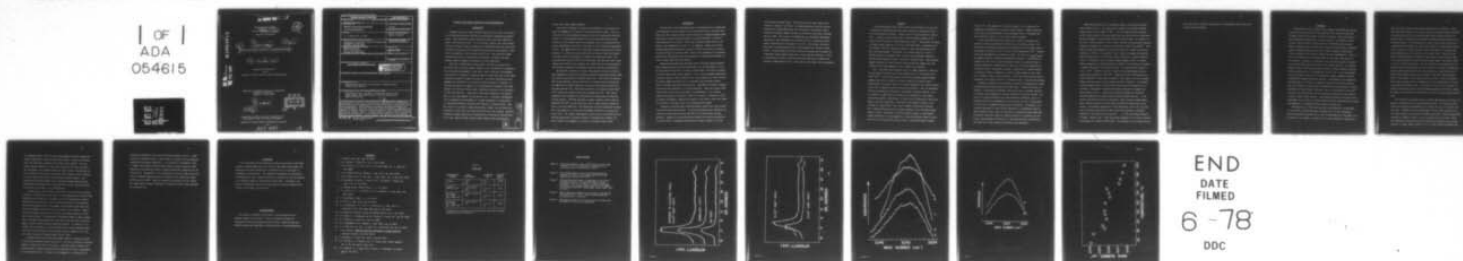
N00014-75-C-0963

UNCLASSIFIED

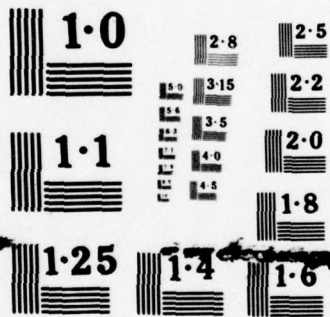
TR-5

NL

1 OF 1
ADA
054615



END
DATE
FILMED
6-78
DOC



NATIONAL BUREAU OF STANDARDS

FOR FURTHER TRAN *TH...*

OFFICE OF NAVAL RESEARCH

Contract No. *15* ~~NO0014-75-C-0963~~

Project No. NR 051-599

12

AD A 054615

6 *9* TECHNICAL REPORT NO. 5

14 TR-5

ELECTRIC FIELD-INDUCED STRUCTURE IN POLY(ACRYLONITRILE)

by

10 S. I. Stupp and S. H. Carr

Prepared for Publication

in the

Journal of Polymer Science, Polymer Physics Edition

Department of Materials Science and Engineering
Northwestern University
Evanston, Illinois 60201

11
15 May 1978

12 23p.

DDC
RECEIVED
JUN 5 1978
B

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

Approved for Public Release; Distribution Unlimited

1473

260 810

LB

AD No.
DDC FILE COPY

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 5 ✓	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) "ELECTRIC FIELD-INDUCED STRUCTURE IN POLY(ACRYLONITRILE)"		5. TYPE OF REPORT & PERIOD COVERED Interim
7. AUTHOR(s) S. I. Stupp and S. H. Carr		6. PERFORMING ORG. REPORT NUMBER 5
9. PERFORMING ORGANIZATION NAME AND ADDRESS ✓ Department of Materials Science and Engineering Northwestern University Evanston, Illinois 60201		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0963 ✓
11. CONTROLLING OFFICE NAME AND ADDRESS ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Project No. NR 051-599
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE May 15, 1978
		13. NUMBER OF PAGES 22
		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Restricted Distribution List		
DISTRIBUTION STATEMENT A Approved for public release; Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Prepared for Publication in the Journal of Polymer Science, Polymer Physics Edition.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Poly(acrylonitrile), electrets, infrared spectroscopy, X-ray diffractometry, paracrystallinity, electrical polarization, dipolar interactions.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Experimental evidence has been obtained for alteration of the molecular organization in polyacrylonitrile which has been given a thermoelectric treatment that creates a persistent elec- trical polarization. These studies have involved infrared spectroscopy and x-ray diffractometry, and their results have been interpreted as suggesting the existence of dipolar clusters in polarized material. These clusters cause poly- acrylonitrile chains to adopt a structure which is different from any previously reported for this material. It is suggested that stability of the polarized state of polyacrylonitrile results, in part, from this new molecular organization.		

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

"ELECTRIC FIELD-INDUCED STRUCTURE IN POLY(ACRYLONITRILE)"

INTRODUCTION

Polymeric solids, as other dielectric materials, will react to the field of an electrical potential difference by developing an opposing polarization charge. This polarization charge persists as long as the solid remains exposed to the electrical field. It is well known, however, that some polymers in the solid state, stored at temperatures considerably lower than their glass transition, retain part of the acquired polarization for long periods of time even in the absence of the electrical field (1-10). The persistent charge is usually the result of both preferred orientation of dipoles and space charges formed by asymmetric mobilization of ionic impurities.

