

AD-A183 411

DR TSDC DSC TMA AND DMA STUDIES IN POLYMERS COMPLEXED
WITH INORGANIC SALT. (U) CASE WESTERN RESERVE UNIV
CLEVELAND OHIO DEPT OF PHYSICS J J FONTANELLA ET AL.
01 JUL 87 TR-28 N00014-87-AF-00001

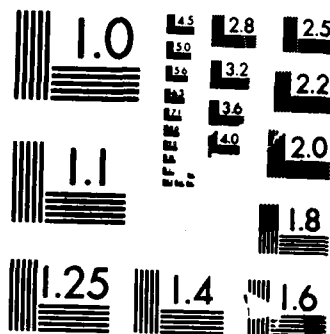
1/1

UNCLASSIFIED

F/G 7/4

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

DTIC FILE COPY

12

AD-A183 411

OFFICE OF NAVAL RESEARCH

Contract N00014-87-AF-00001

R&T Code 413d001—02

Technical Report No. 28

DR, TSDC, DSC, TMA, and DMA Studies in Polymers
Complexed with Inorganic Salts

by

John J. Fontanella & Mary C. Wintersgill

Prepared for Publication

in the

Proceedings of the 16th North American Thermal Analysis
Society Conference

U. S. Naval Academy
Department of Physics
Annapolis, MD 21402-5026

July 1, 1987

DTIC
ELECTE
JUL 27 1987
S D
E

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

* This document has been approved for public release
and sale; its distribution is unlimited

87 7 21 093

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT This document has been approved for public release and sale; its distribution is unlimited.	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 28		7a. NAME OF MONITORING ORGANIZATION	
6a. NAME OF PERFORMING ORGANIZATION U. S. Naval Academy	6b. OFFICE SYMBOL (If applicable)	7b. ADDRESS (City, State, and ZIP Code)	
6c. ADDRESS (City, State, and ZIP Code) Physics Department Annapolis, MD 21402-5026		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	10. SOURCE OF FUNDING NUMBERS	
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217-5000		PROGRAM ELEMENT NO. 61153N	PROJECT NO. RR013-06-OC TASK NO. 627-793 WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) DR, TSDC, DSC, TMA, and DMA Studies in Polymers Complexed with Inorganic Salts (Unclassified)			
12. PERSONAL AUTHOR(S) John J. Fontanella and Mary C. Wintersgill			
13a. TYPE OF REPORT Interim	13b. TIME COVERED FROM 86/10/1 TO 87/9/30	14. DATE OF REPORT (Year, Month, Day) 1987 July 1	15. PAGE COUNT 6
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Prepared for publication in the Proceedings of the 16th North American Thermal Analysis Society Conference	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) In the present note, the relationship between audio frequency dielectric relaxation (DR) and thermally stimulated depolarization current (TSDC) techniques is described. In addition, those methods are compared with differential scanning calorimetry (DSC), thermo-mechanical analysis (TMA) and dynamic mechanical analysis (DMA). The discussion will proceed using data taken on cast film samples of PAREL elastomer.			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL John J. Fontanella		22b. TELEPHONE (Include Area Code) 301-267-3487	22c. OFFICE SYMBOL

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

DR, TSDC, DSC, TMA, AND DMA STUDIES IN POLYMERS COMPLEXED WITH
INORGANIC SALTS

J. J. Fontanella, M. C. Wintersgill, J. P. Calame*
D. R. Figueroa#
C. G. Andeen+



*Physics Dept., U. S. Naval Academy, Annapolis, MD 21402
#Physics Dept., Simon Bolivar University, Caracas, Venezuela
/ +Physics Dept., Case Western Reserve Univ., Cleveland, OH 44106

In the present note, the relationship between audio frequency dielectric relaxation (DR) and thermally stimulated depolarization current (TSDC) techniques is described. In addition, those methods are compared with differential scanning calorimetry (DSC), thermo-mechanical analysis (TMA) and dynamic mechanical analysis (DMA). The discussion will proceed using data taken on cast film samples of PAREL¹ elastomer.

