PL-TR-92-3018

PL-TR--
92-3018

(2)

PROCEEDINGS OF THE FIRST ANNUAL ADVANCED POLYMER COMPONENTS SYMPOSIUM

John J. Rusek

PHILLIPS LABORATORY
RKCP
EDWARDS AFB, CALIFORNIA CA 93523-5000

July 1992

Interim Report

PHILLIPS LABORATORY
Propulsion Directorate
AIR FORCE SYSTEMS COMMAND
EDWARDS AIR FORCE BASE CA 93523-5000

NOTICE

When U.S. Government drawings, specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise, or in any way licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may be related thereto.

FOREWORD

This Interim Report was submitted on completion of the First Annual Advanced Polymer Components Symposium, Febuary 20–22, 1992, by the OLAC -PL/RKCP Branch at the Phillips Laboratory (AFSC), Edwards AFB, CA 93523–50. Project Manager for OLAC Phillips Laboratory was Dr John J. Rusek.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the SF Form 298.

JOHN J. RUSEK
Project Manager

BERGE GOSHGARIAN
Chief, Propellants Branch

WAYNE L. PRITZ
Director
Components Engineering Division

RANNEY G. ADAMS
Public Affairs Director

Accesion For	
NTIS CRA&I	☑
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution /	
Availability	
Dist	Avail and / or Special
A-1	

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	JULY 1992	Interim 21 April 1992

4. TITLE AND SUBTITLE
Proceedings of The First Annual Advanced Polymer Components Symposium

5. FUNDING NUMBERS
PE: 62302F
PR: 5730
TA: 00R9

6. AUTHOR(S)
DR. John Joseph Rusek

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Phillips Laboratory
PL/RKCP
EDWARDS AFB, CA 93523-5000

8. PERFORMING ORGANIZATION REPORT NUMBER
PL-TR-92-3018

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Phillips Laboratory
OLAC-PL/RKCP
Edwards AFB, CA 93523-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
PL-TR-92-3018

11. SUPPLEMENTARY NOTES
COSATI CODES: 21/06; 21/08/01; 21/09/01; 21/08/02; 21/09/02; 07/05; 07/06

12a. DISTRIBUTION/AVAILABILITY STATEMENT
"Approved for Public Release; Distribution is Unlimited"

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Advanced propulsion concepts rely on advanced propulsion materials. The Phillips Laboratory is aggressively pursuing advanced polymeric materials for use in Solid, Liquid, and Nuclear propulsion component applications. Traditional composite materials have high specific strengths, but suffer from high cost and labor intensive processing. The APC program is currently exploring thermotropic liquid crystal polymers. These materials have high specific strength and can be economically processed by traditional high volume routes such as injection molding and blow molding. Applications envisioned for these materials include rocket nozzles, pressure cases, propellant tanks and conduits, nuclear propulsion containment fairings, high pressure tanks and orbit-processed habitats for interplanetary voyages. These proceedings deal with an overview of liquid crystal polymer technology and current art, test article demonstrations and in-depth discussions of the so-called annealing phenomena.

14. SUBJECT TERMS
Liquid Crystal Polymers Liquid Propulsion Synchrotron Radiation
Advanced Materials Solid Propulsion Neutron Scattering
Thermotropic Polyester Nuclear Propulsion Molecular Mechanics

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	SAR

CONTENTS

PREFACE

The Advanced Polymer Components Initiative began in December of 1989. The initial purpose of the program was to explore advanced engineering polymers for use in propulsive applications. Three main objectives were established: apply commercially available materials to solid propulsion needs, apply these materials to liquid propulsion needs and establish a design capability for the new processing techniques envisioned to produce parts. Thermotropic liquid crystal polymers such as VECTRA, XYDAR and others were identified as having the most promise for surviving the rigors identified with space propulsion applications. Within the first few months of the program, it became apparent that these new materials needed significantly more research before final part fabrication could be accomplished.

A team of over two dozen researchers was assembled to attack the fundamental questions raised. The researchers were chosen from government, academia and industry, both nationally and internationally, to focus on specific research areas to quickly enable the Air Force to use these novel materials.

After two years of research, the First Annual Advanced Polymer Components Symposium was held. This initial meeting was conducted at Butler University in Indianapolis, Indiana from February 20-22, 1992. Twenty-four researchers and Air Force users were in attendance from accross the country. This document is the result of that meeting.

In addition to the executive summary and task plan, this report contains the abstracts and content of the twenty-two research papers and Air Force user input. The intent of the report is to indicate the status of Air Force propulsion research using thermotropic liquid crystal polymers. It is anticipated that a second symposium will be held the spring of next year.

The United States Air Force is indebted to all of the participants on this critical program for their goodwill and dedication to this effort.

John J. Rusek
Program Manager
Advanced Polymer Components
Initiative

APC SYMPOSIUM
PRESENTER LIST

Ms Rebecca Ai
Materials Science Department
Northwestern University
Evanston IL 60208
T(708)491-3996
F(708)491-7820

Dr Kevin P. Chaffee
OLAC PL/RKCP
Edwards AFB CA 93523
T(805)275-5740
F(805)275-5144

Mr Tom A. Elkins
OLAC PL/RKAD
Edwards AFB CA 93523
T(805)275-5303
F(805)275-5144

Mr L. Jackson Etheridge
Organic Technologies
Columbus, OH 43220
T(614)459-5000
F(614)459-4372

Mr Chris Frank
SM AL/TIEC
McClellan AFB CA 95652
T(916)643-3810
F(916)643-6800

Mr Terry Fuchser
Mercer University
Engineering Research Center
Warner Robbins, GA 31093
T(912) 929-6400
F(912)929-6406

Cpt Steve Hardy
OO-ALC/TIELM
Hill AFB UT 84056
T(801)777-2874
F(801)777-8049

Prof Dick Hoffman
Physics Department
Case Western Reserve University
Cleveland OH 44106
T(216)368-4012
F(216)368-4671

Mr Paul Jones
OLAC PL/RKFC
Edwards AFB CA 93523
T(805)275-5315
F(805)275-5144

Dr Jordin Kare
L-278 PO Box 808
LLNL
Livermore CA 94550
T(510)423-8300
F(510)423-9178

Prof David Kranbuehl
Chemistry Department
College of William and Mary
Williamsburg VA 23185
T(804)221-2542
F(804)221-1021

Prof Shannon Lieb
Chemistry Department
Butler University
Indianapolis IN 46208
T(317)283-9410
F(317)283-9519

Mr Kevin E. Mahaffy
OLAC PL/RKCC
Edwards AFB CA 93523
T(805)275-5629
F(805)275-5144

Prof J. Mann
Chemical Engineering Department
Case Western Reserve University
Cleveland OH 44106
T(216)368-4150
F(216)368-3016

Prof Laurence Marks
Materials Science Department
Northwestern University
Evanston IL 60208
T(708)491-3996
F(708)491-7820

Mr Hieu Nguyen
OLAC PL/RKCC
Edwards AFB CA 93523
T(805)275-5629
F(805)275-5144

Prof Phil Oldham
Chemistry Department
Mississippi State University
Mississippi State MS 39762
T(601)325-3584
F(601)325-7807

Mr Stephen Osborn
OLAC PL/RKCP
Edwards AFB CA 93523
T(805)275-5741
F(805)275-5144

Prof Tony Palazotto
Astronautics Department
Air Force Institute of Technology
Wright-Patterson AFB OH 45433
T(513)255-2998
F(513)476-4055

Dr John J. Rusek
OLAC PL/RKCP
Edwards AFB CA 93523
T(805)275-5407
F(805)275-5144

Mr Daniel F. Schwartz
OLAC PL/RKCP
Edwards AFB, CA 93523
T(805) 275-5183
F(805) 275-5144

Ms J. Shelley
OLAC PL/RKCC
Edwards AFB CA 93523
T(805)275-5394
F(805)275-5144

1Lt Dave Silver
OLAC PL/RKFC
Edwards AFB CA 93523
T(805)275-5410
F(805)275-5144

Dr E.J. Wucherer
OLAC PL/RKFC
Edwards AFB CA 93523
T(805)275-5759
F(805)275-5144

ADVANCED POLYMER COMPONENTS RESEARCH SYMPOSIUM SCHEDULE

19FEB

1800-2000 Check In

20FEB

0800-0830 APC Overview- J. Rusek
0830-0900 Polymer Synthesis- J. Rusek
0900-0930 Polymer Analysis- K. Chaffee
0930-1000 Molecular Mechanics- S. Lieb
1000-1030 Break
1030-1100 Atomic Force Microscopy- D. Silver
1100-1130 Surface Spectroscopy- J. Mann
1130-1200 Synchrotron Studies- R. Hoffman
1200-1300 Lunch
1300-1330 Reflectance Spectroscopy- P. Oldham
1330-1400 Micromechanics- A. Palazotto
1400-1430 Dielectric Spectroscopy- D. Kranbuehl
1430-1500 Rheology- D. Schwartz
1500-1530 Materials Database- T. Elkins
1530-1600 Break
1600-1630 Macroscopic Analysis- J. Shelley
1630-1700 Thermal Analysis- P. Jones
1700-1730 X-ray/Neutron Reduction- S. Osborn
1730-1800 TEM of Advanced Polymers- L. Marks

21FEB

0800-0830 Mold Design- T. Elkins
0830-0900 Part Design- C. Frank
0900-0930 Injection Molding- R. Griffin
0930-1000 Process Research- N. Schott
1000-1030 Break
1030-1100 Low Temp CVD- E. Wucherer
1100-1130 2x4 Motor- H. Nguyen
1130-1200 Subscale Flight Demonstrator- A. Kenny
1200-1230 Laser Earth to Orbit Vessel- J. Kare
1230-1330 Lunch
1330-1800 Polymer Characterization Discussion

22FEB

0800-1200 Polymer Processing Discussion
1200-1300 Lunch
1300-1800 Polymer Applications/Future Research

EXECUTIVE SUMMARY

The advent of advanced composite materials based on graphite and KEVLAR fibers has shown production articles with very high specific strength and modulus values. The main drawback to these articles are their cost and labor intensive processing. Thermal processing of plastics yields inexpensive parts, but at a significant lowering of performance, in most cases. Thermotropic liquid crystal polymers exhibit ordered behavior in the liquid state; this order can be frozen into the structure of the part thus yielding a "molecular composite" where processing becomes the determinant of the ultimate part strength.

The Advanced Polymer Components Initiative was begun over two years ago to study these advanced materials. Initially, commercial resins were injection molded into test articles for evaluation at the Phillips Laboratory. One anomaly was noted as soon as articles were produced; the properties of the skin of the part were far different from the core region. Sectioned specimens were analyzed and found to be different not only in strength, but chemical and thermal properties as well;most polymers exhibit this, but not to this degree. Chemical compatability with monomethylhydrazine is enhanced dramatically in the skin region.

A second observation is the so-called annealing phenomenon. A part derived from certain resins can be heat treated below the melt transition to yield enhanced solvent resistance and a dramatic increase in the melt temperature. This phenomena could potentially yield rocket nozzles with low erosion, propellant tanks and conduits for use in liquid rockets and moderators and working fluid containment for advanced propulsion scenarios.

On 20-23 February 1992, Phillips Laboratory researchers attended the first national meeting in support of the Advanced Polymer Components Initiative. The purpose of the meeting was to provide an open forum where all researchers and potential users could address issues concerning the use of thermotropic liquid crystal polymers as structural materials for Air Force propulsion applications. The main topics of discussion were fundamental properties, material processing (part design and fabrication), applications and planning.

The symposium was attended by twenty-three engineers and scientists representing three Air Force installations, seven universities, two corporations and one national laboratory. The results or progress reports for each APC task were presented by the task managers. The discussions were logically directed towards understanding how the raw materials fundamental properties affect processability and how the processing techniques in turn determine the mechanical, thermal and chemical properties of the finished product.

The rheological and thermal degradation characteristics of the commercially available polymers are sufficiently understood

to permit test sample production by injection molding. However, the synthesis procedures employed by the manufacturers appear to yield polymer resins with variable impurity content. The polydispersity and the block distribution of the copolymers are also unknown. It is thus difficult to adjust the injection molding parameters to optimize the part properties in a consistant fashion. This fact was made quite evident by the scatter of the measured mechanical properties of injection molded test specimens. One area decided to be of key import is the synthesis of well characterized model polymers.

Like most polymeric materials, the properties of these molecular composites depend upon the specific mechanical and thermal history. Where this is most evident is in the creation of the annealed polymer. The formation and structure of the annealed regions are not well understood. This phenomena is the key to potential applicability of these materials as structural materials and therefore the area where most of the fundamental research in the future will be directed.

Comments elicited after the symposium from all attendees were highly positive. The brainstorming sessions yielded a plethora of new approaches. It is anticipated that a second symposium will be held in the spring of 1993 to continue the communication on this critical research effort.

ADVANCED POLYMER COMPONENTS PROGRAM TASKING

FUNDAMENTAL CONTRACT TASKS

TASK #1 MOLECULAR MECHANICS
S.LIEB, Butler University

Analyze intramolecular minimum energy configurations for model rigid rod polymers. Resolve intermolecular forces thought to occur during polymer annealing.

TASK #2 SURFACE SPECTROSCOPY
J. MANN, Case Western Reserve University

Analyze polymer surfaces using ellipsometric FTIR and Raman spectroscopy to deduce orientation effects in the annealing process. Analyze surface structure of annealed polymers by x-ray reflectivity.

TASK #3 REFLECTANCE SPECTROSCOPY
P. OLDHAM, Mississippi State University

Analyze polymer/solution interfaces by means of the total internal reflection fluorescence phenomena. Understand solvolysis of ordered polymers.

TASK #4 MICROMECHANICS
A. PALAZOTTO, Air Force Institute of Technology

Obtain mechanical property information in the gauge between molecular and macroscopic size domains. Correlate microscopic phenomena to molecular theory and macroscopic results obtained in allied tasks.

TASK #5 DIELECTRIC SPECTROSCOPY
D. KRANBUEHL, College of William and Mary

Determine the macroscopic states, phase transition temperatures and molecular/morphological structure of liquid crystal polymers using dielectric spectroscopy and thermal analysis techniques.

TASK #6 PROCESS RESEARCH
N. SCHOTT, University of Lowell

Obtain commercial resins, mold test specimens as a function of process parameters and perform mechanical testing to directly correlate macroscopic properties to polymer rheology. Explore alternate processing techniques.

FUNDAMENTAL IN-HOUSE TASKS

TASK #7 POLYMER SYNTHESIS
J. RUSEK
K. CHAFFEE

Synthesize model liquid crystal polymers with varying pendant groups in support of the annealing research tasks. Characterize these compounds by LALLS, FTIR, NMR and VPO.

TASK #8 POLYMER X-RAY ANALYSIS
J. RUSEK
K. CHAFFEE
S. OSBORN

Analyze near surface annealing phenomena via low angle x-ray diffraction, high-Z substituent EXAFS and kinetic studies by QEXAFS in full collaboration with researchers at DESY.

TASK #9 POLYMER NEUTRON ANALYSIS
J. RUSEK
K. CHAFFEE
S. OSBORN

Explore the annealed state as a function of depth on as-processed and deuterated polymer samples; study the kinetics of the annealing phenomena in the liquid state in full collaboration with researchers at ANSTO.

TASK #10 ATOMIC FORCE MICROSCOPY
D. SILVER

Observe equilibrium polymer configuration at the atomic level. Correlate polymer morphology with annealing phenomena and support the polymer processing studies.

TASK #11 CHEMICAL VAPOR DEPOSITION
E. WUCHERER

Determine the feasability of low temperature CVD processes to coat advanced polymers with aluminum, nickel and potentially rhenium. Understand mechanisms of adhesion as related to the CVD process.

TASK #12 RHEOLOGY
D. SCHWARTZ

Ascertain appropriate processing conditions for injection molding of liquid crystal polymers by means of mechanical as well as dielectric spectroscopy. Observe and predict cooling anomalies germane to the annealing phenomena.

TASK #13 MACROSCOPIC ANALYSIS
J. SHELLEY
P. JONES
C. FRANK, McClellan AFB

Determine the engineering properties of liquid crystal polymers by mechanical and thermal testing. Assess the sensitivity of these polymers to design variables and gauge their strength efficiencies.

TASK #14 MATERIALS DATABASE
T. ELKINS

Construct a dynamic data storage and retrieval system for mechanical, chemical, thermal, electrical and environmental properties. Specific emphasis is placed on neat resin properties, both as-molded and annealed.

APPLICATION AREA TASKS

TASK #15 INJECTION MOLDING
C. FRANK, McClellan AFB
S. HARDY, Hill AFB
R. GRIFFIN, Hill AFB

Design and fabricate tooling to produce injection molds in support of all phases of the APC program. Injection-mold test articles and final flight products for all allied tasks.

TASK #16 STATIC 2X4 DEMONSTRATOR
H. NGUYEN
C. FRANK, McClellan AFB
R. GRIFFIN, Hill AFB

Study the pressure and ablation effects of liquid crystal polymers by means of the standardized 2X4 test fixture. Quantify the heat transfer properties of the polymers by precise thermal measurements through the case. Results will point to useage of the LCP's as solid rocket motor cases and large launch igniters.

TASK #17 SUBSCALE FLIGHT DEMONSTRATOR
H. NGUYEN
C. FRANK, McClellan AFB
R. GRIFFIN, Hill AFB

Design and fabricate nominal 100 # thrust boosters incorporating total polymer case and nozzle closures. Nozzle assemblies are CVDed to reduce erosion; boosters will be launched at Colorado Springs CO. Results will assess flight-weight useage.

TASK #18 BLOW-MOLDING
J. SHELLEY
J. RUSEK
C. FRANK, McClellan AFB
H. COX, General Motors Research
I. ABU-ISA, General Motors Research

Assess the feasability of thermotropic LCP's as blow-molding resins to impart biaxial orientation to cast pressure vessels. Test these vessels to failure with defined liquid propellants. Results will show potential as OTV high pressure tanks, Mars mission shrouds and LLV propellant tanks.

TASK #19 LASER EARTH TO ORBIT DEMONSTRATOR
J. KARE, Lawrence Livermore National Laboratories
J. RUSEK
J. SHELLEY
C. FRANK, McClellan AFB

Design and produce a biaxially oriented 2-liter hydrogen storage vessel using blow-molding technology and commercial LCP's. Launch test vehicle at Kirtland AFB using MW-class chemical lasers. Results will point to useage in the storage of liquid hydrogen and tethered flight operations.