Given that a biased spatial orientation of dipoles is induced by the electrical field, one must question whether or not polarization is accompanied by a structural rearrangement in the solid. Such a structural rearrangement could involve, for example, an enhanced degree of local order due to the common orientation acquired by neighboring dipoles. Two recent investigations have suggested the possibility of electrically induced structure in polymers. It has been discovered, for example, that poly(bisphenol-A-carbonate) thin films exposed to an electrical field reveal a significant increase in the elongation at break and elasticity. These effects have been attributed to the development of local order domains in this material (11). A different investigation (12) has suggested the development of a slight enhancement of crystallinity in polarized polyethylene containing small amounts of sodium chloride. This was inferred on the basis of Raman spectroscopic studies, and the effect was attributed to electrical fields associated with ionic space charges. Generally speaking, one might suppose that susceptibility to electrically induced structure is most likely in those polymers which possess strong intermolecular

Section	☒
Section	☐
	☐
Y CODES	
SPECIAL	

A

forces due to their chemical make-up.

The present investigation explores the possibility of electrically induced rearrangements of structure in poly(acrylonitrile) (PAN). PAN is instructive for this investigation because it has the following two characteristics: 1) the strong dipole moment of its nitrile groups which are substituents on every other carbon in the backbone, and 2) its paracrystalline nature, hypothesized previously on the basis of x-ray diffraction experiments (13-15). The significance of the large dipole moment associated with nitrile groups is, of course, the strong torque that an external field could impose on polymer chains, thus leading to a highly polarized state in PAN. The paracrystalline nature of PAN, on the other hand, indicates that these chains possess some ability to pack together even though they are not stereoregular, thus possibly permitting a considerable degree of molecular reorganization.

The possible occurrence of electric field-induced structure in PAN has been suggested by previous work involving thermally stimulated discharge (TSD) and infrared spectroscopy of polarized films (16). TSD involves the measurement of depolarization currents and thus is a technique which characterizes the magnitude and thermal stability of electrical polarization acquired by any given material (17). PAN films polarized by low intensity fields ($5 \times 10^4 \text{ Vcm}^{-1}$) reveal upon heating a TSD current maximum near 90°C . This current maximum has been proposed to be associated with randomization of partially oriented dipoles. PAN films polarized by higher intensity fields (order of magnitude 10^5 Vcm^{-1}), on the other hand, tend to reveal smaller currents or none at all below 100°C (16). This observation has been interpreted as being due to the presence of a structural arrangement induced by the strong electrical field. The present investigation involving both x-ray diffraction and infrared spectroscopy is therefore aimed at obtaining direct evidence for such a possible rearrangement of structure in polarized films of PAN.

EXPERIMENTAL

The PAN used in this investigation was a custom-made batch of homopolymer kindly supplied to us by courtesy of the Vistron Corporation, Cleveland, Ohio. Films were cast on glass surfaces from 2% solutions in dimethylformamide (DMF). Evaporation of solvent was accomplished by exposing solutions to vacuum at room temperature for 24 hours. Films, whose thickness ranged from 20 to 80 microns, were subsequently cut into 1" x 1" segments. Samples were placed between glass plates and exposed to vacuum at 40°C for 24 hours in an effort to reduce further the content of DMF. Prior to any thermoelectric treatments, samples were covered with thin gold overlayers in a high vacuum evaporator in order to assure good electrical contact.

Samples were annealed and polarized using an "Electret Thermal Analyzer" (ETA), manufactured by Toyo-Seiki Seisaku-Sho, Ltd. and distributed in U.S.A. by Atlas Electric Devices Co., Chicago, Illinois 60613. This device includes a DC power supply whose output ranges to 4 kV, a U-line programmed temperature controller coupled to power regulator, and a dual channel strip chart recorder. The sample chamber provided with this instrument holds specimens between platen electrodes under mild spring pressure. Specimens are coated on opposite surfaces with gold deposited in a vacuum evaporator: these gold layers (~50Å thick) serve as the actual electrodes in the experiments. All polarized samples were exposed to electrical fields for a period of 30 minutes at 145°C. Following this exposure, samples were allowed to cool slowly, while still under the influence of the field, until room temperature was reached.

Analyses of polarized and/or annealed samples involved both x-ray scattering and ATR infrared spectroscopy. Scattering experiments were carried out in a reflective mode using a Phillips XRG 5000 x-ray diffractometer and CuK_α radiation. Samples for x-ray analysis were mounted with double-stick tape on the open surface of polystyrene cups having the proper diameter to fit the

diffractometer specimen holder. Diffraction scans of these samples were recorded at speeds of $1(2\theta)^{\circ}/\text{min}$. The spectrophotometer used for infrared analysis was a Perkin Elmer Model 180, fitted with a twin-parallel mirror reflection attachment (TPRMA) from Harrick Scientific Corporation, Ossining, New York 10562. The accuracy of transmittance and wavenumber measurements specified for this instrument are $\pm 0.4\%$ and $\pm 0.25 \text{ cm}^{-1}$ respectively (wavenumber resolution was in the range of 0.7 cm^{-1}). The internal reflection plate used for ATR spectroscopy was a parallelepiped zinc selenide crystal ($\theta=45^{\circ}$). Contact between the internal reflection element and the sample was accomplished using pressure plates and a torque-limiting screwdriver. Prior to spectroscopic analysis, thin gold electrodes evaporated on samples were removed by rubbing gently with a cotton swab that was lightly wet with methanol.