1. Dielectric Relaxation

Audio frequency DR studies at various temperatures were taken over the frequency range 10 to 100,000 Hz. The equipment used to make the measurements is the latest in a long series of capacitance bridges developed by one of the authors (CGA). Results from early versions of the apparatus appeared in the literature as early as 1970.² The key element of the present system is a CGA-83 capacitance bridge which is fully automated for measurements over the range 10 to 100,000 Hz. This bridge is more sensitive and accurate than any commercially available bridge. Electrodes are either sputtered or evaporated onto the samples in two- or three-terminal configurations, and the sample holder can accommodate eight samples simultaneously. The sample holder is then bolted to the cold finger of a Precision Cryogenics CT-14 dewar. The temperature is controlled by a Lake Shore Cryotronics DRC-82C temperature controller using a silicon diode temperature sensor. The overall system is controlled by an Apple II+ microcomputer.

The results of a typical data run are shown in Fig. 1a, in this case for a sample of uncomplexed PAREL. Data are normally

taken isothermally at seventeen frequencies in approximately equal logarithmic intervals, where the capacitance, C , and the conductance divided by the frequency, G/ω are measured. Values of the real part of the complex dielectric constant, $\epsilon^* = \epsilon' - j\epsilon''$, at 1000 Hz and room temperature are calculated from the usual expression for a perfect parallel plate capacitor:

$$\epsilon' = Cd/\epsilon_0 A \quad (1)$$

where A is the area of the plates, d is the sample thickness, and ϵ_0 is the permittivity of free space. Next, since thermal expansion coefficients were not measured, values of ϵ' at other temperatures and frequencies were calculated using the approximation that the relative shift in ϵ' is proportional to the relative shift in capacitance. Finally, values of ϵ'' are generated from:

$$\epsilon'' = \epsilon' G/\omega C \quad (2)$$

The results for PAREL elastomer using these procedures are shown in Figs. 1a and 1b. The strong alpha relaxation associated with the glass transition can be clearly seen. The 1000 Hz data have been shown previously.³ In fact in that paper, data at 1000 Hz are also shown for pressures up to 0.3 GPa (3kbar). The high pressure data allowed the shift in glass transition temperature with increase in pressure to be determined. Data are not usually analyzed in the variable temperature format although for some systems such techniques have been developed.⁴ It is more usual to analyze the data in terms of the frequency variation.⁵ This type of analysis shows that for PAREL the maximum of the loss peak, ω_p , varies with temperature according to the WLF⁶ or VTF⁷ equations:

$$\log_{10}(\omega_p) - 1.076 = 11.6(T-211)/(38.3+T-211) \quad (3)$$

$$\omega_p = 10^{12.68} \exp(-1023/(T-172.7)) \quad (4)$$

where T is in Kelvins and the WLF equation utilizes the "central" glass transition temperature of 211K.⁵ For the present purpose, these results are of interest as they relate to the TSDC as discussed in the next section.

2. Thermally Stimulated Depolarization Currents

The equipment used to carry out the TSDC studies has been described elsewhere.⁸ Briefly, the technique consists of placing a voltage across a sample, cooling it down and removing the voltage. The temperature is then increased and the current flowing through a large resistor connected across the sample is monitored. In the experiments discussed here, a linear heating rate is achieved using digital techniques. The results for a

typical TSDC run are shown in Fig. 1c. Two peaks are observed. The position of the higher temperature peak depends strongly on the polarization temperature and hence is attributed to space charge effects. This is to be expected as PAREL is relatively conductive, presumably due to ionic trace impurities. Further evidence of these impurities can be seen in the DR results, since the low frequency (10 Hz) values of ϵ'' rise rapidly at high temperatures. This reflects the electrical conductivity, σ , because:

$$\sigma = \epsilon_0 \epsilon'' \omega \quad (5)$$

In fact, related behavior is the motivation for studying PAREL, which is primarily poly(propylene oxide) (PPO), as it represents a prototype amorphous, ionic conductor or solid electrolyte. The authors have carried out several studies of PPO containing Li and Na salts^{3,9} and in one case have found a significant relationship between the DR and the ionic conductivity.⁵

The position of the lower temperature peak, at 206 K, is independent of the polarization temperature and corresponds to the α -relaxation. These results demonstrate that TSDC can be related to low frequency DR. Specifically, the position of a TSDC peak is about where a DR peak would be expected at low frequency. For the present case, the VTF or WLF equations predict that the 206 K DR peak would appear at a frequency of about 34 mHz. This is similar to the situation described for an ionic crystal.¹⁰