TASK #20 NUCLEAR PROPULSION

J. SHELLEY
J. RUSEK
K. CHAFFEE
C. FRANK, McClellan AFB

Assess the feasability of LCP's as candidate materials for nuclear propulsion. Thermal properties will be measured using laser thermal analysis techniques. Results will point to containment for nuclear propulsion applications.

GLOSSARY

AFM-Atomic Force Microscopy
ANSTO-Australian Nuclear Science and Technology Organisation
AP-Ammonium Perchlorate
APC-Advanced Polymer Components
ASTM-American Society for Testing of Materials
CHQ-Chlorohydroquinone
CVD-Chemical Vapor Deposition
DBMS-Database Management System
DESY-Deutsches Elektronen-Synchrotron
DMA-Dynamic Mechanical Analyzer
DSC-Differential Scanning Calorimetry
EDC-Ethylene Dichloride
EXAFS-Extended X-ray Absorption Fine Structure
FDEMS-Frequency Dependent Electromagnetic Sensing
FEA-Finite Element Analysis
FTIR-Fourier Transformed Infrared Spectroscopy
IDEAS-Integrated Design Engineering Analysis Software
IR-Infrared
LALLS-Low Angle Laser Light Scattering
LB-Langmuir-Blodgett Film
LCP-Liquid Crystal Polymer
LH2-Liquid Hydrogen
LN2-Liquid Nitrogen
LTA-Laser Thermal Analyzer
Me-Methyl
MHQ-Methylhydroquinone
MMH-Monomethylhydrazine
NEMESIS-New Eng. Materials Eval./Surface & Interface Studies
NMR-Nuclear Magnetic Resonance Spectroscopy
NTO-Nitrogen Tetroxide
ODE-Ordinary Differential Equations
OTV-Orbit Transfer Vehicle
PAS-Photoacoustic Spectroscopy
PBO-Polybenzoxamide
PBZT-Polybenzthiazole
PEHQ-2(1-Phenylethyl)hydroquinone
Ph-Phenyl
PhEt-Phenylethyl
PHQ-Phenylhydroquinone
PMT-Photomultiplier Tube
QEXAFS-Quick Acquisition EXAFS
RDA-Rheometrics Dynamic Analyzer
RF-Radio Frequency
SDRC-Structural Dynamics Research Corporation
TA-Terephthalic Acid
TEM-Transmission Electron Microscopy
TIRF-Total Internal Reflection Fluorescence
TMA-Thermal Mechanical Analyzer
UV-Ultraviolet
VATIRF-Variable Angle TIRF Analysis
VPO-Vapor Phase Osmometry
XAFS-X-ray Absorption Fine Structure
XANES-X-ray Absorption Near Edge Structure
XRD-X-ray Diffraction

APC OVERVIEW

J.J. Rusek
OLAC PL/RKCP
Edwards AFB CA 93523

Advanced propulsion concepts rely on advanced propulsion materials. The Phillips Laboratory is aggressively pursuing advanced polymeric materials for use in solid, liquid and nuclear propulsion component applications. Traditional composite materials have high specific stengths, but suffer from high cost and labor intensive processing. The APC program is currently exploring thermotropic liquid crystal polymers. These materials have high specific strength and can be economically processed by traditional high volume routes such as injection molding and blow molding. Applications envisioned for these materials include rocket nozzles, pressure cases, propellant tanks and conduits, nuclear propulsion containments, fairings, high pressure tanks and orbit-processed habitats for interplanetary voyages.

This paper will deal with an overview of liquid crystal polymer technology and current art, test article demonstration and an introduction to the so-called annealing phenomena. Finally, next-generation space applications will be discussed germane to the Space Exploration Initiative.

ADVANCED POLYMER COMPONENTS

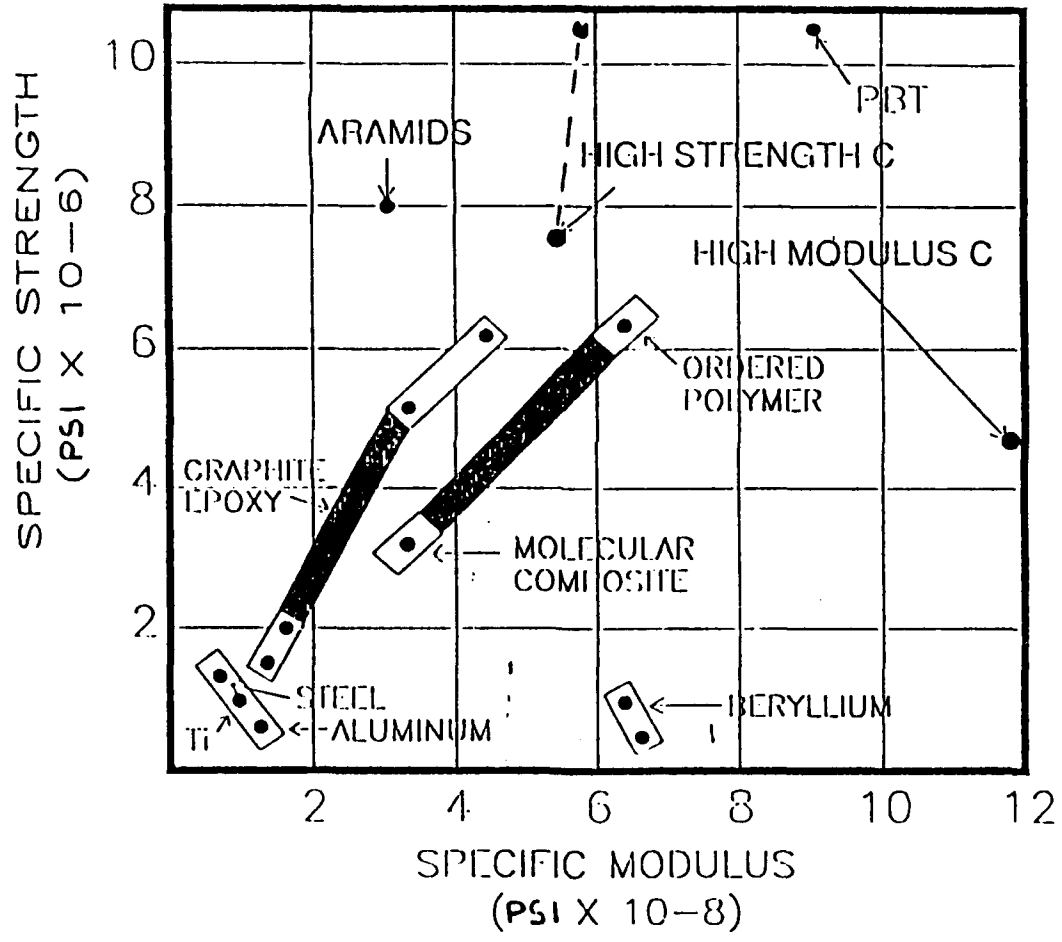
A1051.03

OBJECTIVES....

- UNDERSTAND THE FUNDAMENTAL MECHANISMS OF LIQUID CRYSTALLINE BEHAVIOR IN POLYMERS AND PREDICT STRUCTURE/ PROPERTY RELATIONSHIPS TO YIELD FULLY ENGINEERED ARTICLES

- DEMONSTRATE THE FEASIBILITY OF THERMOTROPIC LIQUID CRYSTAL POLYMERS AS SYSTEM COMPONENTS FOR BOTH SOLID AND LIQUID PROPULSION

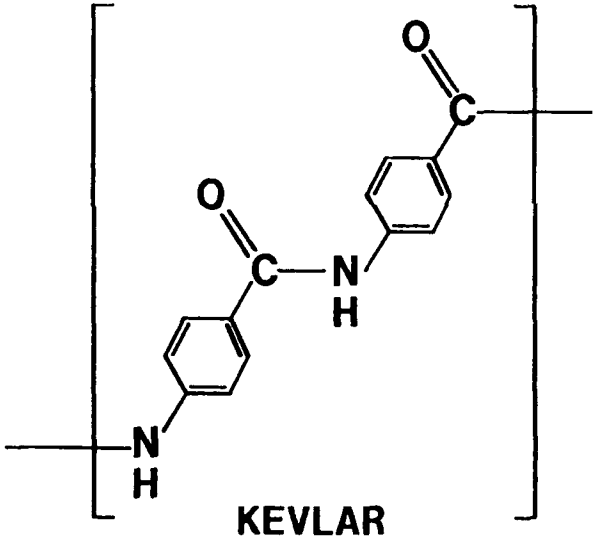
ORDERED POLYMERS/MOLECULAR COMPOSITES



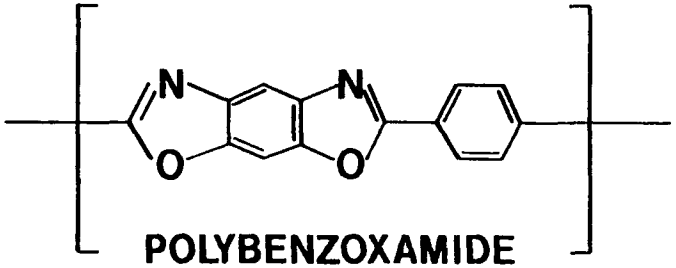
COMPARATIVE MATERIALS PROPERTIES FOR DEVELOPED STRUCTURES

ADVANCED POLYMER COMPONENTS....

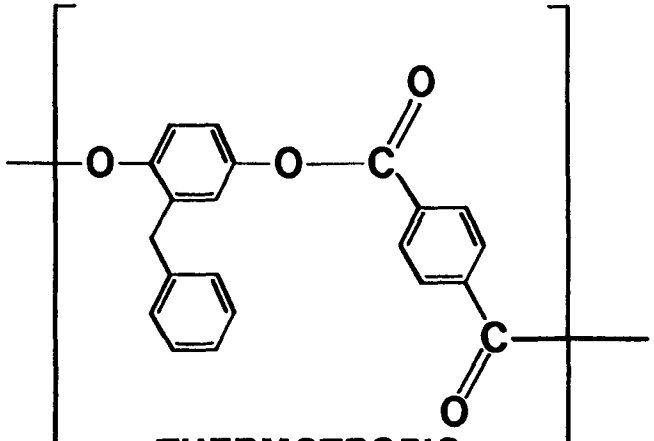
C0301.13



KEVLAR



POLYBENZOXAMIDE



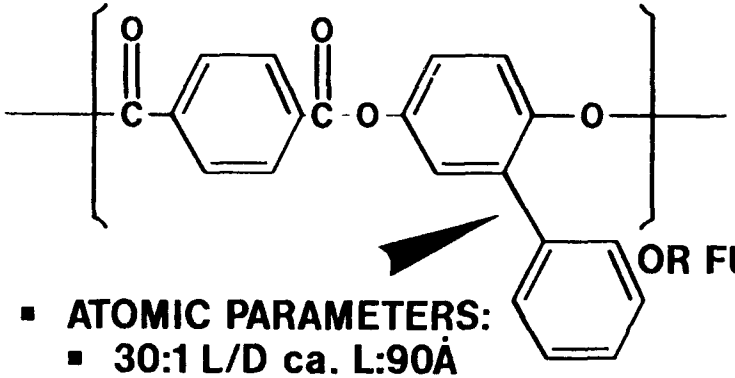
THERMOTROPIC
POLYESTER

ADVANCED POLYMER COMPONENTS

C0301.14

TECHNOLOGY....

- MOST THERMOTROPIC LCP'S ARE BASED ON:



OR FUSED RING PRECURSORS

- ATOMIC PARAMETERS:
  - 30:1 L/D ca. L:90Å
  - VIRTUALLY RIGID ROD
- "STACKING" AND/OR INTERMOLECULAR FORCES CAUSE ANNEALING

  ONCE ANNEALED:
  - INTRACTABLE BY THERMAL/SOLVENT INTERACTION
- WHICH ANNEAL?
- HOW IS IT DONE?
- MECHANISM?

ADVANCED POLYMER COMPONENTS

APPROACH

IDENTIFY UNIQUE ATTRIBUTES
EXPLORE MOLECULAR PHENOMENA
COUPLE TO MACROSCOPIC PROPERTIES
COMPILE DATABASE
DESIGN COMPONENTS
FABRICATE COMPONENTS
PROPULSIVE TESTING

" THE MOST BEAUTIFUL THING WE CAN EXPERIENCE IS THE MYSTERIOUS. IT IS THE TRUE SOURCE OF ART AND SCIENCE." - ALBERT EINSTEIN

ADVANCED POLYMER COMPONENTS

RESEARCH QUESTIONS

WHAT IS PHYSICO - CHEMICAL ANNEALING?

- STRUCTURE
- ASSEMBLY
- KINETICS

HOW IS IT MEASURED?

HOW ARE PARTS FABRICATED?

WHAT DEMONSTRATION ARTICLES ARE IMPORTANT?

- HYBRID MOTOR
- 2X4 MOTOR
- AFA MOTOR
- LETO VEHICLE

ADVANCED POLYMER COMPONENTS

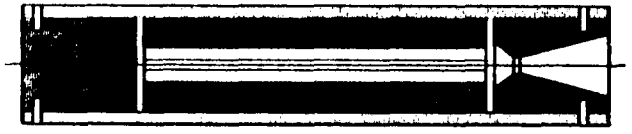
CRITICAL BREAKTHROUGHS

ANNEALING OBSERVED BY CHEMICAL/THERMAL ANALYSIS
RELATIONAL DATABASE GENERATED
2X4 CASES/HYBRID NOZZLES FIRED
LOW TEMP CVD ACCOMPLISHED ON POLYMERS
CHLORINE SHELL XAFS SUCCESSFUL
ATOMIC RESOLUTION OBTAINED BY TEM

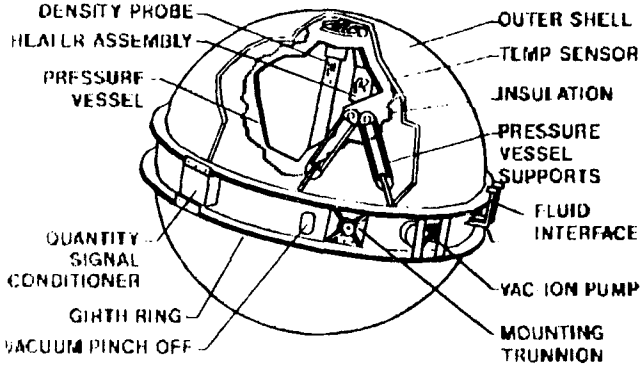
FIGURES OF MERIT

18 PAPERS PRESENTED
2 NATIONAL SYNCHROTRON LIGHT SOURCE PROPOSALS ACCEPTED
3 DEUTSCHES ELEKTRONEN-SYNCHROTRON PROPOSALS ACCEPTED
1 AUSTRALIAN NUCLEAR SCIENCE & TECHNOLOGY ORGANISATION PROPOSAL ACCEPTED
5 SIGNIFICANT EVENTS
ANNUAL APC RESEARCH REVIEW - FEB 1992