RESULTS

X-ray diffractometer scans were obtained from PAN films in as-cast form or annealed at temperature-time conditions identical to those used in electrical polarization procedures. Typical scans for these samples are shown in Fig. 1. Scans of as-cast films reveal a broad scattering maximum in the range of $2\theta=17^\circ$ as well as a weak maximum near $2\theta=30^\circ$. These maxima correspond to average repeat distances of $5.1\text{\AA}$ and $2.9\text{\AA}$ respectively. Annealing of as-cast films at 145°C for 30 minutes appears to cause some sharpening of the main scattering maximum. Furthermore, this maximum appears to acquire a doublet character in annealed films. Finally, the scattering intensity of the high angle maximum is found to increase in annealed films. These observed changes correlate well with previously reported data and suggest that some ordering at the chain segmental level is induced upon annealing.

Fig. 1 also shows diffractometer scans of a sample annealed to 145°C and one electrically polarized at the same temperature by a low-strength field ($5 \times 10^4 \text{ Vcm}^{-1}$). The different shape of the main scattering maximum strongly suggests some effect on physical structure caused by the applied field; specifically, the doublet character of the main maximum is more easily resolved in the case of samples that were electrically polarized. Given the difficulty involved in measuring 2θ positions of the maxima in annealed samples, it is not possible to assess with any certainty any differences in this respect between both samples. Nonetheless, if there are such differences, they do not appear to be very significant. Both peaks of the doublet do appear to be narrower to a small extent in the case of samples electrically polarized. Fig. 2 shows scattering curves for samples exposed to low- and high-strength fields at 145°C . Scattering of x-rays by samples exposed to high-strength fields ($5 \times 10^5 \text{ Vcm}^{-1}$) is also suggestive of some field-induced change in structure, but in this case there is also a shift of scattering maxima to higher

values of 2θ . The magnitude of this shift amounts to ~ 0.7 degrees in 2θ , suggesting a densification of laterally ordered regions. Angular positions for the main scattering maxima and corresponding values of d-spacings have been tabulated in Table 1 for the various types of samples.

X-ray scattering curves were analyzed in an effort to determine any changes in overall crystallinity brought about by electrical fields. For this purpose, integrated intensities were measured for both the main scattering maxima in the range of $2\theta=17^\circ$ as well as the maximum near $2\theta=30^\circ$. Results from these measurements are presented in Table 1 as ratios of $I_{2\theta=30^\circ}/I_{2\theta=17^\circ}$ for samples exposed to different thermoelectric histories. The observed increments for this ratio in polarized samples relative to annealed films is possibly significant, considering these values are internally normalized for irradiated volume. The apparent increase of these ratios in samples exposed to electrical fields is suggestive of either a higher degree of local order or an increase in size of ordered regions. Given the overlap between scattering maxima in the range of $2\theta=17^\circ$, no attempt was made to measure peak breadths.

Additional evidence for field-induced structural rearrangements was sought by high-resolution infrared spectra from PAN films. Internal reflection, as opposed to conventional transmission, was used in order to maximize expansion of ordinate scales (absorbance) and thus resolution of spectral details. The nitrile stretching absorption has a high extinction coefficient, and it is therefore difficult in transmission to keep the band in scale at high signal to noise ratios in samples having practical thicknesses. Furthermore, it is virtually impossible to record nitrile absorption in transmission using expanded ordinate scales. This is contrasted with absorbance measurements made by internal reflection, where the limited penetration of radiation into the film at the wavelength of interest ($\sim 1\mu$) decreases absorbance substantially and allows use of both ordinate and abscissa scale expansions.

High-resolution scans in the wavenumber range of the nitrile peak maximum are shown in Fig. 3. All spectra were recorded at the normal operating temperature for the instrument (-35°C). The first general feature revealed by the various spectra is the possibility that more than one nitrile absorption maximum is present in the spectrum of PAN in the solid state. For example, in the case of films annealed at 145°C , careful analysis of the absorbance spectrum suggests the presence of a doublet with maxima at $\sim 2241\text{cm}^{-1}$ and 2239cm^{-1} . This doublet becomes more apparent in the spectrum shown for a sample electrically polarized at 145°C by a low-intensity field. Spectra of samples polarized by high-intensity fields at 145°C reveal, rather distinctly, a doublet character as well. Furthermore, scans from these samples suggest a shift to slightly higher frequencies for the high-frequency component of the doublet with respect to samples polarized by low-intensity fields. The observed shift amounts to $\sim 1.0 - 1.5\text{cm}^{-1}$. Moreover, spectra of high-field polarized samples reveal a possible third maximum at $\sim 2243.5\text{cm}^{-1}$. These rather subtle differences were found reproducible in many scans recorded for each sample, and also in several samples polarized under any given temperature/field conditions. The possible relation between electric field induced structure and the appearance (or enhancement) of absorbance at higher vibrational frequencies is suggested by spectra shown in Fig. 4. These nitrile absorbance maxima for high-field polarized samples were recorded using polarized infrared radiation. In the spectrum recorded with parallel polarization, higher frequency maxima appear better resolved relative to the spectrum recorded with perpendicular polarization. The possible significance of this observation lies in the fact that only reflectivity with parallel light contains the absorption coefficient component in the direction of the applied electric field (thickness direction of films). Finally, Fig. 5 shows the thermal dependence of the nitrile stretching frequency in solvent-cast PAN films. As discussed in the following section,

these data offer a possible interpretation of experimental results from electrically polarized samples.