3. Thermal Analysis

The TSDC result is particularly important in the light of DSC, TMA and DMA studies, the data for which were obtained using Dupont 910, 943, and 982 cells which were controlled by Dupont 990 consoles which were interfaced with Apple II+ computers. Results for all four techniques are shown in Fig. 2. In each case, an event is seen in the vicinity of 206 K. This is not at all surprising since the heating rates in all four experiments are similar. In some experiments, the variety of thermal analysis techniques has proved invaluable. For example, in the presence of an extraneous thermal absorption in the DSC, perhaps due to water, the DMA or TMA will be usually be unaffected. Similarly, when the contribution to the DR signal from DC ionic conductivity masks the α -relaxation, in the case of ion containing materials for example, alternative techniques are essential to identify the glass transition temperature. These results, then, emphasize some of the relationships between low frequency DR and thermal analysis.

ACKNOWLEDGMENTS

The authors would like to thank Hercules, Inc. for providing the samples of PAREL. This work was supported in part by the Office of Naval Research.

REFERENCES

1. PAREL is a registered trademark of Hercules, Inc.
2. C. Andeen, J. Fontanella, and D. Schuele, Rev. Sci. Instr. 41, 1573 (1970).
3. J. J. Fontanella, M. C. Wintersgill, J. P. Calame, M. K. Smith, and C. G. Andeen, Solid St. Ionics 18&19, 253 (1986).
4. C. Andeen, D. Link, and J. Fontanella, Phys. Rev. 16, 3762 (1977).
5. J. J. Fontanella, M. C. Wintersgill, M. K. Smith, J. Semanick, and C. G. Andeen, J. Appl. Phys. 60, 2665 (1986).
6. H. Vogel, Phys. Z. 22, 645 (1921); V. G. Tammann and W. Hesse, Z. Anorg. Allg. Chem. 156, 245 (1926); G. S. Fulcher, J. Am. Ceram. Soc. 8, 339 (1925).
7. M. L. Williams, R. F. Landel, and J. D. Ferry, J. Am. Chem. Soc. 77, 3701 (1955).
8. J. P. Calame, J. J. Fontanella, M. C. Wintersgill, and C. G. Andeen, J. Appl. Phys. 58, 2811 (1985).
9. S. G. Greenbaum, Y. S. Pak, M. C. Wintersgill, J. J. Fontanella, J. W. Schultz, and C. G. Andeen, J. Electrochem. Soc., to be published.
10. D. R. Figueroa, M. C. Wintersgill, J. J. Fontanella, D. A. Beam, and C. G. Andeen, Cryst. Latt. Defects and Amor. Mat., to be published.

Figure 1. Real (a) and imaginary (b) parts of the dielectric constant at five frequencies (features from left to right): 10 Hz-short dashed lines; 100 Hz-long dashed lines; 1000 Hz-solid lines; 10,000 Hz-dot dash (chain) lines; 100,000 Hz-dotted lines. Straight line segments connect the datum points. Curve (c) is a TSDC spectrum. A voltage of 200 V was applied to the sample for 15 min at a polarization temperature of 190K and the heating rate was 6 K/min.