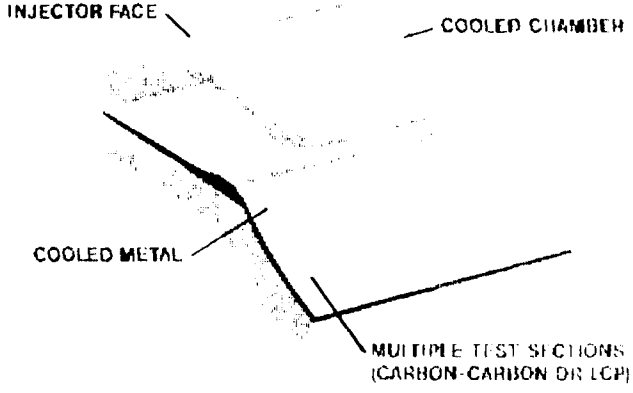
PROPELLANT GRAIN AND TUBE

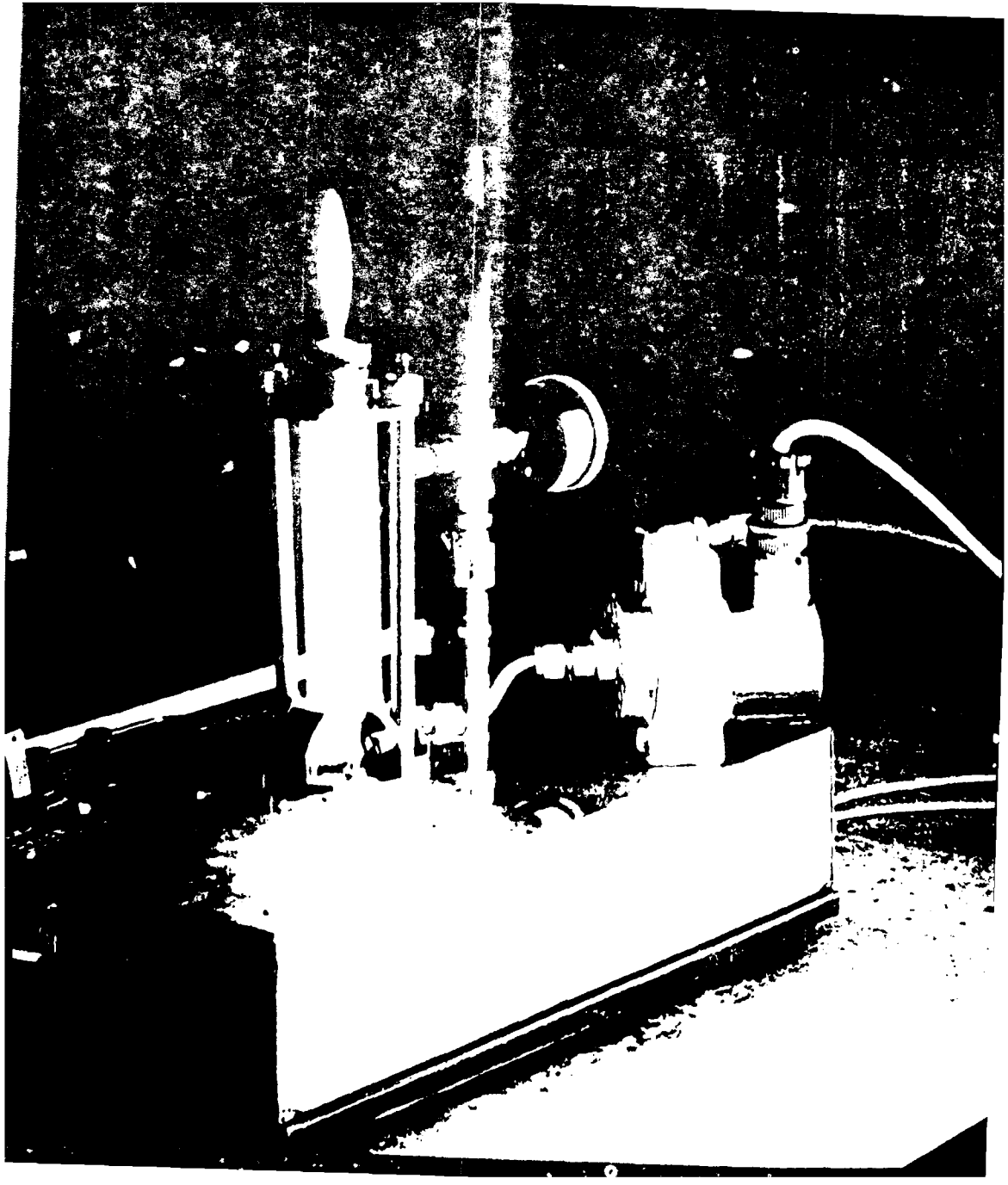


BOOSTER ASSEMBLY



NASPLAS 2-D TEST ARTICLE

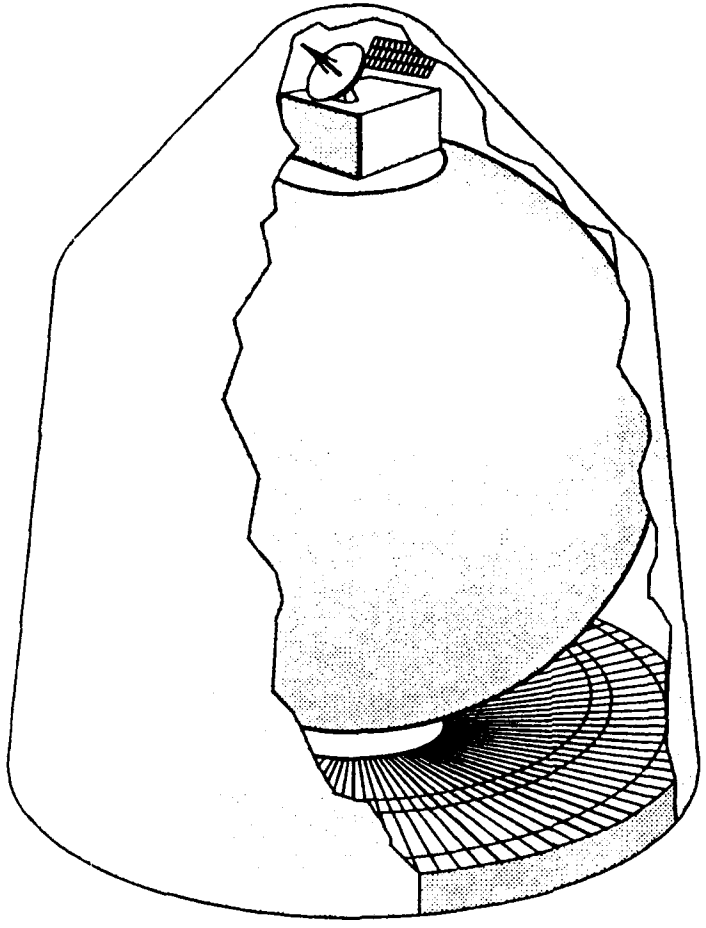


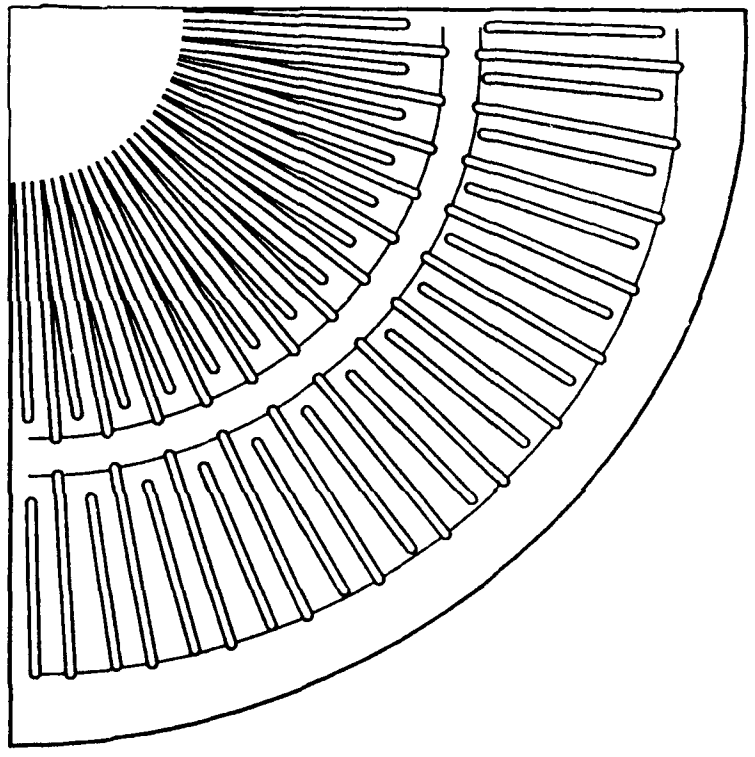


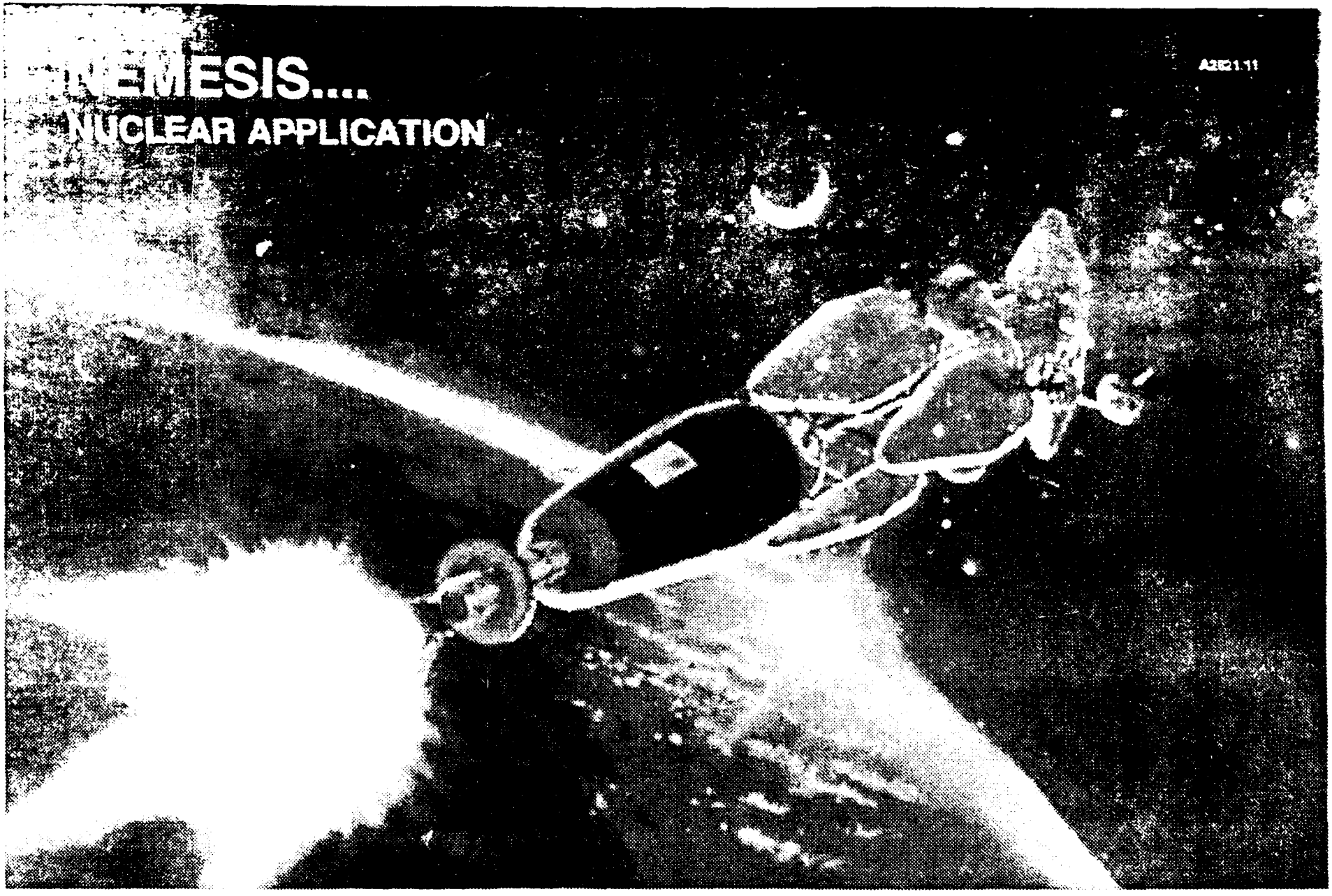
NEMESIS....

A2821.14

LASER EARTH-TO-ORBIT APPLICATION






NEMESIS....
NUCLEAR APPLICATION
A3E1.11

POLYMER SYNTHESIS

J.J. Rusek
OLAC PL/RKCP
Edwards AFB CA 93523

A concept coined polymer annealing was observed in DuPont HX-4000 and Granmont GRANLAR. These polymers, when appropriately heat treated, exhibit significant elevation of the melt temperature and greatly increased solvent resistance. The HX-4000 could be thought of as chain extending during treatment, since it is synthesized from the melt, however, the GRANLAR species is fully reacted in solution and exhibits an obviation of the melt entirely. It is thought that the size and the polarity of the pendant group in the polyester is the prime determinant in the ability to anneal.

This paper will address the annealing phenomena by looking at the molecular structure of the liquid crystal polyesters. Synthetic schemes are presented as well as the polymers synthesized to date. The critical nature of polymer synthesis as it supports the rest of the APC effort is stressed.

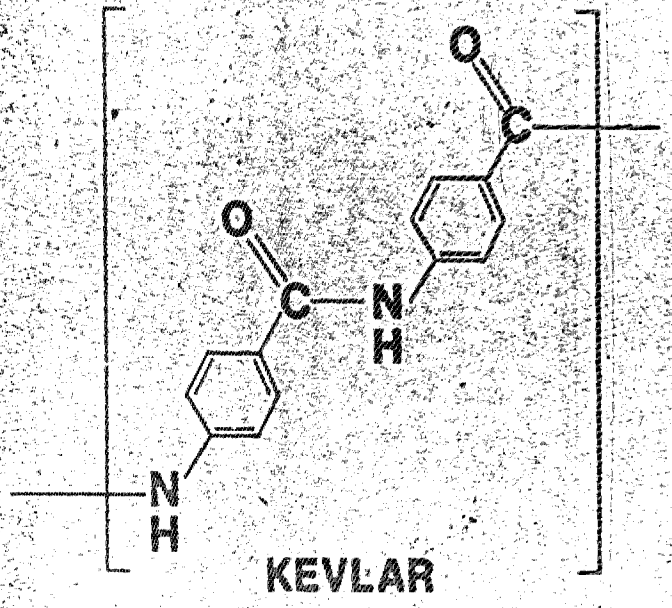
ADVANCED POLYMER COMPONENTS

TASK #1

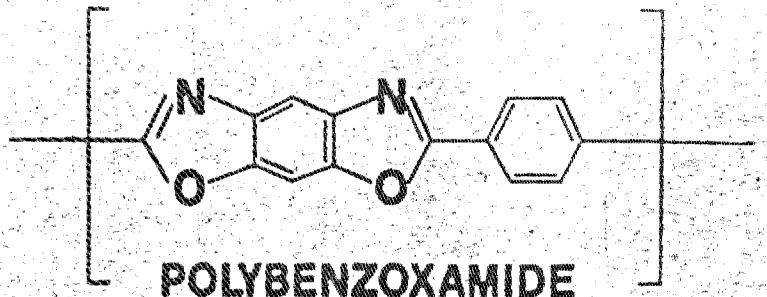
POLYMER SYNTHESIS

ADVANCED POLYMER COMPONENTS....

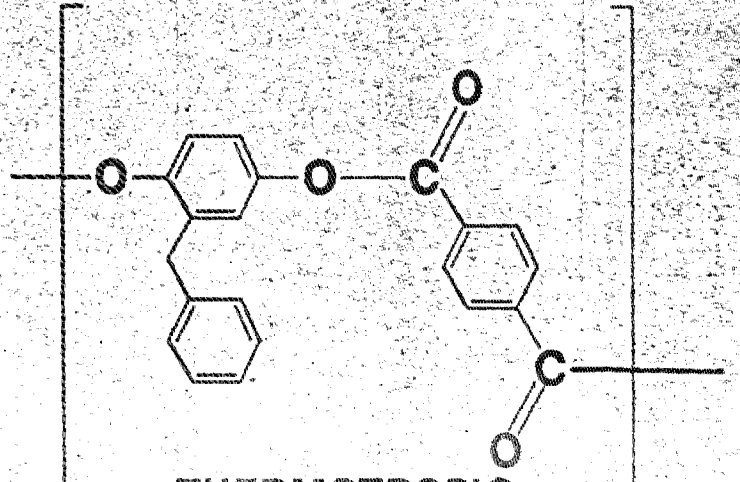
C0301.13



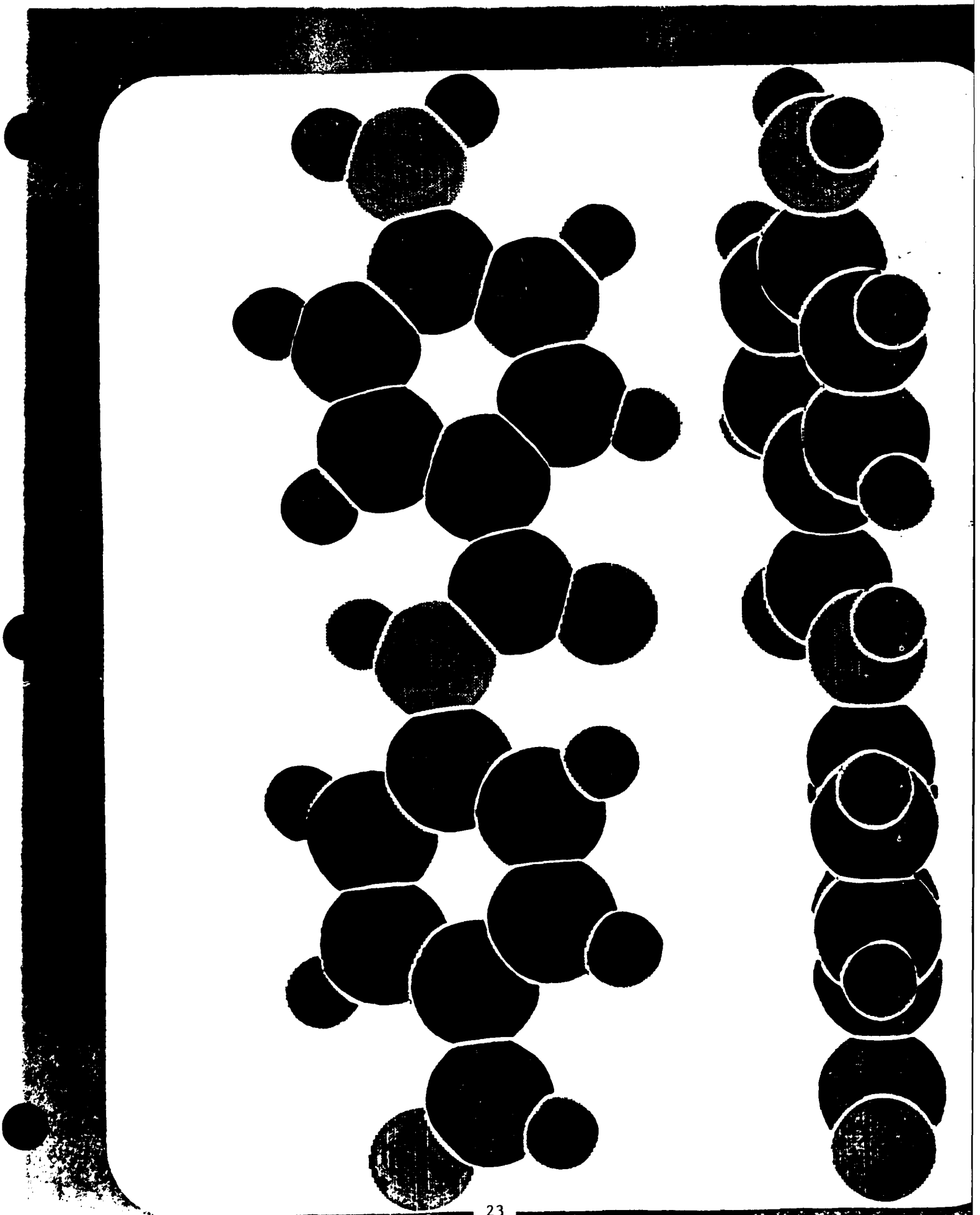
KEVLAR



POLYBENZOXAMIDE

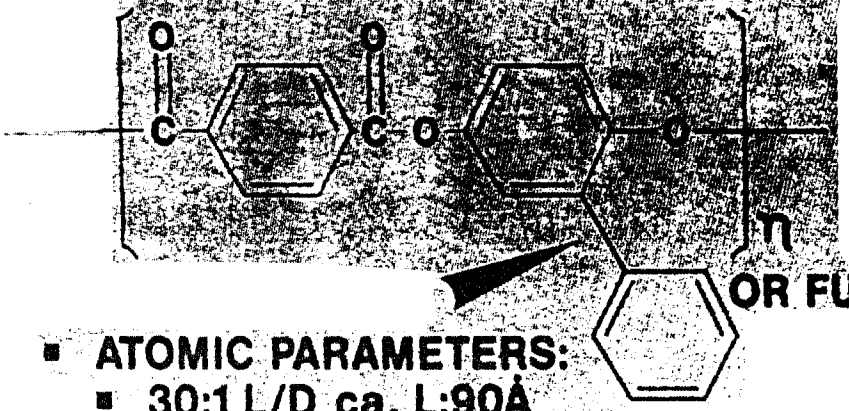


THERMOTROPIC POLYESTER



TECHNOLOGY...