DISCUSSION

Data presented in the previous section suggests the possibility that the electrically polarized state of PAN, especially that induced by high field strengths, involves some change in physical structure. Before proceeding to analyze possible interpretations of data reported, it is helpful to review previous research aimed at characterization of PAN solid state structure. Despite extensive x-ray scattering work carried out over the past two decades, complete characterization has been only partially achieved. Nonetheless, certain conclusions can be safely derived from past investigations. First of all, it is evident that some limited degree of structural order exists in this material. Secondly, the possibility that more than one phase is present in solid state PAN cannot be excluded at the present time (18). The limited degree of order in PAN has been associated with a laterally ordered structure in which chains pack in a two-dimensional lattice (13). It has been assumed that order along the chain axis is absent due to highly irregular molecular conformations (randomly kinked and twisted). Experimentally, this suggestion has been based on the absence of meridional maxima in x-ray fiber patterns. The actual origin of conformational irregularity has been attributed to strong intermolecular dipole-dipole repulsions. Thus, in the context of this interpretation, the macromolecules can be envisioned as symmetrical rods spaced at a regular lateral repeat distance. The observed splitting of the main scattering maximum into a doublet in annealed material has been interpreted as a change from hexagonal to rectangular lateral packing of chains (15).

The complexity of solid state structure in PAN should not be surprising in view of the strong dipole moment possessed by its nitrile side-groups. Strong dipole-dipole associations, as well as repulsions, will inevitably occur. In addition, the irregular conformation of the chain backbone is dominated by

some balance which exists between these associations and repulsions. When a solid like PAN is exposed to an electric field, the question raised is how does this external force alter the balance between dipolar associations and repulsions and its consequent chain backbone conformations which existed in the unpolarized state. If the system were to exist in some stable state prior to a thermoelectric treatment, the result might simply be a biased spatial orientation of dipoles, and this situation would only persist for as long as the system remains under the influence of the electric field. Naturally, this biased orientation would also persist in the absence of the electrical field for as long as molecular relaxation motions remain highly constrained, unable to return to that previous state. On the other hand, one envisions that the external electrical field might actually be capable of driving the system over some activation energy barrier into a metastable state, specifically one in which dipolar groups interact more favorably. Then, when this material is heated in the absence of the external electrical field, a kind of hysteresis effect might accompany dipolar randomization as the system returns to its previous electrically neutral state. The reason for this is that the onset of molecular motions may actually require higher temperatures in order to achieve an energy level sufficient for the system to return to its electrically neutral state.

The activation of molecular motion at higher temperatures could cause, for example, a densification of closely packed PAN chains. It follows that this densification should be accompanied by an increase in order at the repeat unit size scale. Evidence for such an improvement in local order is found in the x-ray data, where it is noted that the higher angle peak at $2\theta=29^\circ$ progressively increases in intensity relative to the scattering from the 17° peak. X-ray data presented in the previous section, involving the increase in scattering intensity at higher angles relative to the 17° peak, would be consistent with

this suggested model. This structural rearrangement involving, among other things, maximization of dipolar associations should, at least in principle, affect the vibrational frequencies of nitrile groups in PAN. It is not readily obvious, however, how local order induced by the field will affect the interatomic force constants within the nitrile group. Interactions due to an increase in local order could either simply change the force constant, or lead to coupled vibrational motions between adjacent dipoles. Such coupling effects would probably lead to absorption maxima spaced by small differences in wavelength, due to the large force constant association with the $C\equiv N$ bond (on the order of 18 millidynes/cm).

Wolfram, *et al.*, (19) reported a small shift for the nitrile stretching frequency to lower values (on the order of a few wavenumbers) in PAN near 90°C. This shift was attributed by the authors to loss of intermolecular bonding between nitrile side-groups. Their conclusion was based on the assumption that nitrile groups would have the highest electron density when associated with their neighbors and, therefore, have a higher force constant. However, an actual frequency splitting for the nitrile stretching absorption in PAN has not been reported. The appearance of subsidiary maxima at higher frequencies in the high-field polarized PAN could result from just such an enhanced degree of dipolar bonding between neighboring nitriles. In addition, it is possible that the presence of several maxima within a narrow frequency range could result from vibrational coupling amongst nearest neighbors due to the local order induced by the high-strength electric field.