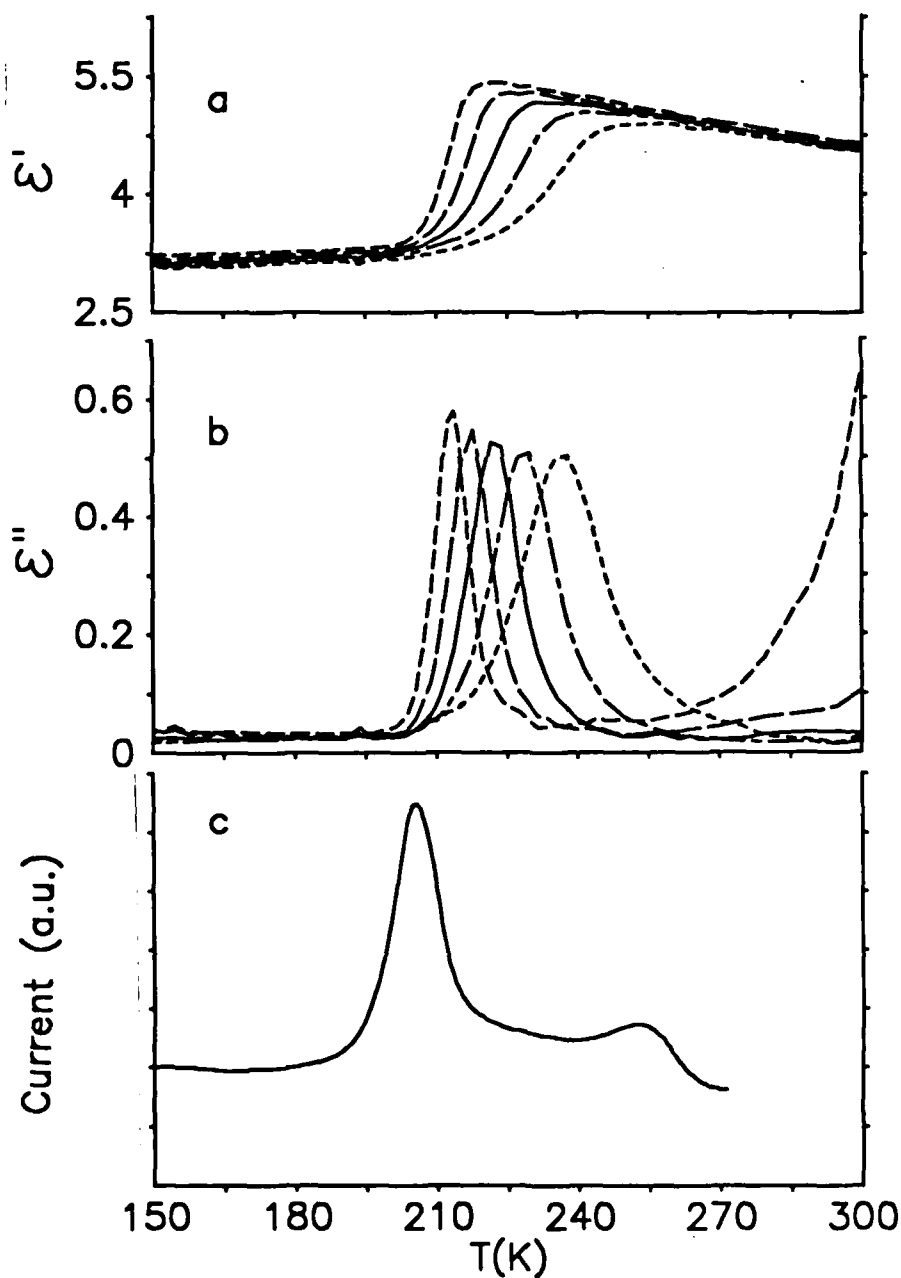
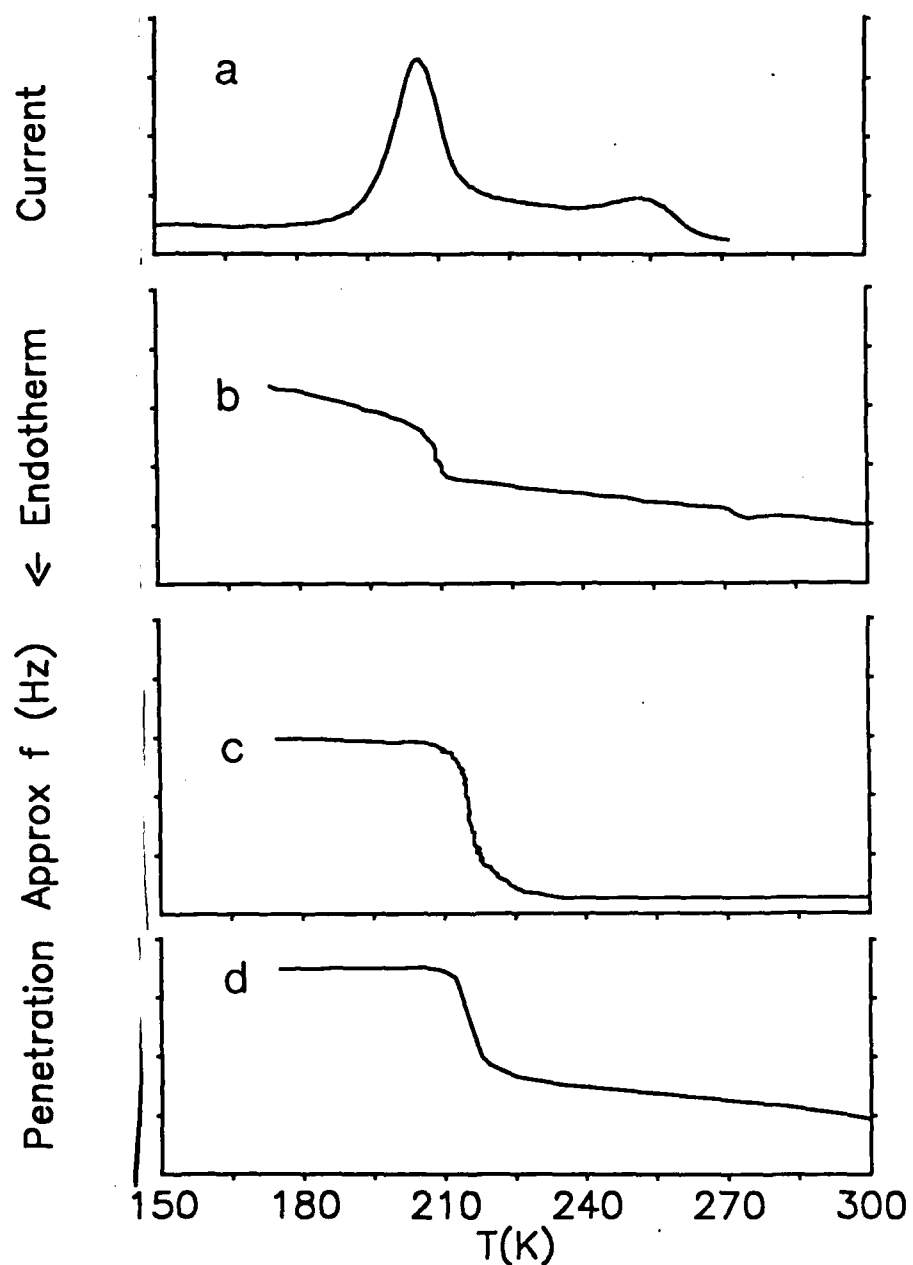