- **MOST THERMOTROPIC LCP'S ARE BASED ON:**



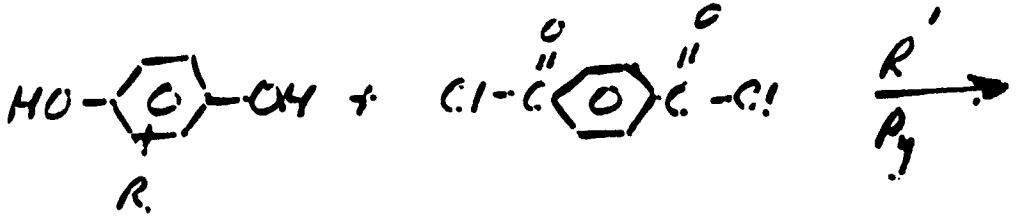
OR FUSED RING PRECURSORS

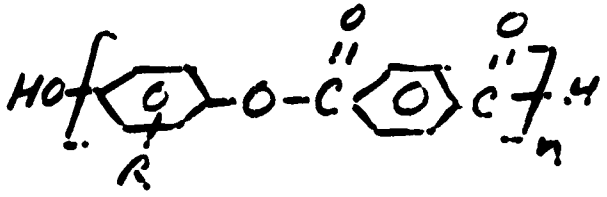
- **ATOMIC PARAMETERS:**
  - **30:1 L/D ca. L:90Å**
  - **VIRTUALLY RIGID ROD**
- **"STACKING" AND/OR INTERMOLECULAR FORCES CAUSE ANNEALING**

ONCE ANNEALED:

- **INTRACTABLE BY THERMAL/SOLVENT INTERACTION**

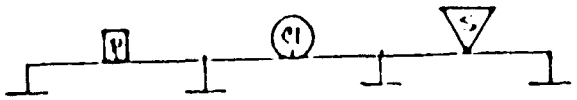
- WHICH ANNEAL?
- HOW IS IT DONE?
- MECHANISM?



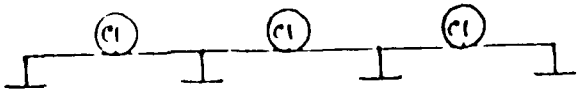


where R = H
Me
PhEt
Ph
Cl

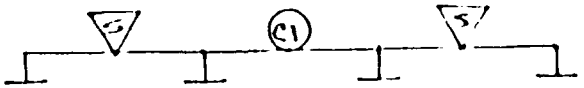
R' = Methylene Chloride
Ethylene Dichloride



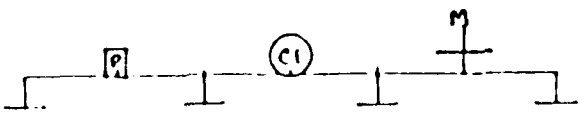
SYN 11



SYN 12



SYN 13



SYN 14

SYN 2 MHQ/TA MC

SYN 3 PHQ/TA MC

SYN 4 PHQ/TA MC Ci

SYN 5 CHQ/TA

SYN 6 MHQ/PHQ/TA

SYN 7 MHQ/TA

SYN 8 PHQ/PEHQ/TA

SYN 9 PHQ/PEHQ/TA

SYN 10 PEHQ/TA

SYN 11 PEHQ/PHQ/CHQ/TA

SYN 12 CHQ/TA

SYN 13 PEHQ/CHQ/TA

SYN 14 MHQ/CHQ/PHQ/TA

SYN 15 CHQ/TA

SYN 16 PEHQ/PHQ/TA

SYN 17 MHQ/TA

SYN 18 PHQ/TA

CF_3COOH / CH_2Cl_2 50 % w/w IS PREFERRED SOLVENT FOR ALL THERAPEUTICS UP TO 4 mg/ml

CURRENT ACTIVITIES:

Monomer purification

LALLS experimentation

LTA experimentation

CRYOGEN TESTING

K.P. Chaffee
OLAC PL/RKCP
Edwards AFB, CA 93523

ABSTRACT

The objective of tasks 12,13 and 14 was to examine the mechanical integrity and stability of the commercially available thermotropic liquid crystal polymers (LCP) at cryogenic temperatures. The liquid oxygen (LOX) testing was conducted at the NASA White Sands Test Facility by Harold Beeson and Richard Shelley. The liquid hydrogen (LH2) mechanical testing was performed by Tom Eisenreich of General Dynamics Space Systems Division. Finally, the liquid nitrogen (LN2) burst tests were performed at the Phillips Laboratory by Eric Schmidt.

The LOX test results imply that the injection molded commercially available LCP materials are not suitable for liquid oxygen use. Although the materials compared favorably to Teflon (PTFE) in the autoignition test, the LCPs relatively high reactivity to mechanical impact and combustible gaseous emissions make them poor canidates for tank materials. Vectra A950 had the overall best properties while DuPont HX4000 had the poorest.

The longitudinal XYDAR SRT-500 had the highest tensile and flexural strength and modulus at LH2 temperatures. All materials displayed anisotropic mechanical behaviour, as expected. General Dynamics reports considerable scatter in all results. This is perhaps a result of the injection molding process.

VECTRA A950 had the highest ambient temperature burst pressure of 7.38 MPa while the XYDAR SRT-300 had the highest LN2 burst pressure at 9.21 MPa.