A detailed vibrational analysis that might explain the observed position of the nitrile absorption maxima (especially in the case of high-field polarized samples) is beyond the scope of this paper. One might suggest, however, that enhanced degree of dipolar bonding between neighboring nitriles is responsible for the observed effects. The basis of this suggestion is provided by the

temperature dependence of the nitrile stretching frequency (Fig. 4). These data show a progressive shift to lower values of frequency for the absorption maximum with increasing temperature. It is perhaps not unreasonable, then, to suggest that thermally induced dissociations of dipolar clusters in PAN (parallel or anti-parallel) result in lowered vibrational frequencies for the nitrile group. Furthermore, it is interesting to note that slight discontinuities in frequency-temperature data are observed in the temperature ranges, 60-70°C and on 30-150°C. These are essentially coincident with the temperature ranges where transition phenomena are observed in PAN by other experimental techniques (20).

CONCLUSIONS

X-ray scattering and high-resolution infrared spectroscopy of PAN films exposed to high-strength electrical fields at high temperatures suggest the possibility that such thermoelectric treatments lead to a structural rearrangement in this material. The suggested rearrangement is envisioned as one involving not just a biased orientation of dipoles, but also the formation of an additional number of dipole-dipole associations. Furthermore, the electric field-induced structure is interpreted as having an enhanced level of order at the repeat unit size scale.

ACKNOWLEDGEMENTS

The authors are indebted to the Office of Naval Research for its generous support of this project. Use of the Central Facilities of Northwestern University's Materials Research Center, supported under the NSF-MRL program grant DMR76-80847, facilitated much of the experimentation.

REFERENCES

1. M. Eguchi, Phil. Mag., 49, 178 (1925).
2. M. L. Miller, J. Polym. Sci., A-2, 4, 685 (1966).
3. P.K.C. Pillai, V. K. Jain and G. K. Vij, Electrochem. Soc. J., 116, (6), 836 (1969).
4. R. A. Creswell and M. M. Perlman, J. Appl. Phys., 41, 2365 (1970).
5. P.K.C. Pillai and V. K. Jain, Brit. J. Appl. Phys., Ser. 2, 3(1), 829 (1970).
6. M. Kryszewski, H. Kasica, J. Patora, and J. Piotrowski, J. Polym. Sci., Part C, No. 30, 243 (1970).
7. T. Takamatsu and E. Fukada, Polym. J., 1, 101 (1970).
8. A. C. Lilly, Jr., L. L. Stewart, and R. M. Henderson, J. Appl. Phys., 41, 2007 (1970).
9. J. van Turnhout, Polym. J., 2, 173 (1971).
10. M. Latour, J. Appl. Phys., 46, 42 (1975).
11. G. A. Lushcheikin, V. E. Gul, V. K. Shatalov, E. A. Tsoi, and I. G. Kuznetsova, Dokl. Akad. Nank SSSR, 225 (4), 801 (1975).
12. M. Latour and G. Donnet, Journal de Physique-Lettres, No. 6, 145 (1976).
13. C. R. Bohn, J. R. Schaefgen, and W. O. Statton, J. Polym. Sci., 55, 531 (1961).
14. W. O. Statton, J. Polym. Sci., 41, 153 (1959).
15. P. H. Lindenmeyer and R. Hosemann, J. Appl. Phys., 34, 42 (1963).
16. S. I. Stupp and S. H. Carr, J. Polym. Sci., Polym. Phys. Ed., 16, 13 (1978).
17. J. van Turnhout, Thermally Stimulated Discharge of Polymer Electrets, Elsevier Scientific, New York (1975).
18. E. Hinrichsen, J. Polym. Sci., Part C, 38, 303 (1972).
19. L. E. Wolfram, J. E. Grasselli, and J. L. Koenig, Appl. Polym. Symposia, No. 25, Ed. John Wiley & Sons, 1974.
20. R. J. Comstock, S. I. Stupp, and S. H. Carr, J. of Macromol. Sci.-Phys., B13(1), 101 (1977).

Table 1

X-RAY DATA

THERMOELECTRIC HISTORY	PEAK POSITIONS (2 θ)	D-SPACINGS ($\text{\AA}$)	$\frac{I_{2\theta=30^\circ}}{I_{2\theta=17^\circ}}^*$
As-Cast	$\sim 17^\circ$, $\sim 29^\circ$	~ 5.2 , ~ 3.1	0.088
Annealed 145°C , 0 Vcm^{-1}	17.1 , 17.5 ± 0.3 17.1° , 17.5 , $\sim 29^\circ$	5.2 , 5.0 , ~ 3.1	0.131
Polarized $T_p = 145^\circ\text{C}$ $E_p = 5 \times 10^4 \text{ Vcm}^{-1}$	16.8° , 17.2 ± 0.2 $\sim 29^\circ$	5.3 , 5.2 , 3.1	0.134
Polarized $T_p = 145^\circ\text{C}$ $E_p = 5 \times 10^5 \text{ Vcm}^{-1}$	17.5 , 18.0 ± 0.2 $\sim 30^\circ$	5.1 , 4.9 , 3.0	0.183

*Intensities were obtained by integrating the area under the peak and above its local "baseline".