Figure 2. (a) TSDC spectrum from Fig. 1c. (b) DSC thermogram. The heating rate was 10 K/min. (c) DMA results. The heating rate was 5 K/min. (d) TMA penetration results. The heating rate was 5 K/min.



TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Stanislaw Szpak
Naval Ocean Systems Center
Code 633, Bayside
San Diego, California 95152

Dr. Gregory Farrington
Department of Materials Science
and Engineering
University of Pennsylvania
Philadelphia, Pennsylvania 19104

~~Dr. John Fontanella
Department of Physics
U.S. Naval Academy
Annapolis, Maryland 21402-5062~~

Dr. Micha Tomkiewicz
Department of Physics
Brooklyn College
Brooklyn, New York 11210

Dr. Lesser Blum
Department of Physics
University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Dr. Joseph Gordon, II
IBM Corporation
5600 Cottle Road
San Jose, California 95193

Dr. Joel Harris
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Dr. J. O. Thomas
University of Uppsala
Institute of Chemistry
Box 531 Baltimore, Maryland 21218
S-751 21 Uppsala, Sweden

Dr. John Owen
Department of Chemistry and
Applied Chemistry
University of Salford
Salford M5 4WT UNITED KINGDOM

Dr. O. Staffsudd
Department of Electrical Engineering
University of California
Los Angeles, California 90024

Dr. Boone Owens
Department of Chemical Engineering
and Materials Science
University of Minnesota
Minneapolis, Minnesota 55455

Dr. Johann A. Joebstl
USA Mobility Equipment R&D Command
DRDME-EC
Fort Belvoir, Virginia 22060

Dr. Albert R. Landgrebe
U.S. Department of Energy
M.S. 6B025 Forrestal Building
Washington, D.C. 20595

Dr. J. J. Brophy
Department of Physics
University of Utah
Salt Lake City, Utah 84112

Dr. Charles Martin
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dr. Milos Novotny
Department of Chemistry
Indiana University
Bloomington, Indiana 47405

Dr. Mark A. McHugh
Department of Chemical Engineering
The Johns Hopkins University
Baltimore, Maryland 21218

Dr. D. E. Irish
Department of Chemistry
University of Waterloo
Waterloo, Ontario, Canada
N2L 3G1