CRYOGEN TESTING

K.P. CHAFFEE
PHILLIPS LABORATORY
EDWARDS AFB, CA

CRYOGEN TESTING

1. LOX TESTING / NASA WHITE SANDS
2. LH2 TESTING / GENERAL DYNAMICS
3. LN2 BURST TESTING / PL

LOX TESTING

1. Mechanical Impact
2. Auto-Ignition
3. Promoted Combustion

MECHANICAL IMPACT RESULTS
20 TESTS

MATERIAL	REACTIONS
Vectra A950	3
Dupont HX4000	18
Xydar RC210	19
Teflon	0

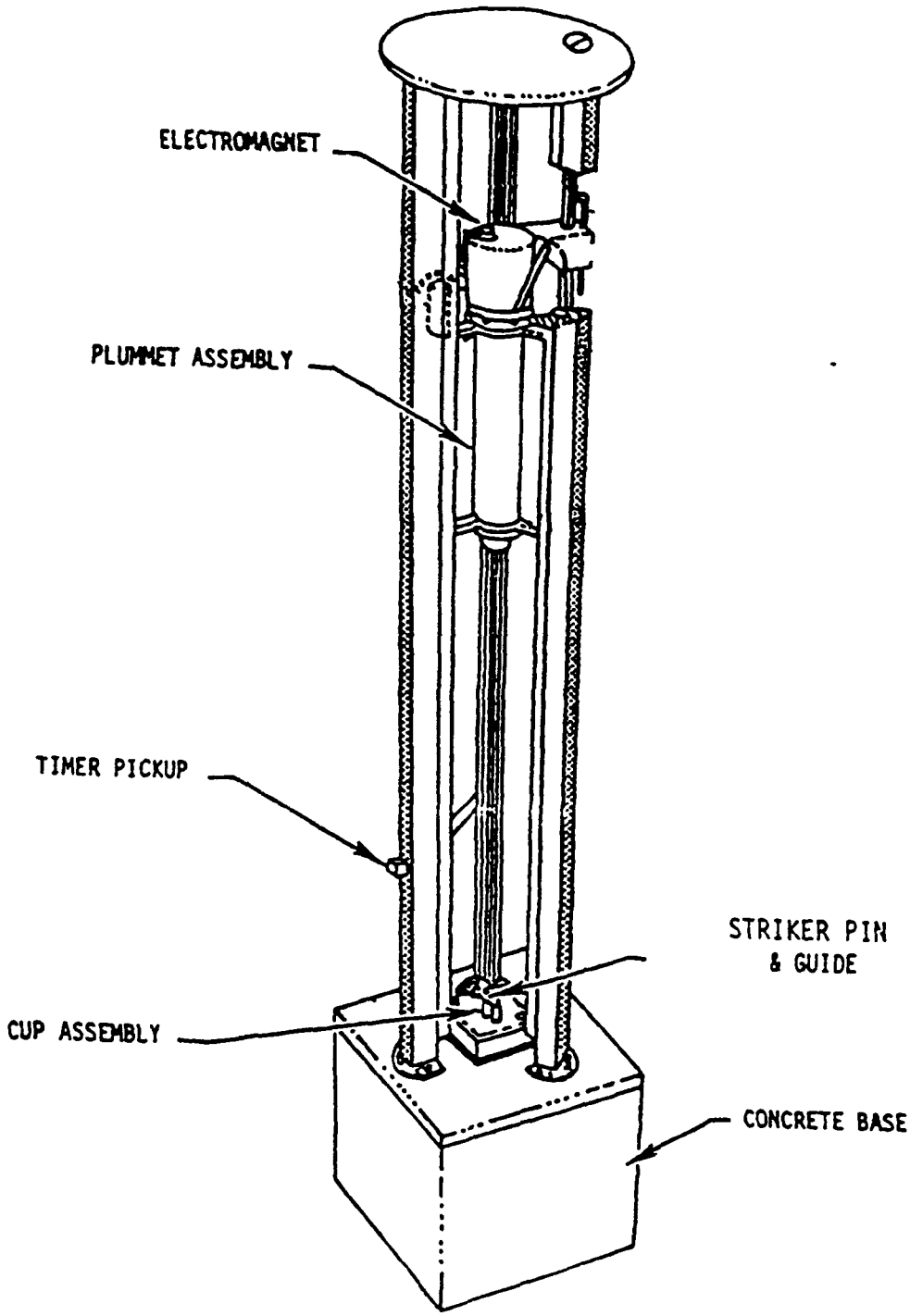


Figure 1. Mechanical Impact Testing Apparatus

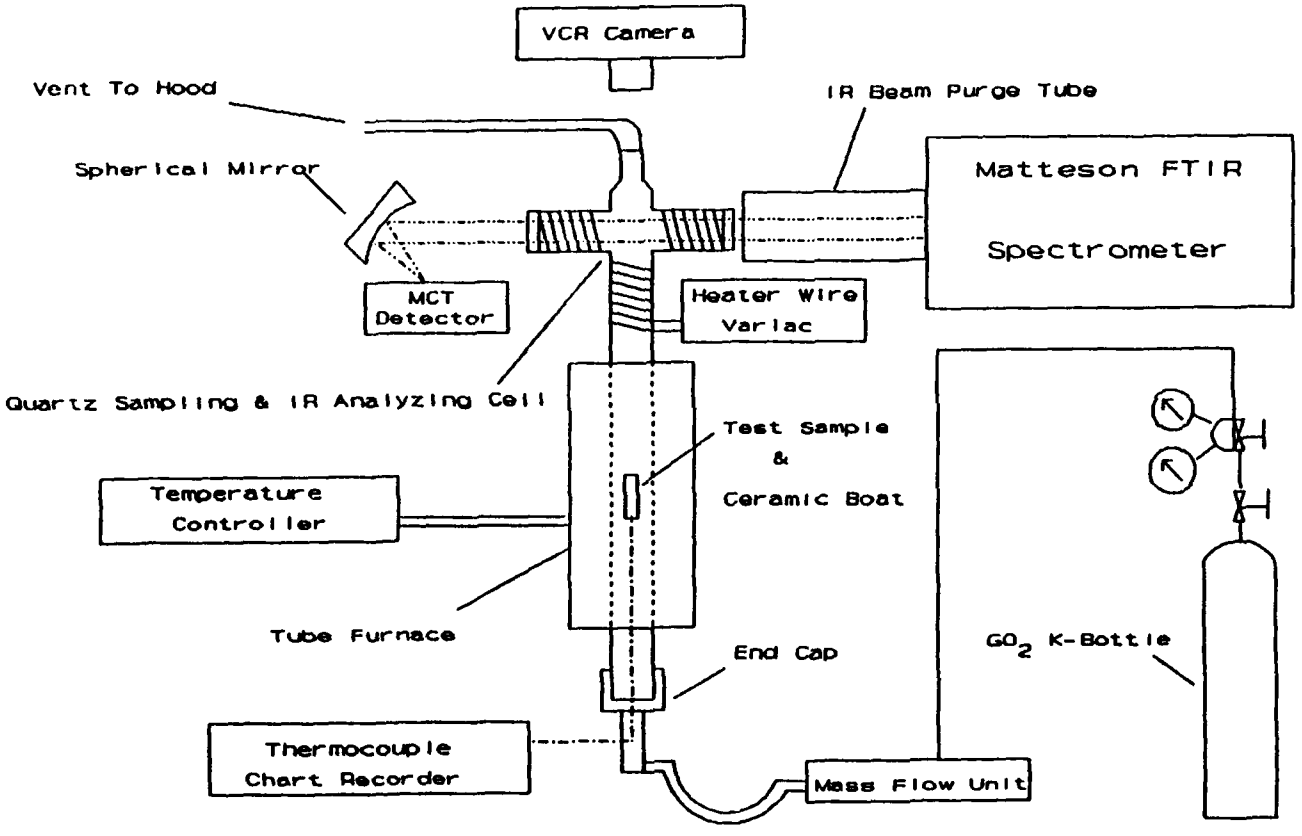


Figure 2. FTIR Tube Furnace

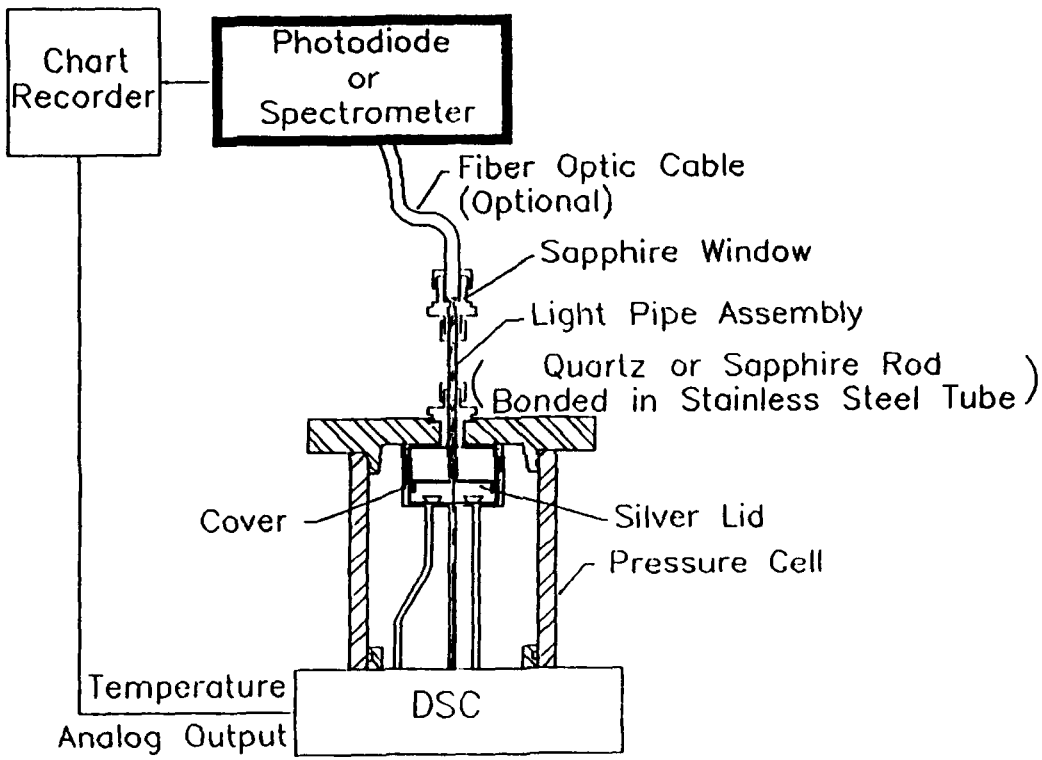


Figure 3. DSC/Light Pipe Assembly

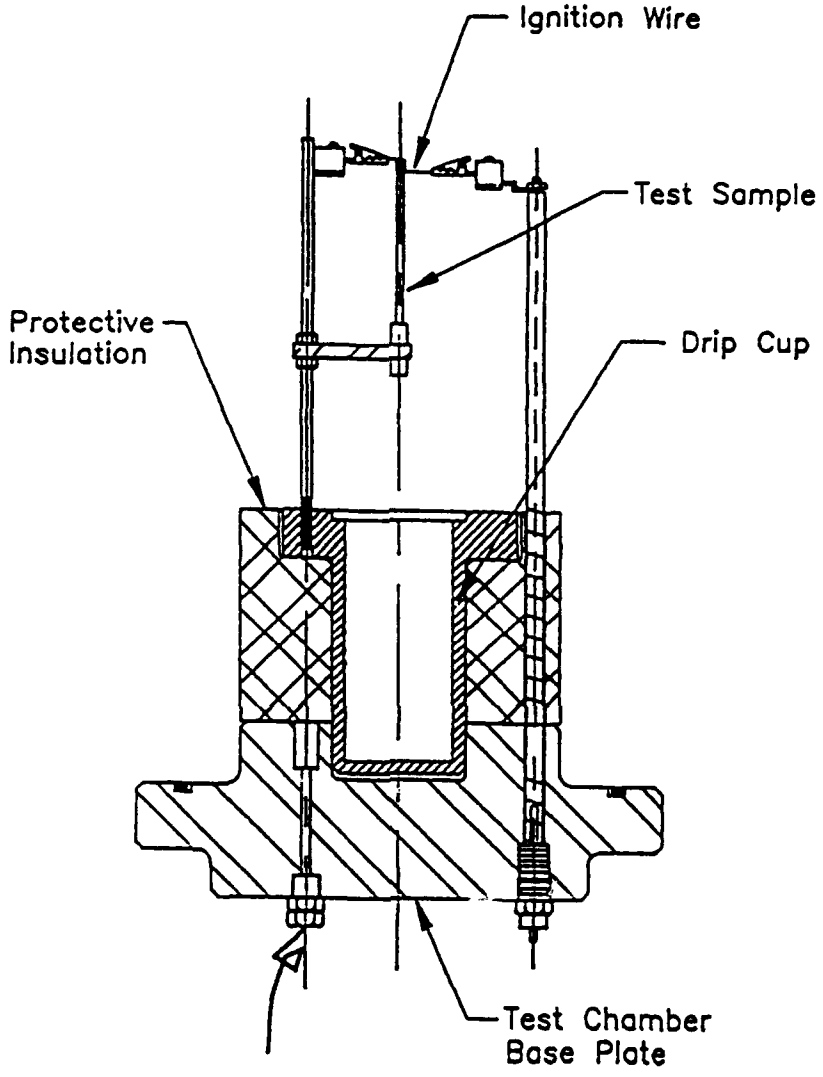


Figure 4. Promoted Combustion Test Apparatus

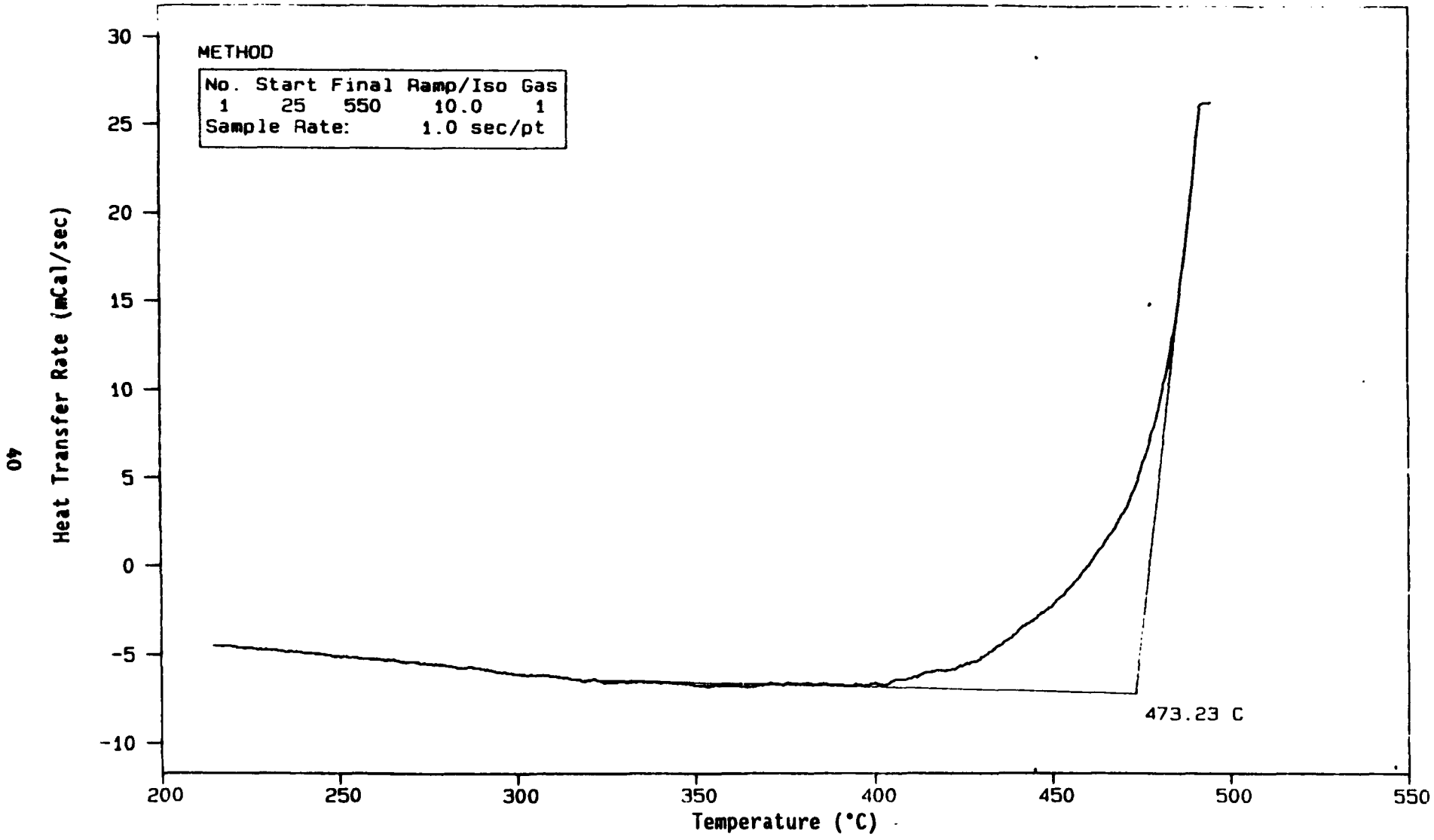


Figure 5. Vectra A950 DSC Trace

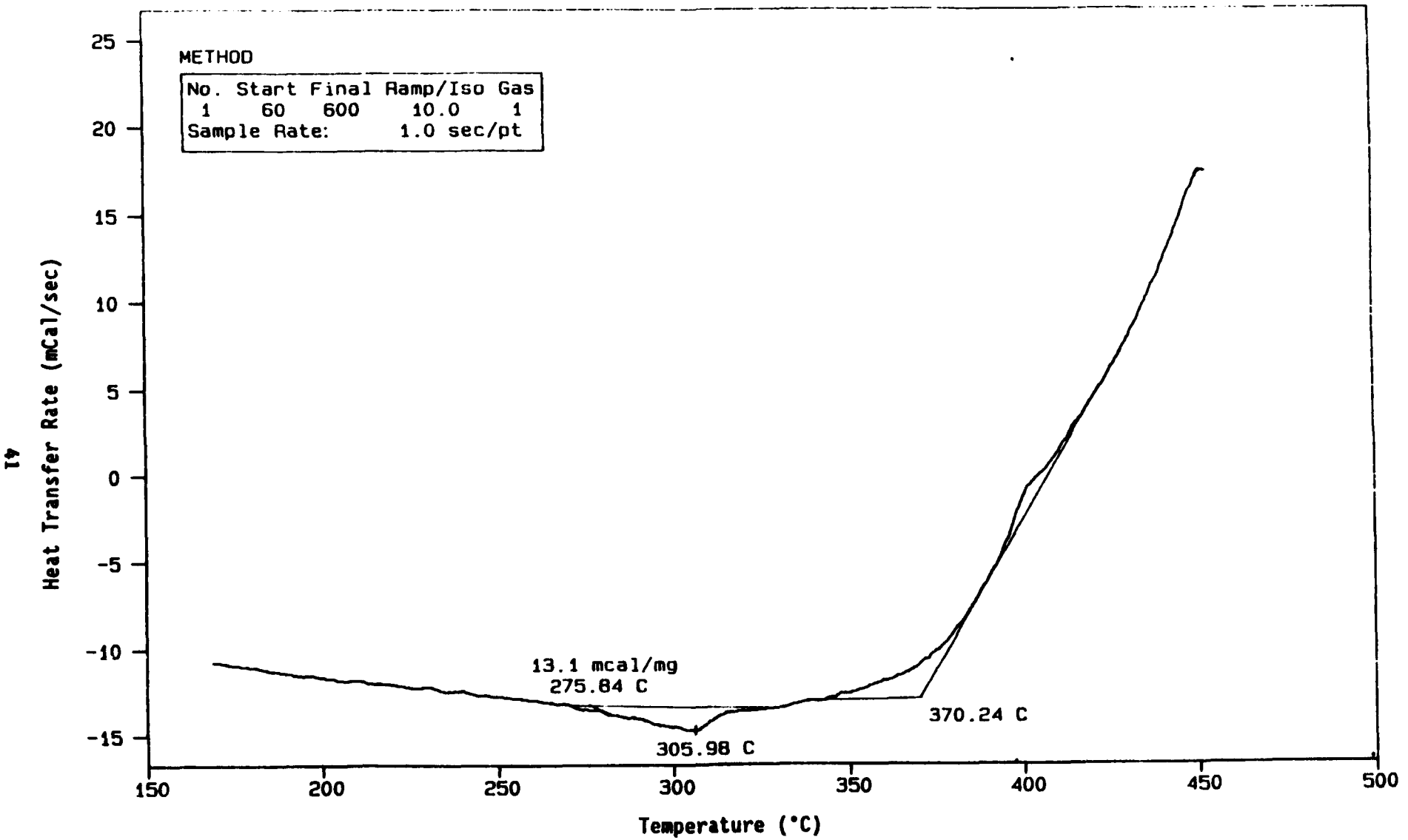


Figure 6. DuPont HX400 DSC Trace

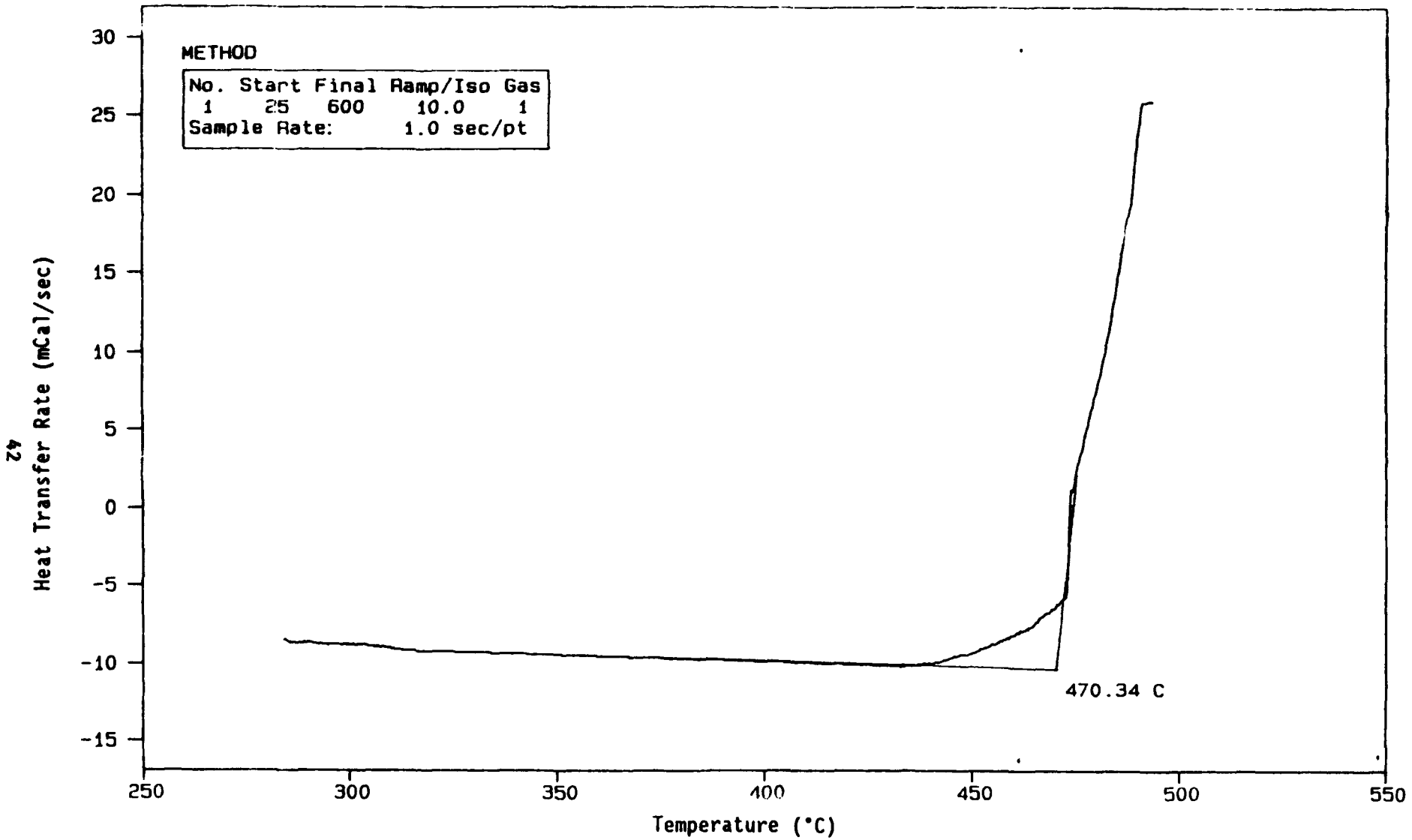


Figure 7. Xydar RC210 DSC Trace

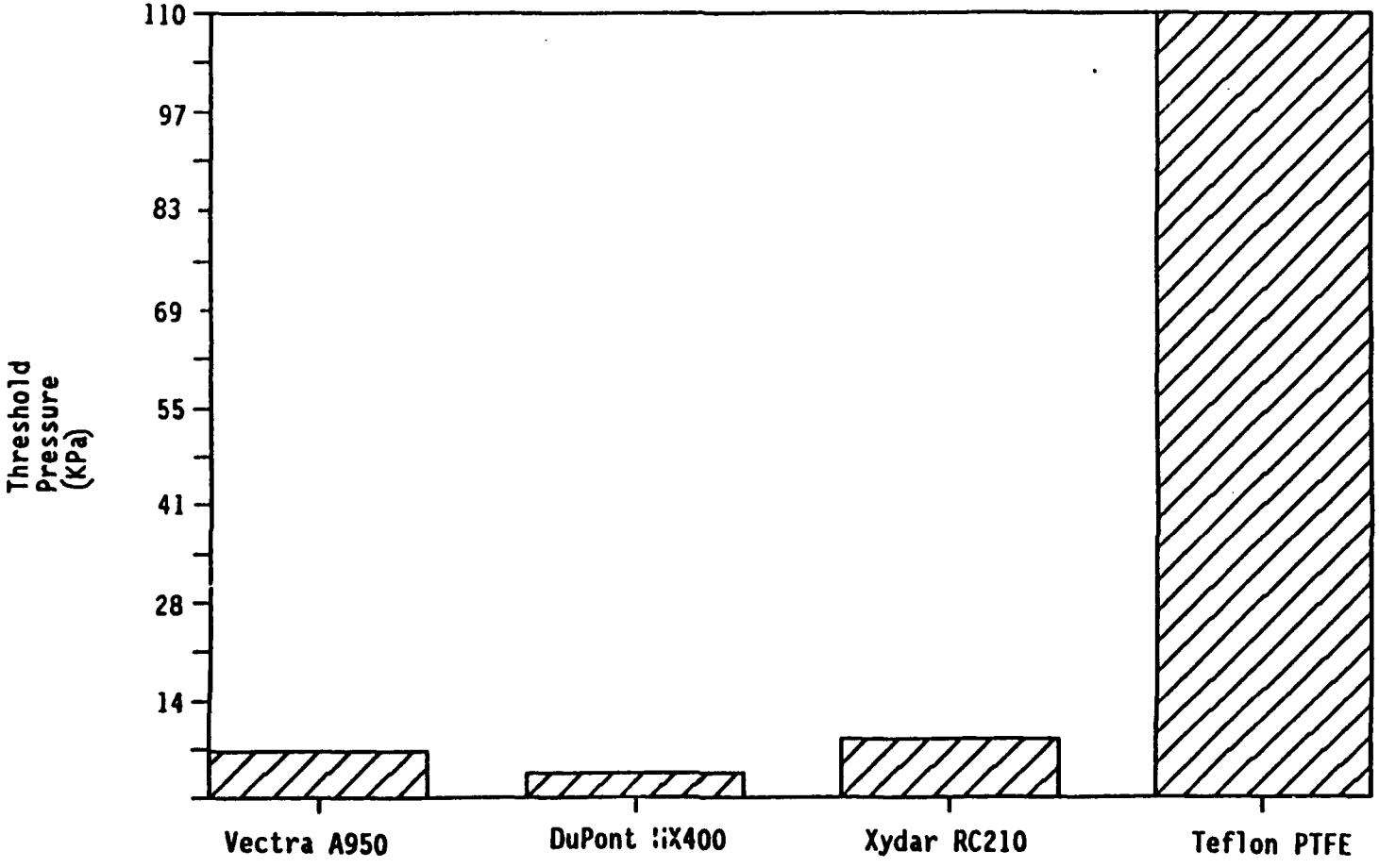


Figure 8. Threshold Pressure Comparison
Vectra A950, DuPont HX400, Xydar RC210, and Teflon

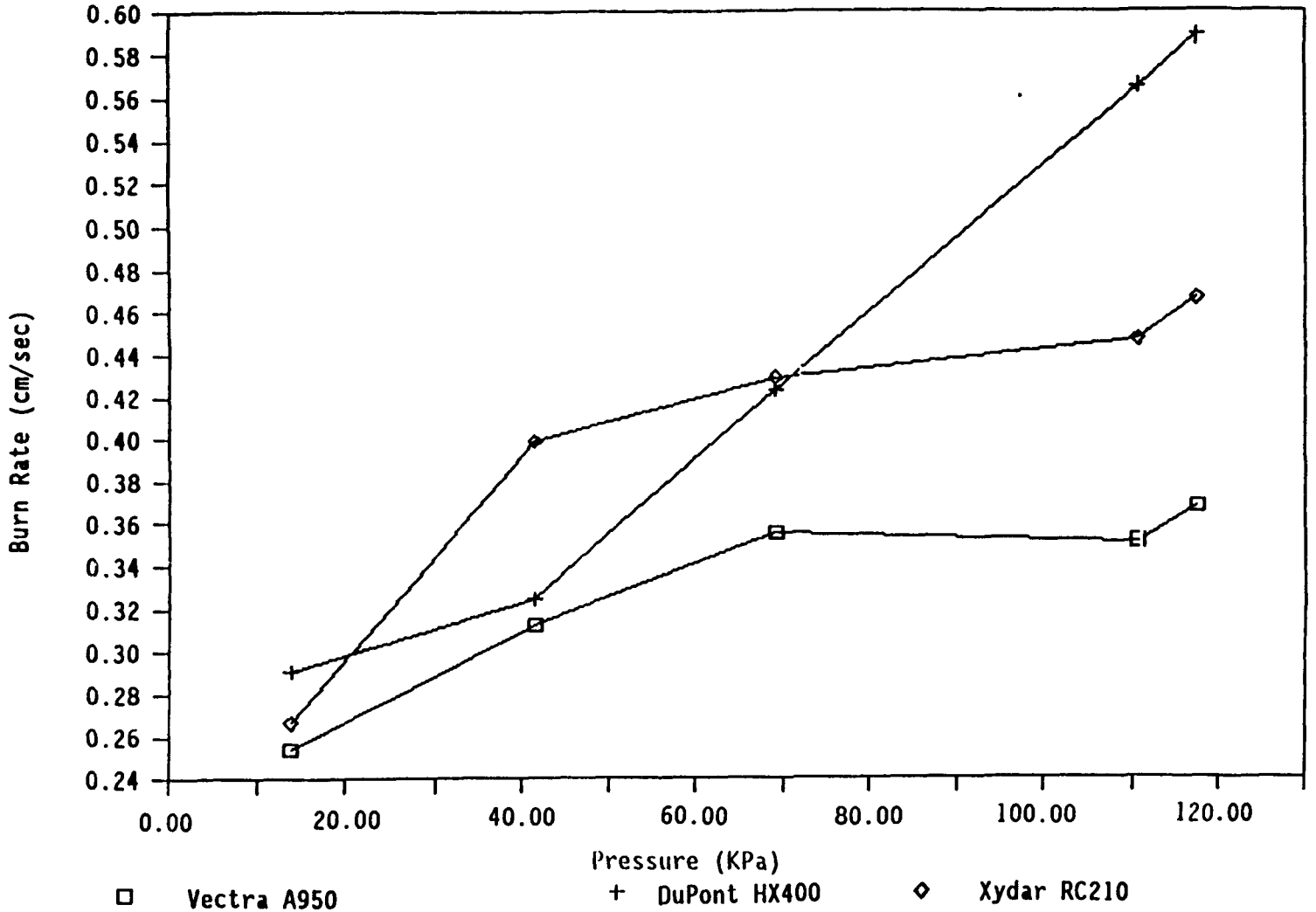


Figure 9. Burn Rates in Oxygen for Vectra A950, DuPont HX400, Xydar RC210

LH2 TESTING

1. Tensile Testing
2. Flexure

Table 1. Liquid Hydrogen Flexure Test Results on Liquid Crystal Polymers.