FIGURE CAPTIONS

- Figure 1. X-ray diffractometer scans of PAN films in as-cast form, annealed at 145°C for 30 minutes, and exposed to an electrical field of $5 \times 10^4 \text{ Vcm}^{-1}$ at 145°C.
- Figure 2. X-ray diffractometer scans of PAN films electrically polarized at 145°C by low strength ($5 \times 10^4 \text{ Vcm}^{-1}$) and high-strength fields ($5 \times 10^5 \text{ Vcm}^{-1}$).
- Figure 3. Infrared absorption maxima corresponding to the nitrile stretching band for a) as-cast PAN films, b) films annealed at 145°C for 30 minutes, c) films electrically polarized by low-strength fields ($5 \times 10^4 \text{ Vcm}^{-1}$ at 145°C), and d) films polarized by high-strength fields ($5 \times 10^5 \text{ Vcm}^{-1}$ at 145°C).
- Figure 4. Nitrile absorption maxima from electrically polarized PAN films ($5 \times 10^5 \text{ Vcm}^{-1}$, 145°C), using polarized radiation: a) perpendicular, b) parallel.
- Figure 5. Stretching frequency of the nitrile group in solvent-cast PAN films as a function of temperature.

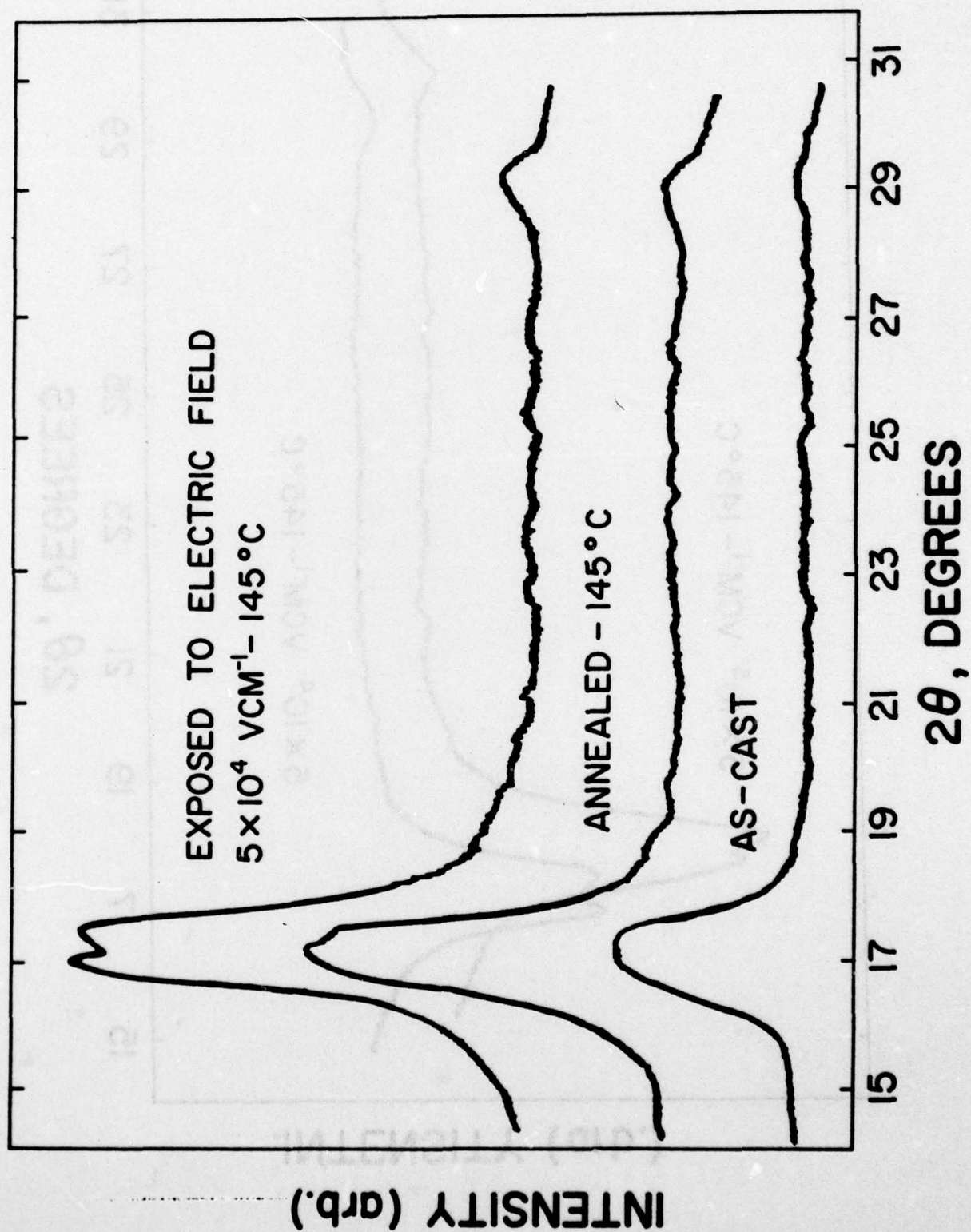


Figure 1.