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton SO9 5H UNITED KINGDOM

Dr. John Wilkes
Department of the Air Force
United States Air Force Academy
Colorado Springs, Colorado 80840-6528

Dr. R. A. Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. Janet Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. A. J. Bard
Department of Chemistry
University of Texas
Austin, Texas 78712

Dr. Steven Greenbaum
Department of Physics and Astronomy
Hunter College
695 Park Avenue
New York, New York 10021

Dr. Donald Sandstrom
Boeing Aerospace Co.
P.O. Box 3999
Seattle, Washington 98124

Mr. James R. Moden
Naval Underwater Systems Center
Code 3632
Newport, Rhode Island 02840

Dr. D. Rolison
Naval Research Laboratory
Code 6171
Washington, D.C. 20375-5000

Dr. D. F. Shriver
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Dr. Alan Bewick
Department of Chemistry
The University of Southampton
Southampton, SO9 5NH UNITED KINGDOM

Dr. Edward Fletcher
Department of Mechanical Engineering
University of Minnesota
Minneapolis, Minnesota 55455

Dr. Bruce Dunn
Department of Engineering &
Applied Science
University of California
Los Angeles, California 90024

Dr. Elton Cairns
Energy & Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Dr. Richard Pollard
Department of Chemical Engineering
University of Houston
Houston, Texas 77004

Dr. M. Philpott
IBM Research Division
Mail Stop K 33/801
San Jose, California 95130-6099

Dr. Martha Greenblatt
Department of Chemistry, P.O. Box 939
Rutgers University
Piscataway, New Jersey 08855-0939

Dr. Anthony Sammells
Eltron Research Inc.
4260 Westbrook Drive, Suite 111
Aurora, Illinois 60505

Dr. C. A. Angell
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. Thomas Davis
Polymers Division
National Bureau of Standards
Gaithersburg, Maryland 20899

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Manfred Breiter
Institut für Technische Elektrochemie
Technischen Universität Wien
9 Getreidemarkt, 1160 Wien
AUSTRIA

Dr. E. Yeager
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

Dr. R. Sutula
The Electrochemistry Branch
Naval Surface Weapons Center
Silver Spring, Maryland 20910

Dr. R. A. Marcus
Department of Chemistry
California Institute of Technology
Pasadena, California 91125

Dr. J. J. Auborn
AT&T Bell Laboratories
600 Mountain Avenue
Murray Hill, New Jersey 07974

Dr. M. S. Wrighton
Chemistry Department
Massachusetts Institute
of Technology
Cambridge, Massachusetts 02139

Dr. B. Stanley Pons
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Dr. Bernard Spielvogel
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709

Dr. Mel Miles
Code 3852
Naval Weapons Center
China Lake, California 93555

Dr. P. P. Schmidt
Department of Chemistry
Oakland University
Rochester, Michigan 48063

Dr. Roger Belt
Litton Industries Inc.
Airtron Division
Morris Plains, NJ 07950

Dr. Ulrich Stimming
Department of Chemical Engineering
Columbia University
New York, NY 10027

Dr. Royce W. Murray
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Dr. Michael J. Weaver
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. R. David Rauh
EIC Laboratories, Inc.
Norwood, Massachusetts 02062

Dr. Edward M. Eyring
Department of Chemistry
University of Utah
Salt Lake City, UT 84112

Dr. M. M. Nicholson
Electronics Research Center
Rockwell International
3370 Miraloma Avenue
Anaheim, California

Dr. Nathan Lewis
Department of Chemistry
Stanford University
Stanford, California 94305

Dr. Hector D. Abruna
Department of Chemistry
Cornell University
Ithaca, New York 14853

Dr. A. B. P. Lever
Chemistry Department
York University
Downsview, Ontario M3J 1P3

ABSTRACTS DISTRIBUTION LIST, 359/627

Dr. Henry S. White
Department of Chemical Engineering
and Materials Science
151 Amundson Hall
421 Washington Avenue, S.E.
Minneapolis, Minnesota 55455

Dr. Daniel A. Buttry
Department of Chemistry
University of Wyoming
Laramie, Wyoming 82071

Dr. W. R. Fawcett
Department of Chemistry
University of California
Davis, California 95616

Dr. Peter M. Blonsky
Eveready Battery Company, Inc.
25225 Detroit Road, P.O. Box 45035
Westlake, Ohio 44145

END

9-87

Dtic