Material	Specimen I.D.	Width (in)	Thickness (in)	Ultimate Load (lb)	Ultimate Strength (ksi)	Modulus (msi)	Failure Strain (%)	Failure Location
Vectra B950 Long	A1	1.0263	0.1237	127.3	47.42	2.99	1.59	Tension
	A3	1.0298	0.1226	110.8	41.88	2.56	1.64	Tension
	A5	1.0289	0.1238	110.8	41.40	3.02	1.36	Tension
	Avg	1.0283	0.1234	116.3	43.47	2.86	1.53	
	Std. Dev.	0.0018	0.0007	9.5	3.45	0.26	0.15	
	COV	0.18%	0.54%	8.17%	7.93%	9.01%	9.58%	
Vectra A950 Long	B2	1.0424	0.1204	94.5	39.40	3.33	1.18	Tension
	B4	1.0270	0.1396	105.4	33.18	2.28	1.46	Tension
	B5	1.0249	0.1374	97.3	31.63	2.23	1.42	Tension
	Avg	1.0314	0.1325	99.1	34.73	2.61	1.35	
	Std. Dev.	0.0096	0.0105	5.7	4.09	0.62	0.15	
	COV	0.93%	7.93%	5.71%	11.78%	23.77%	10.95%	
Vectra B950 Trans	C1	1.0308	0.1187	63.1	12.38	0.99	1.25	Tension
	C3	1.0232	0.1211	89.8	17.06	1.23	1.39	Tension
	C4	1.0311	0.1201	72.1	13.82	1.15	1.20	Tension
	Avg	1.0284	0.1200	75.0	14.42	1.12	1.28	
	Std. Dev.	0.0045	0.0012	13.6	2.39	0.12	0.10	
	COV	0.44%	1.00%	18.11%	16.61%	10.88%	7.50%	

Table 1. Continued

Material	Specimen I.D.	Width (in)	Thickness (in)	Ultimate Load (lb)	Ultimate Strength (ksi)	Modulus (msi)	Failure Strain (%)	Failure Location
XY DAR	D2	1.0285	0.1213	97.8	39.75	4.02	0.99	Shear
SRT-500	D3	1.0291	0.1322	129.8	44.38	5.44	0.82	Shear
Long	D4	1.0207	0.1326	1900	41.12	4.43	0.93	Shear
	Avg	1.0261	0.1287	115.9	41.75	4.63	0.91	
	Std. Dev.	0.0047	0.0064	16.4	2.38	0.73	0.09	
	COV	0.46%	4.98%	14.15%	5.71%	15.78%	9.63%	
DuPont	E2	0.9938	0.1244	44.5	17.36	2.73	0.64	Shear
HX 4000	E4	0.9948	0.1260	55.0	20.89	2.41	0.87	Shear
Long	E5	0.9907	0.1240	64.8	24.34	2.27	1.07	Shear
	Avg	0.9931	0.1248	53.8	20.87	2.47	0.86	
	Std. Dev.	0.0021	0.0011	8.7	3.49	0.24	0.22	
	COV	0.22%	0.85%	16.21%	16.73%	9.55%	25.43%	

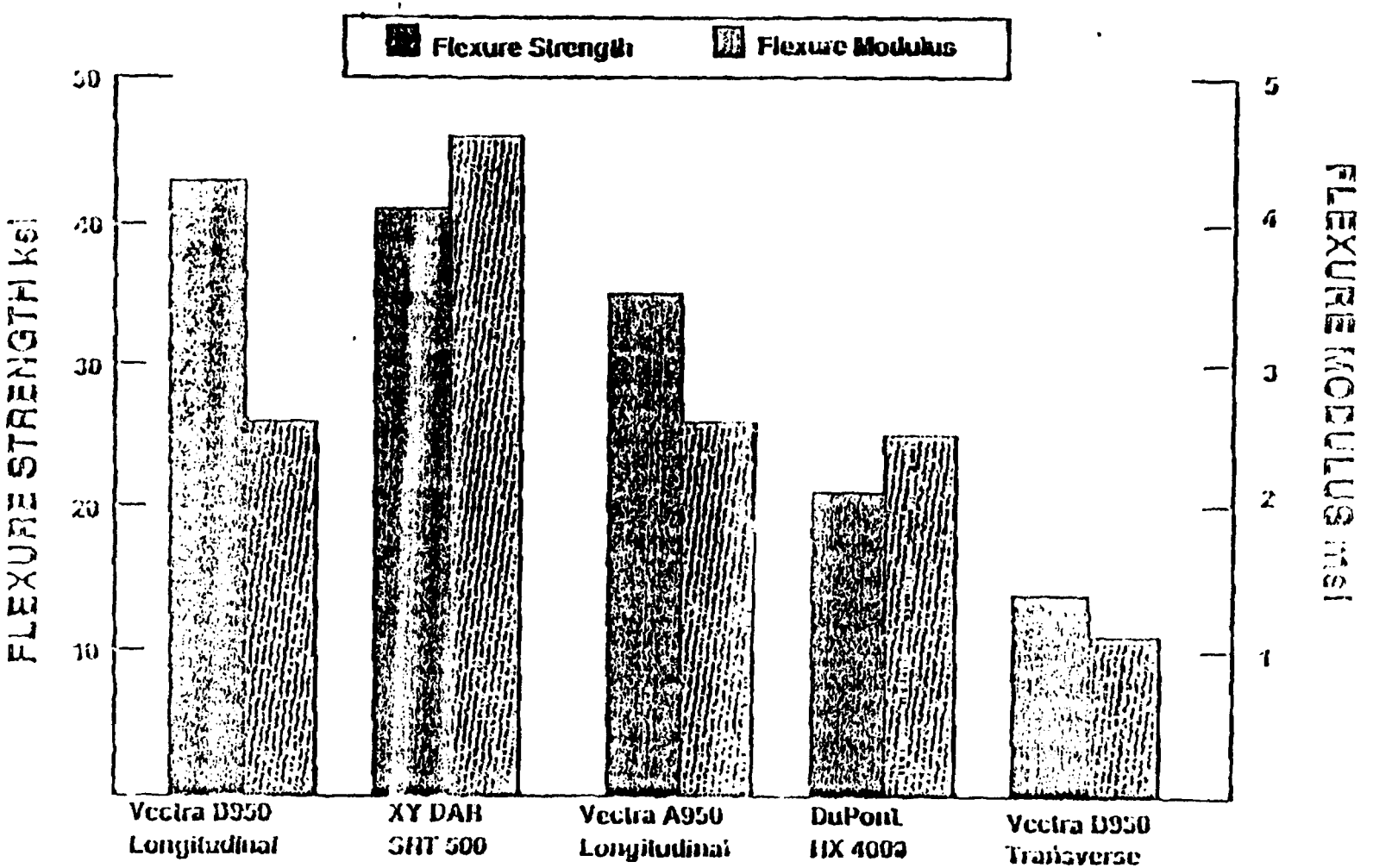


Figure 2. Comparison of the flexure strength and modulus of the various Liquid Crystal Polymers Generated in Liquid Hydrogen.

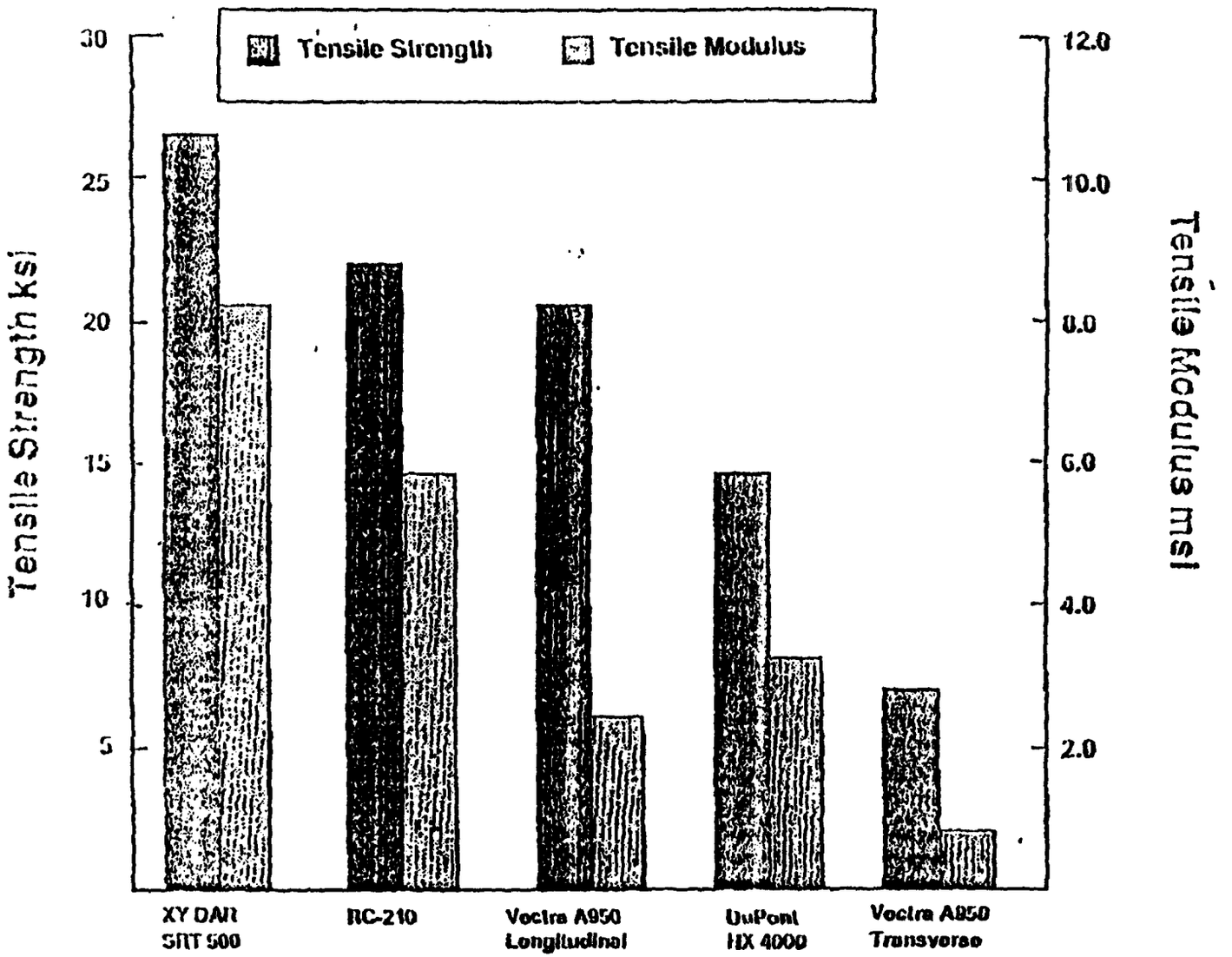


Figure 2. Comparison of the Tensile Strength and Modulus for the Various Liquid Crystal Polymers Generated in Liquid Hydrogen. Note that the Tensile Strength for XY DAR SRT 500 Shown Is Not Ultimate Strength But Maximum Stress Obtained.

Table 1. Liquid Hydrogen Tensile Test Results on Liquid Crystal Polymers.

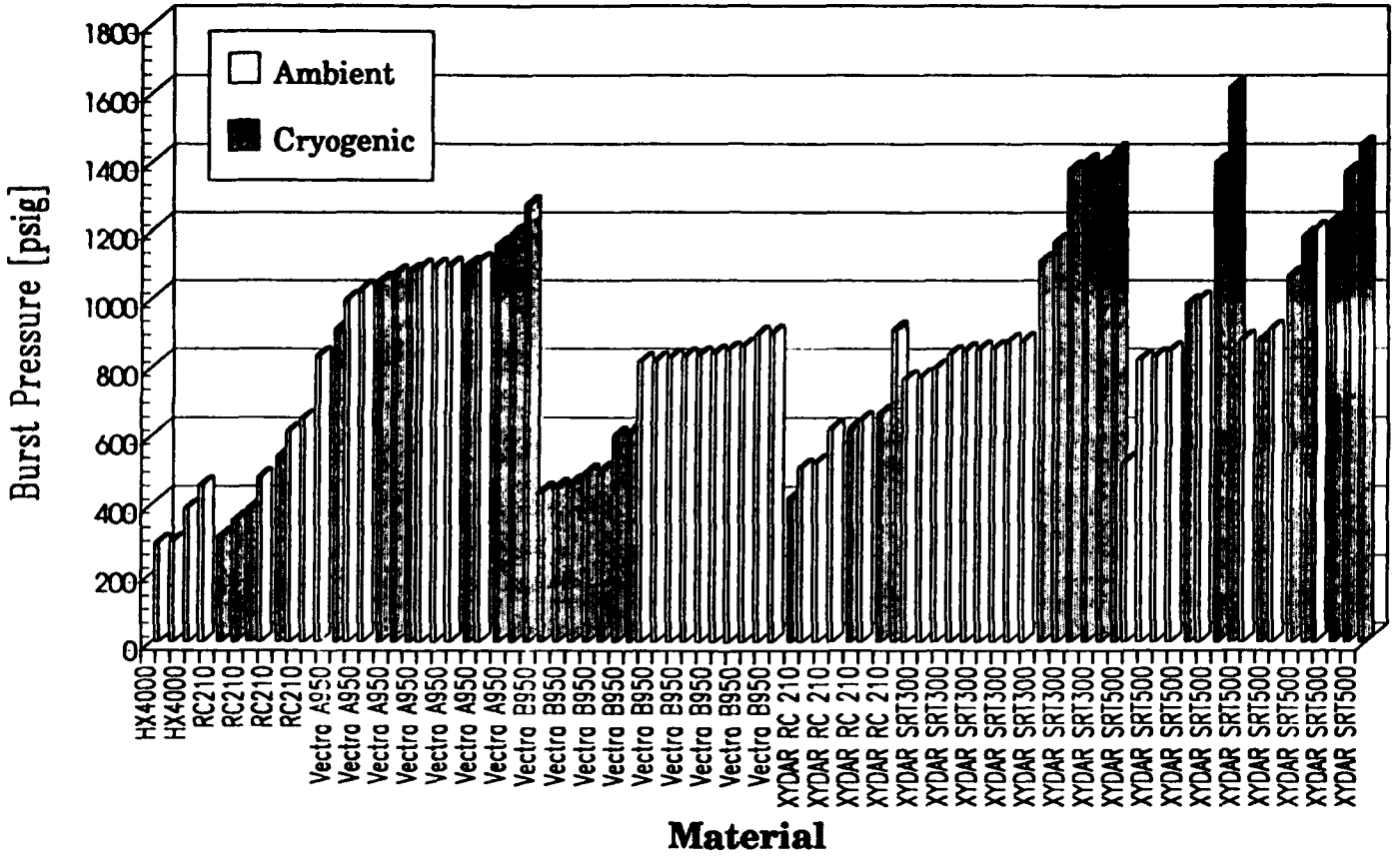
Material	Specimen I.D.	Width (in)	Thickness (in)	Ultimate Load (lb)	Ultimate Strength (ksi)	Modulus (msi)	Failure Strain (με)	Failure Location
Vectra A950 Longitudinal	H1	0.5495	0.1231	1379	20.39	2.30	8864	III
	H2	0.5505	0.1232	1507	22.22	2.05	10839	I
	H4	0.5509	0.1235	1332	18.82	2.70	6969	I
	Avg	0.5503	0.1249	1406	20.47	2.35	8891	
	Std. Dev.	0.0007	0.0031	91	1.70	0.33	1935	
	COV	0.13%	2.47%	6.44%	8.32%	13.95%	21.77%	
Vectra A950 Transverse	F1	0.5631	0.1210	553	8.12	0.85	9549	III
	F2	0.5690	0.1206	653	9.52	0.95	10017	III
	F3	0.5790	0.1216	377	5.35	0.82	6530	III
	Avg	0.5704	0.1211	528	7.66	0.87	8698	
	Std. Dev.	0.0080	0.0005	140	2.12	0.07	1892	
	COV	1.41%	0.42%	26.48%	27.64%	7.79%	21.76%	
DuPont HX 4000 Longitudinal	G2	0.5631	0.1200	839	12.42	2.73	4548	III
	G3	0.5690	0.1191	952	14.05	3.23	4349	III
	G4	0.5476	0.1193	1103	16.88	3.55	4756	I
	Avg	0.5599	0.1195	965	14.45	3.17	4551	
	Std. Dev.	0.0111	0.0005	132	2.26	0.41	203	
	COV	1.97%	0.40%	13.73%	15.65%	13.04%	4.47%	

Table 1. Liquid Hydrogen Tensile Test Results on Liquid Crystal Polymers.