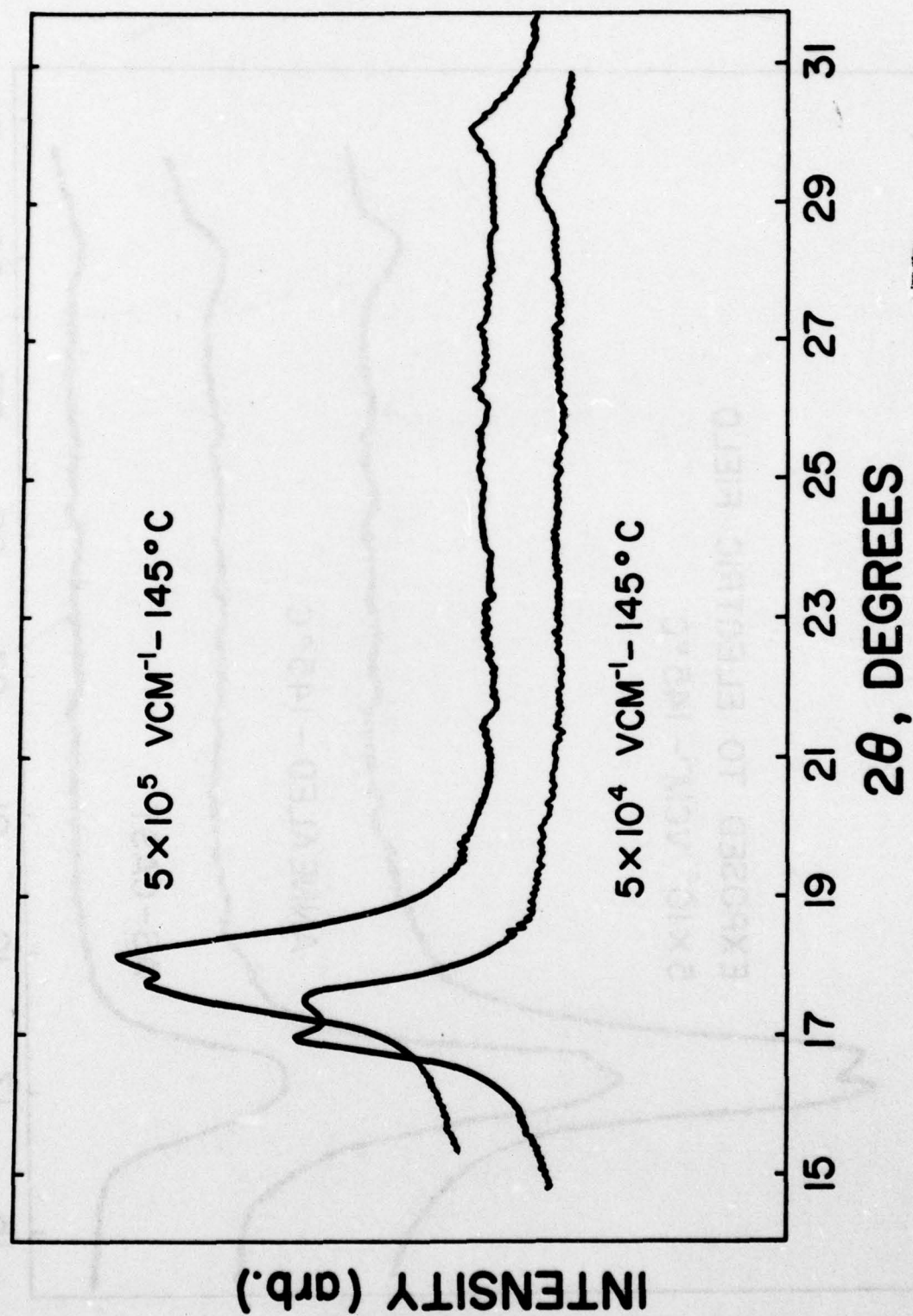


Figure 2.

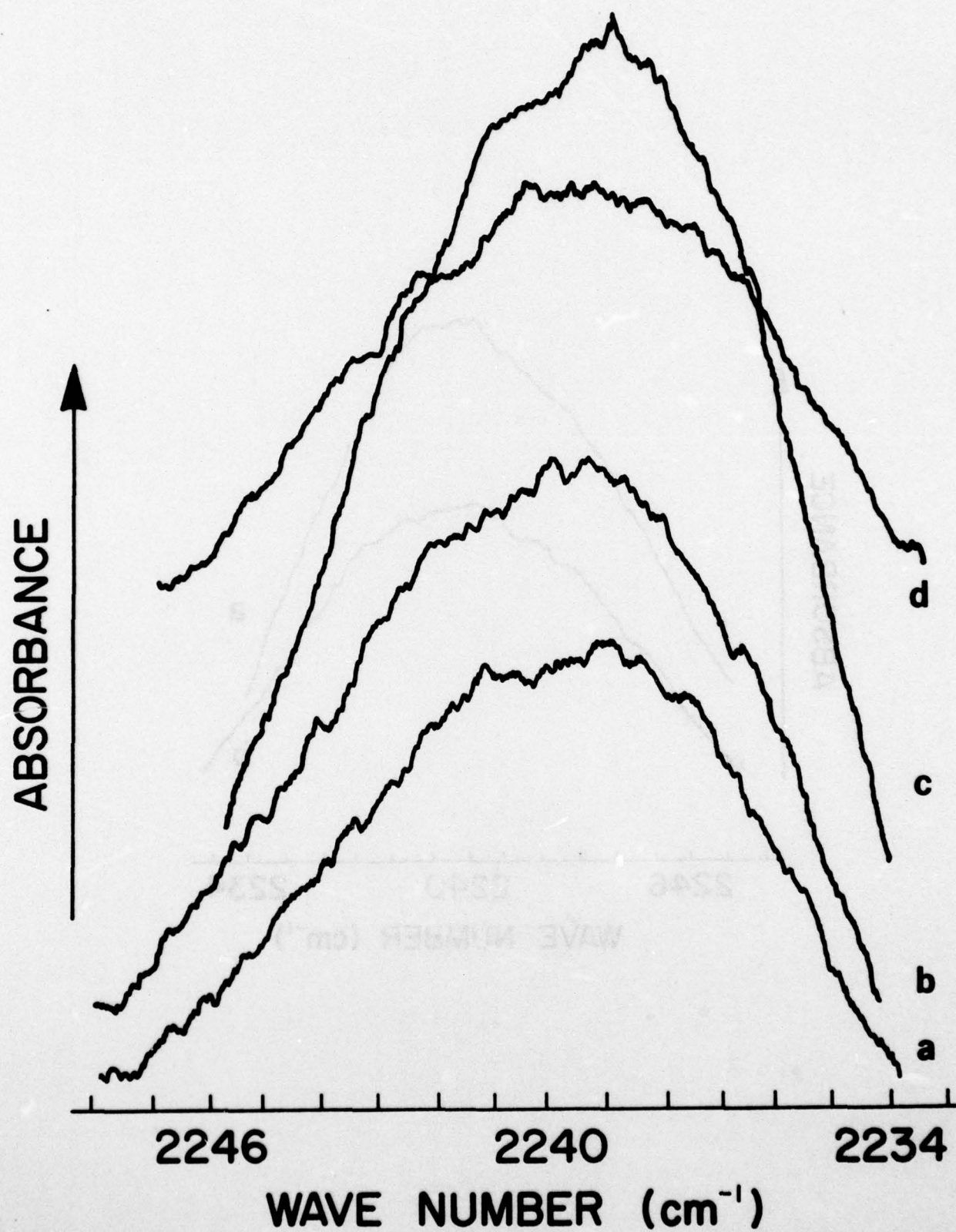


Figure 3.

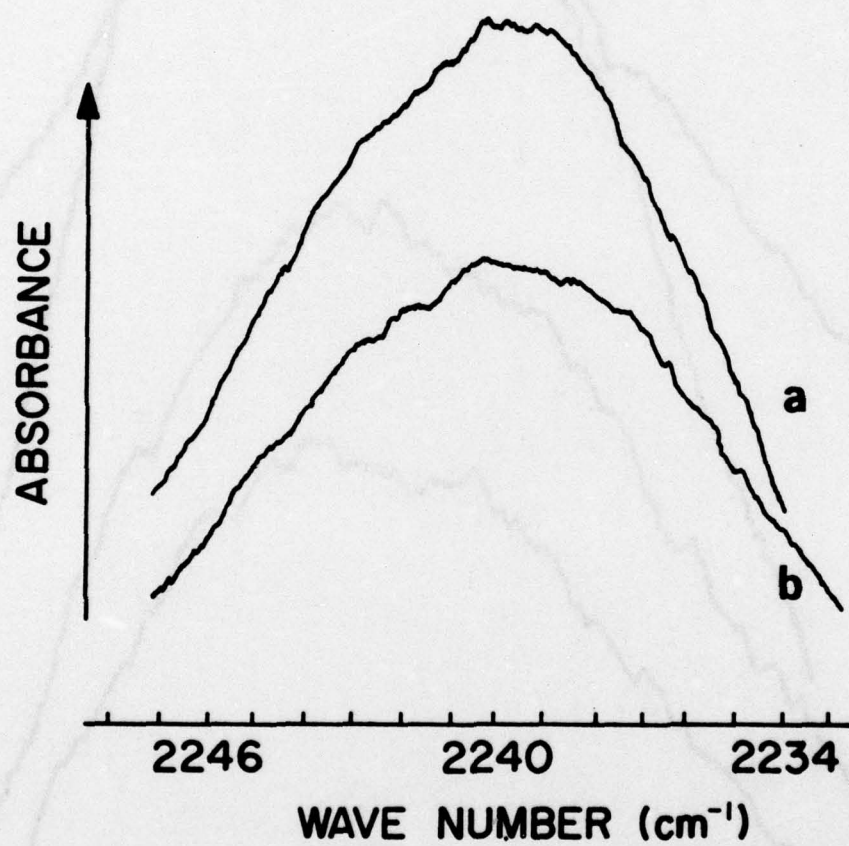


Figure 4.

Figure 5.