Material	Specimen I.D.	Width (in)	Thickness (in)	Ultimate Load (lb)	Ultimate Strength (ksi)	Modulus (msi)	Failure Strain (με)	Failure Location
XYDAR SRT-500 Longitudinal	I1	0.5494	0.1201	1798	27.25	8.11	3360	*
	I2	0.5487	0.1185	1894	29.13	8.25	3531	*
	I3	0.5493	0.1191	1490	22.78	8.48	2686	*
	Avg	0.5491	0.1192	1727	26.38	8.28	3192	
	Std. Dev.	0.0004	0.0008	211	3.26	0.19	447	
	COV	0.07%	0.68%	12.22%	12.37%	2.26%	14.00%	
RC-210 Longitudinal	J3	0.5533	0.1241	1239	18.04	5.42	3329	III
	J4	0.5512	0.1234	1665	24.48	5.98	4093	II
	J6	0.5514	0.1234	1547	22.74	5.95	3821	III
	Avg	0.5520	0.1236	1484	21.75	5.78	3748	
	Std. Dev.	0.0012	0.0004	220	3.33	0.32	387	
	COV	0.21%	0.33%	14.82%	15.30%	5.45%	10.33%	

* Specimen did not reach ultimate load. Failure occurred in bond between doubler and specimen.

Comparison of Liquid Crystal Polymer Burst Pressure in Ambient and Cryogenic Environments



LN2 Burst Test Reference:

"The Application of Liquid Crystal Polymers to Turbomachinery", M.A. Mueller and E.E. Schmidt, Proceedings of the 1992 JANNAF Propulsion Meeting, Indianapolis IN.

Presenter: Shannon G. Lieb
Department of Chemistry
Butler University
4600 Sunset Avenue
Indianapolis, IN 46208
Phone: (317) 283-9410
FAX: (317) 283-9519
Bitnet: Lieb@ButlerU

Abstract

Molecular Dynamics Investigation of Polymer Annealing

Polymers have an essential use in the making of casings of solid rocket boosters. An investigation into the molecular structure and the resulting macroscopic properties is necessary in order to modify existing technology for the production of casing material for present and future uses. The "annealing" process of some liquid crystal polymers (synthesized from a monosubstituted hydroquinone and terephthalic acid) produces a polyester whose physical characteristics do not seem attributable to the usual further "cross-linking" explanations. The annealing process of holding the polymer at a temperature just below the melting point for five or so hours produces a material that does not melt at its original melting point, but can be raised to its decomposition temperature without melting. The label of order-disorder phase transition seems a more appropriate term for this process. The object of this theoretical investigation is to uncover the importance of the substituent of the hydroquinone in the action of producing this phenomenon. This ongoing investigation is divided into two tracks. The first is a molecular dynamics simulation of the annealing process. The second is the use of of some spectroscopic techniques to aid in the proper parametrization of the theoretical modeling, as well as, lending some bench marks by which the theory can be gauged. As the project unfolds it is anticipated that the theoretical modeling will serve as a predictive tool in suggesting other liquid crystal polymer structures that may or may not have this phase transition inherently built into them.

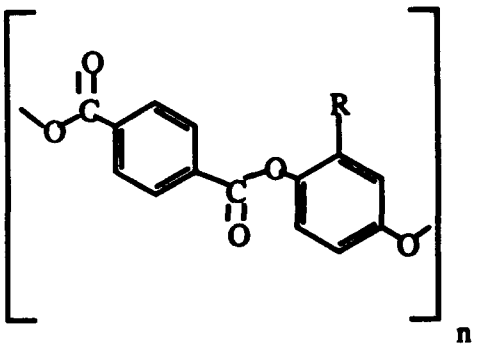


Figure 1. A typical monomer unit for a monosubstituted hydroquinone terephthalic acid polyester. The R group can be in either of the two unique positions available to it in the hydroquinone portion of the structure. The model systems proposed for study have R = CH_2-CH_2-C_6H_5 (phenethyl), CH_3 (methyl) and Cl (chloro).

As a liquid crystal polymer this material behaves as a rigid rod molecule. Interestingly, of the three polymers shown in figure 1 (differentiated by their "R" groups) the phenethyl derivative demonstrates the annealing behavior and the other two show only a "partial annealing". Because of the rigid rod characteristics and lack of many functionalities (only the two end groups) left over for the typical cross-linking, it seems more appropriate to view this as a phase transition (i.e., an order-disorder phase transition). It is further my contention that this phase transition is enhanced by the freely rotating phenethyl group interacting with neighboring aromatic rings whether it be those found on the polymer backbone or other phenethyl groups. The crystal structure of benzene has been found to have the benzene molecules stacking such that the edge of one ring is perpendicular to the face of its nearest neighbors as depicted in figure 2.

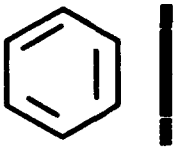


Figure 2. The perpendicular arrangement of two benzene molecules as found in the solid state. The second benzene molecule is to the right with its edge coming directly out of the page.

Introduction

This problem is best modeled at a theoretical level using a general approach that has been explored for the past 15 years or so by those interested in biopolymers (i.e., biochemists). The technique used in that case was to acknowledge that the problem was well

beyond the computational limits of *ab initio* (first principles) calculations and one had to rethink what questions could be answered with the computing power available. The obvious answer is to push the techniques that made molecular modeling "fashionable" to begin with. The elucidation of the double helix structure of DNA was in no small part accomplished by the use of "hand-held" molecular models which piece together and indicate the 3-dimensional ramifications of placing atoms together in molecules using accepted bonds lengths and angles for various combinations of atoms. There are several obvious omissions from this approach. Although torsional motions (those motions accompanying rotations of groups stuck to either end of a bonded pair of atoms) are allowed, there is no restriction of motion about a single bond which is an unpleasant event for long stretches of singly bonded atoms; take polymethylene for example. There is no convenient way to represent interactions between different molecules. There is an average bond length used to represent every pair of atom interactions. Even though the average length takes into account the nature of the two atoms and the nature of the bonding between them (i.e., single, double or triple bonds), it does not allow the bond angles, lengths and torsions to readjust to each new chemical environment. The next obvious step is to devise a computer image of the molecular structure under question and set down rules for accommodating each of the aforementioned drawbacks. This extension allows a very wide latitude for development of a molecular model. The obvious drawback is that the model is Newtonian - that is, it creates a molecule that is a classical mechanics model of the molecule rather than a quantum mechanical model. One can, in part, set that objection aside by insisting on the use of inter and intramolecular forces that are based on quantum mechanical potential models that have developed over the years. The issues that remain unsettled are the violation of the Uncertainty Principle which does not allow for the trajectory description of the classical model and when does a classical model begin to mimic a statistical average of a large ensemble of molecules. These philosophical issues need to be born in mind while pushing of the frontiers of the relationship between **structure and reactivity** - the keywords found at the front of every introductory general chemistry text.

So much for background and philosophical issues, there remains the description of the Newtonian mechanics applied to molecular systems. This is referred to as Molecular Mechanics. The quantum mechanical potentials typically used are shown on the next page.

Molecular Mechanics Potentials

Non-bonding interactions

$$V_{nb} = \sum_{i,j} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{\varepsilon r_{ij}} \qquad (1\text{-}6\text{-}12)$$

Bonding interactions

$$V_{bond} = \sum_{1,2} \frac{1}{2} k_b (b - b_o)^2$$

$$V_{bond\ angle} = \sum \frac{1}{2} k_\theta (\theta - \theta_o)^2$$

$$V_{torsion} = \sum k_\phi \left[1 + \cos(n\phi + \delta)\right]$$

Van der Waal radii are used to detect when atoms are coming too close together and a high repulsive energy penalty is added for interactions which infringe on the van der Waal sphere.

To cut down on the amount of computation, extended atom approaches can be applied for C-H groups (i.e., a C-H or CH_2 or CH_3 group can be replaced by a single "extended" atom)

Newton's equations of motion for quantum mechanical potentials:

$$m_i \frac{d^2 r_i}{dt^2} = -\nabla_i\left[U(r_1, r_2, \ldots, r_N)\right] \qquad i = 1,N$$

One solves the N coupled differential equations numerically to obtain the trajectories of the atoms of the system.

The definition of the temperature of the system at some time, t, is defined as:

$$T(t) = \frac{1}{(3N - n)k_B} \sum_{i=1}^{N} m_i \left| v_i \right|^2$$

where k_B is the Boltzmann constant, 3N-n is the number of unconstrained degrees of freedom in the system and v_i is the velocity of atom i at time t.

By way of explanation, one can see that the first equation on the previous page uses the Lennard-Jones 6-12 potential to describe the dispersive forces between molecules and an electrostatic term is added in as well because those forces are of equal or greater importance in describing intramolecular interactions. Since we are free to make the charges (qi and qj) non-integer, a semiempirical estimate of charges is warranted for a more accurate simulation of the molecular mechanics (dynamics) of polymer systems. The next three equations relate to the intermolecular forces found between two (bond), three (bond angle) and four (torsion) atoms. The first two interactions of this set are cast in the harmonic oscillator formulation and do not allow molecules to dissociate. This has the advantage that one can raise the "temperature" of the system (as defined in the last equation on the previous page) to several thousand Kelvins and preserve the molecular integrity of the system under study. Not that one supposes that ordinary organic molecules would not dissociate, but this allows for the search of other equilibria configurations of the molecular system under study through the mathematical device referred to as "simulated annealing". By "heating" the molecular system to very high temperatures, one can push the molecular conformations past very high potential barriers and sample other potential minima. This allows a more thorough search of configuration space when looking for a global energy minimum. The torsional potential function is definable for all sets of four atoms which are chemically bonded. A simple cosine series allows the description of torsional barriers and wells. In ethane, for instance, there are 3 trans and gauche conformations about the carbon - carbon single bond and hence the value of "n" in the cosine function is set at 3. One could add multiples of the fundamental value of "n" if different trans or gauche positions are not equivalent (as in the case of 1,2 dichloroethane). For a rather general and thorough treatment of the development of molecular dynamics programs, one is best referred to the Advances in Chemical Physics[1] series. Although the title indicates a specialization in biopolymers, the background chapters are quite general and the extension to industrial polymers is obvious.

---

[1] C.L. Brooks III, M. Karplus and B.M. Pettitt, "Proteins: A Theoretical Perspective of Dynamics, Structure, and Thermodynamics", Advances in Chemical Physics, Volume LXXI, 1988.

Annealing in Polyester Liquid Crystals

Up to this point there has only been a ground work description of why and how to apply molecular dynamics calculations to polymer systems. It is time to address the problem at hand for this conference. An ideal candidate for study of the annealing phenomena mentioned in the abstract is the oligomer derived from the reaction between phenethyl hydroquinone and terephthaloyl chloride. An oligomer of 4 monomer units is shown below (figure 3).

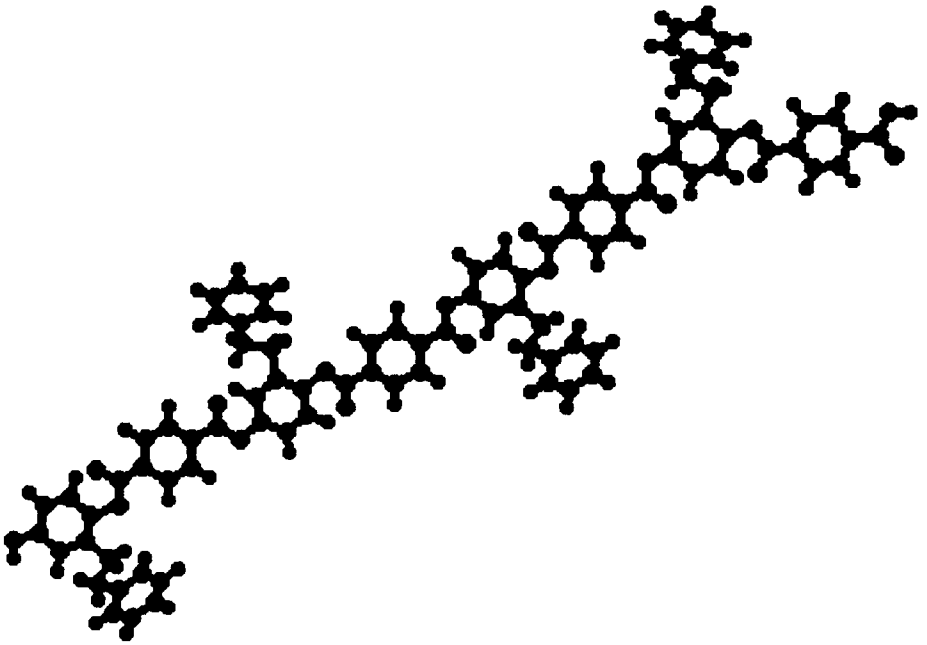


Figure 3. The above oligomer is comprized of 4 ester units of terphthaloyl chloride and phenethyl hydroquinone.

There are several key features to note on this figure. The phenethyl groups are relatively free to move about from a position of just above a phenyl ring in the backbone of the oligomer to other backbones or phenethyl groups on adjacent, parallel chains. These phenethyl groups can readily assume an orthogonal orientation to other aryls found in the vicinity. This orthogonal orientational preference is demonstrated in the crystallization of benzene[2] and has

---

[2] (a) D.E. Williams, "Calculated Energy and Conformationa of Clusters of Benzene Molecules and Their Relationship to Crystalline Benzene", Acta Cryst. A36, 715-23 (1980); (b) N.L. Allinger and JH Lii, "Benzene, Aromatic Rings, Van der Waals Molecules, and Crystals of Aromatic Molecules in Molecular

been incorporated in molecular mechanics parametrization schemes. The primary effect is that due to the acidity of the hydrogens on one benzene ring being drawn to the aromatic pi electron cloud of a neighboring ring. This type of relatively weak interaction is significant in the solid phase and when accompanied by many other like interactions, one gets a large total effect.

Another point of reference in figure 3 is to note that on the average there is one carbonyl belonging to an acid functional group and the other carbonyls belong to ester functional groups. If one does his or her arithmetic correctly, he or she will see that there is a ratio of 2n-1 to 1 ester to acid carbonyls where n = the number of polyester units. If one performs an FTIR (Fourier Transform InfraRed) spectrum of the polyester and fits the carbonyl peaks to the two different carbonyl stretches, the areas under the curve are directly related to the ratio of 2n-1 to 1. One can thereby compute the value of n and the average molecular weight (MW) and average degree of polymerization (DP). The value of n is currently thought to be about 10. If one assumes that the spread of the number of units per polymer is not very wide (which is typical for condensation polymerizations such as this one), there is a simple equation that relates the fraction of conversion (p) to the average DP[3].

$$DP = \frac{1}{1 - p}$$

One can easily verify that an average DP of 10 would result in the consumption of 90% of the reacting materials.

In order to compare the intensities of two different carbonyl groups, one should correct the intensity of the two different carbonyls so that they properly reflect the true concentrations of the two different peaks. The intensity of a particular absorption is proportional to the change in dipole moment during the vibrational excitation. This comparison of dipole intensity can be obtained using a semiempirical scheme to compute the charges on each center (noted earlier as important in the electrostatic intramolecular interaction). The scheme under consideration presently is that proposed by Rappe and Goddard[4]. This not only allows for the charge calculation at the atomic sites, but also an analytic expression

---

Mechanics (MM3)", J. Comp Chem, 8, 1146-53; (c) E.G. Cox, F.R.S., D.W.J. Cruickshank and J.A.S. Smith, "The Crystal Structure of Benzene at -3°C", Proc Royal Soc London, A247, 1-21 (1958).

[3] Malcomb P. Stevens, **Polymer Chemistry, An Introduction**, 2nd Edition, page 15, Oxford University Press, New York (1990)

[4] A.K. Rappe and W.A. Goddard III, "Charge Equilibration for Molecular Dynamics Simulations", J. Phys. Chem., 95, 3358-63 (1991).

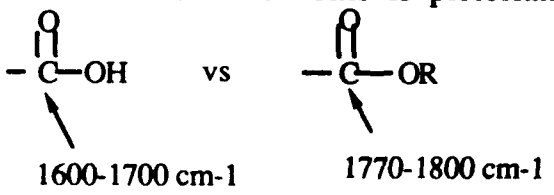
of the change in charge with atomic displacement. Using that information along with the normal mode analysis, one can compute the relative dipole moment changes (intensities) for the two different carbonyls. For an intuitive sketch of this method look at appendix A of this paper.

If one looks further at figure 3, one will note that it would be interesting to substitute the oxygen in the ester linkage with a N-H group to form the amide to see the effects of substitution with heteroatoms of similar electronegativity. This results in the synthesis of Kevlar, the tradename given to condensation reaction between terephthaloyl chloride and 1,4 diamino benzene. See figure 4 (next page) for a pictorialization of three short segments of Kevlar sitting side by side with the backbone rings parallel to one another and notably there is the chance of hydrogen bonding between the amide hydrogen of one oligomer and the carbonyl of an adjoining oligomer. This hydrogen bonding is expected based on the formation of hydrogen bonding found between beta pleated sheets of proteins[5].

Experimental

To emphasize the interaction of undergraduates in this project, this section will deal with experimental approaches to this problem that are under investigation. Undergraduates best benefit from an experience to which they can ascribe some ownership. I have found that undergraduates can more readily appreciate interpreting results that come from turning the correct knobs and mixing the right reagents. The concrete operational skills leave them with more of a sense of accomplishment and understanding. Providing undergraduates an opportunity to perform research is key to encouraging them into scientific careers.

Resuming with the thrust of this proceeding, there are two instruments that play a key role in structure analysis that are available at Butler. The first is an FTIR, which has been mentioned above in connection with DP. This is pictorialized below



[5] Lubert Stryer, **Biochemistry**, 3rd edition, page 28, W.H. Freeman and Company, New York (1988).

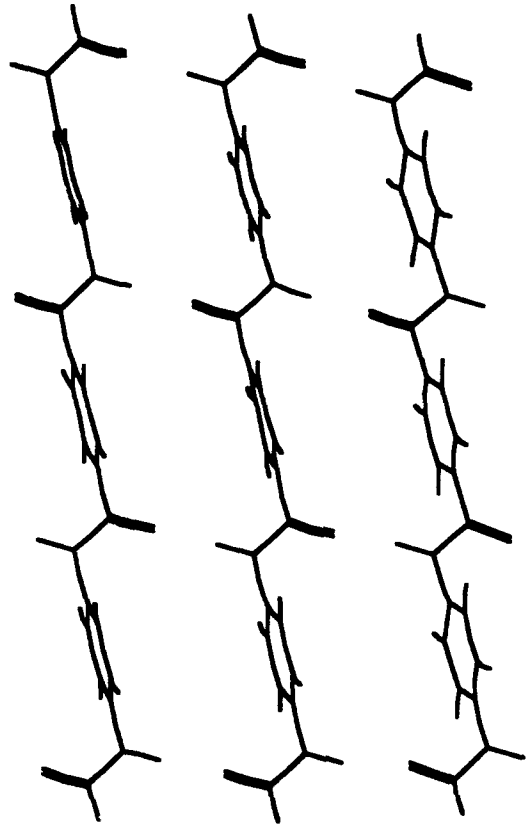


Figure 4. Hypothetical stacking of Kevlar oligomers with hydrogen bonding interactions shown in analogue with β-pleated sheets found in proteins

Another experiment that will soon be possible is the use of a catalytic chamber which allows the infrared monitoring of solid materials at reduced or elevated pressures and elevated temperatures. One can perform diffuse reflectance on a sample held at 5-10 degrees below the melting point for an extended period of time to observe infrared changes that would hint at structural changes associated with annealing of annealable LCPs.

The second instrument available to us is an NMR which can be used to test chemical environmental changes for different protons or ^{13}C or ^{19}F. The ^{19}F would require the synthesis of the appropriate fluorocarbon to allow the specific site to be labeled for NMR work. An interesting alternate study would be Magic Angle Spinning NMR which would look direct at the solid state material. Otherwise it is a matter of dissolving sufficient oligomer to get sharp enough peaks for analysis. Here again one could observe the integrated intensity of

the aryl groups relative to the acid proton or the hydroxyl proton found (on the average) at either end. If each unit is the same as all others (i.e., there is not a mixture of copolymers), then the number of aromatic protons times the DP would be equal to the ratio of the aryl integrated intensity to the acidic or hydroxyl proton.

Theoretical

Currently, there has been the acquisition of a Silicon Graphics Personal IRIS workstation along with the software CHARMm and Polymer Dynamics (Polygen Corp. is the software vendor for these products). Along with this the purchase of MOPAC (a semiempirical molecular orbital software package) has been made and that program has been installed and tested for bugs. Last but not least is the writing and testing of the code for the calculation of electrostatic point charges associated with atoms in a molecule according to the prescription of Rappe and Goddard. The formalism and code for the dependence of charge on atomic coordinate displacement has been completed. This when implemented into code can be used with the normal mode coordinate analysis generated by MOPAC to produce the relative intensities of infrared fundamental transitions. The IRIS is setup and the time consuming process of learning how to operate the software as well as discovering all the software options is now in progress.

Concluding Remarks

One might ask, "Could the (global) energy minimized structure be obtained by starting with an arbitrary structure and use simulated annealing to produce the structure of minimum energy?". To answer this question, one might first consider obtaining the α-helix structure of a protein from a random coil configuration. Consider a protein consisting of five amino acid residues (an unrealistically small protein) which starts in a random coil configuration. Proteins structures are characterized by two torsional angles as shown below:

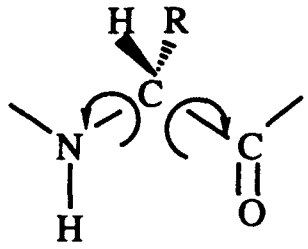


Figure 5. The two torsional angles that need to be described per amino acid residue are indicated by the curved arrows above. This unit represents a monomer of a biopolymer. There is essentially no torsional motion about the C--N bond around body temperature or lower.

The reason to pick 5 residues is that there are 3.5 residues per helical turn, so the ability to recognize a helical structure requires at least 5 or more residues. The final ingredient in this analysis is to note that there are at least two energy minima per torsional angle. Therefore the two torsional angles per residue times the five residues leads to the number of configurations of energy minima as 2^{10} (i.e., the number of energy minima raised to the total number of torsional angles) which is approximately 10^3. That is a large number of configurations for a small number of residues in a protein, especially when the energy search proceeds in a random fashion. As one can see, it is fruitful to at least narrow the field of configurations by some judicious choice (i.e., chemical intuition) of configurations to study. This does not even address the question of whether the global minimum energy is the only structure to be investigated. Protein structure has been determined over many years of many experimental and theoretical approaches to come up with some criteria for reasonableness of structure. In the final analysis, it is the synthesis of theory and experiment that produces a coherent picture of structure and reactivity.

Appendix A

I. Electrostatics (Rappe and Goddard)

Single atom dependence on charge:

$$E_A(Q) = E_{A0} + Q_A \frac{\delta E}{\delta Q}_{A0} + \frac{1}{2} Q_A^2 \frac{\delta^2 E}{\delta Q^2}_{A0}$$

or

$$E_A(Q) = E_{A0} + \chi_A^o Q_A + \frac{1}{2} J_{AA}^o Q_A^2$$

where $\chi_A{}^o$ is the electronegativity of element A and $J_{AA}{}^o$ is the self-coulomb potential.

Applying this to molecules and allowing for charge equilibration through coulombic interactions:

$$E_Q(Q_1,\ldots,Q_N) = \sum_A \left(E_{A0} + \chi_A^o Q_A\right) + \sum_{A,B} Q_A Q_B J_{AB}$$

where $J_{AA}(R) \rightarrow J_{AA}^o$ as $R \rightarrow 0$

where $J_{A,}$ is the two electron-two center coulomb integral which is analogous to Coulomb's law except that the point charges are replaced with electron probability densities which must be integrated over all space in order to include the entire electron density. Ultimately, the above equations coupled with the condition that the total charge on the molecular species equals the sum of the individual atomic charges are reduced to a matrix equation which depends on evaluation of the two electron-two center coulomb integrals, and input of the atomic properties of electronegativity and the self-coulomb energy. Solution of the matrix formulation yields the atomic charges in the given molecule. This method has been written into FORTRAN code and currently runs on a VAX at Butler University. There is under development the writing of the code for the assessment of the first derivative of the charge dependence with respect to change in the atomic coordinates. With this information and the normal mode coordinate analysis of the vibrational modes of a molecule, one can compute the relative intensities of all the fundamental vibrational modes.

THERMOTROPIC LIQUID CRYSTAL POLYMER IMAGING USING THE ATOMIC FORCE MICROSCOPE

Several thermotropic liquid crystal polymers were studied using the Atomic Force Microscope (AFM), one of several scanning-probe microscopes introduced by Gerd Binnig and Calvin F. Quate of Stanford University in 1986. Each LCP is observed along two sections of its material, one being immediately below the exterior portion of the skin, and the other being within the interior or core region. Samples from each section is cut to approximately 2mm by 2mm dimension and then taped onto a magnetic disk which rests on the AFM scanner. The AFM, a Digital Instruments Nanoscope II product, generally tracks over smooth surfaces only, and the flow lines of each sample were oriented perpendicular to the direction of the scanning tip. Images are obtained using a silicon nitride tip, attached to the end of a triangular shaped cantilever that is either 100um or 200um in length. A laser beam at 670nm reflects from the back of the cantilever foil and focuses into a photodiode sensor. Cantilever deflections, as the tip scans over surface topography, cause the laser beam reflecting from the cantilever to deflect. These deflections are measured by changes in the light falling on different parts of the photodiode. The AFM images are in the 'force mode', meaning that the 'z' scale is in nanonewtons. The AFM process is time-consuming due to the rough nature of these samples. Successful images, however, were reproducible and the scan rate was no more than 3.5Hz.

Unlike the Scanning Tunneling Microscope (STM), the AFM senses non-conductors, as well as conductors or semi-conducting materials. The tip and sample are brought close enough together such that electron clouds between the two repel. This electrostatic repulsion is responsible for the cantilever deflections as the tip 'drags' over the surface. The atomic forces involved are of the order of 10-9 Newtons.

Incremental movements in the 'x', 'y', and 'z' directions are made possible by rigid piezoelectric tubing which acts as the scanner element. Piezoelectrics have the property of exhibiting mechanical strains, e.g. expansion and contraction, when subjected to an electric field. The 'z' movement is controlled by a feedback loop which uses the deflected beam as an input parameter. Voltages along the 'z' direction vary in response to these deflections.

Illustrations of AFM images of HX-4000, SRT-300, A950, and SRT-500 are depicted in Figures below. In each case scan sizes are 5um in dimensions. Skin and core regions appear to show structural differences; the skins contains smaller nodules and lumps than their corresponding core regions. The latter exhibits large faceted domains more frequently than their counterparts. These observations are in agreement with x-ray results.

The AFM images of HX-4000 for both skin and core regions show the same orientation. A significant difference between the two is the crystallite size. Average nodules on the skin are 1x1 elliptical

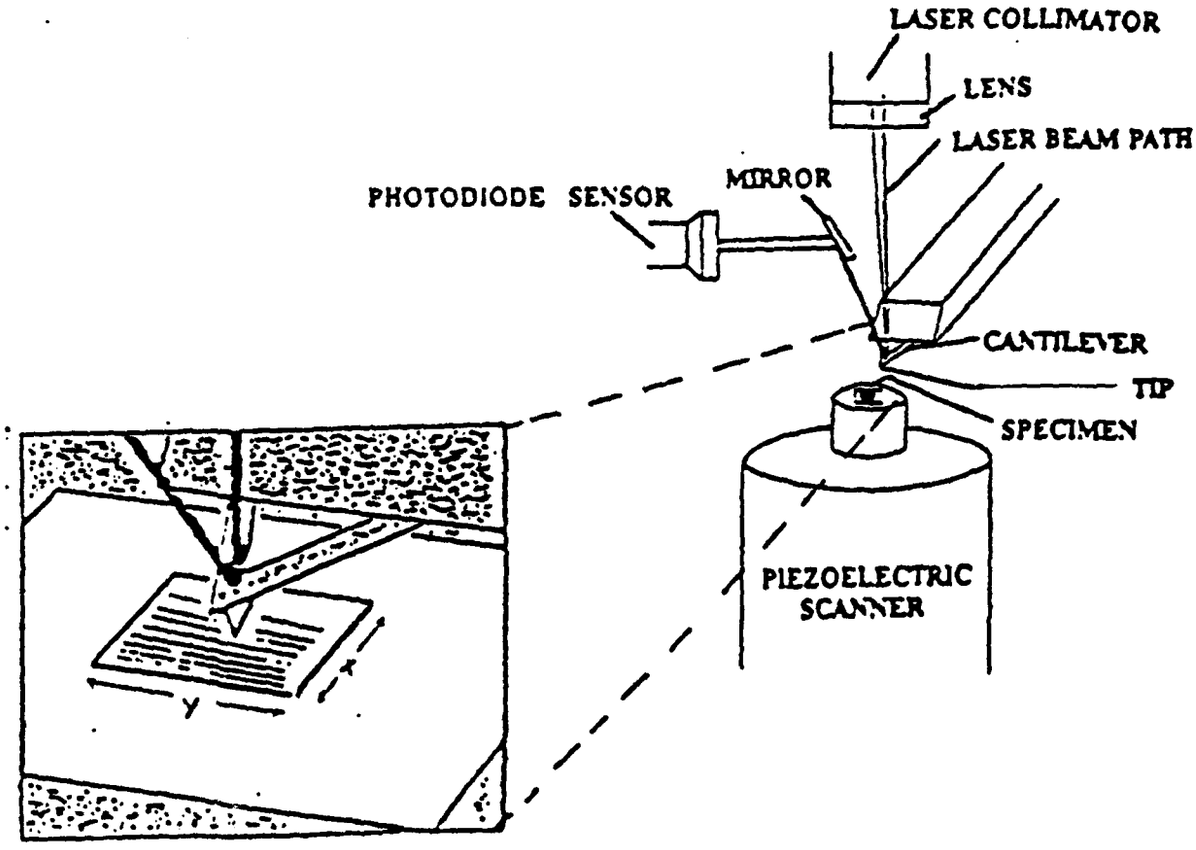
configurations that average 300nm in width along most of the surface. The core, however, shows elliptical regions that average 1000nm in width.

AFM images of SRT-300 reveal high orientation for both skin and core surfaces. Small crystallites on the skin region are 1x1 ellipses that average 300nm while those existing on the core region appear to be 10X1 ellipses that average 400nm in width.

The polymer, A950, reveals a skin region that is highly oriented along the flow axis. Nodules tend to be 1X1 nodules of 200nm width. The core region tends to be isotropic and containing a multitude of large crystalline regions of 10X1 geometry averaging 1000nm width. These regions are often oriented at random.

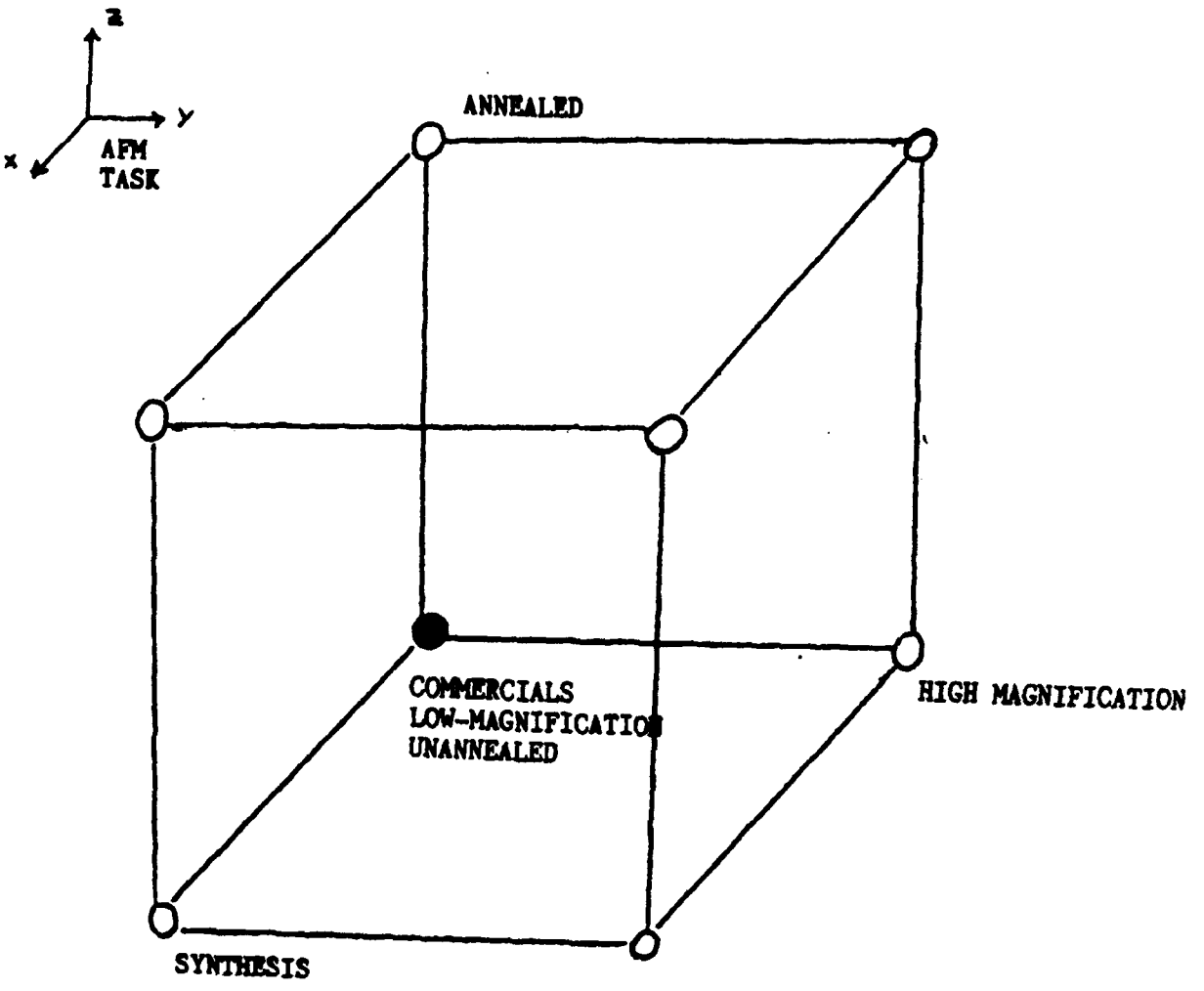
The companion polymer of SRT-300, SRT-500, reveals the most pronounced differences between the skin and core regions. Small crystallites in the skin region appear as 200nm, 1X1, ellipses. The core region reveals larger crystallite structures, averaging 400nm in width and grown as 10X1 ellipses.

Schematic of Atomic Force Microscope



LIQUID CRYSTAL POLYMER

DAVID S. SILVER



X = COMMERCIAL - SYNTHESIS

Y = MAGNIFICATION

Z = ANNEALING

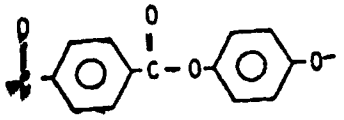
COMMERCIAL POLYMERS

SRT500
A950
C130
HX4000
SRT300
GRANLAR

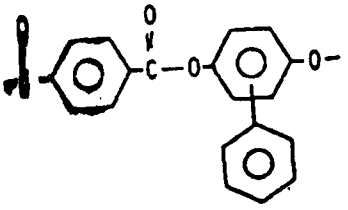
Solid/nematic

T (Melting) °C

Bulky Side Group



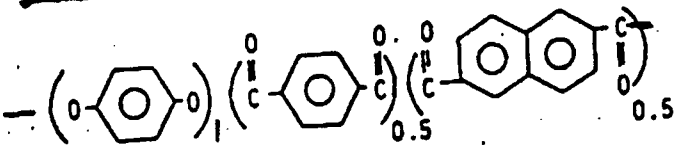
> 600



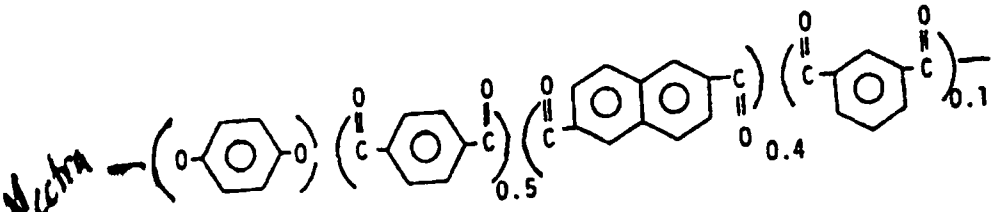
≈ 340

T (Melting) °C

Bent Monomer



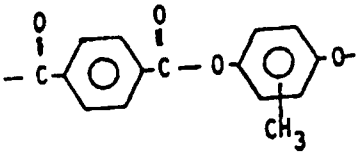
≈ 400



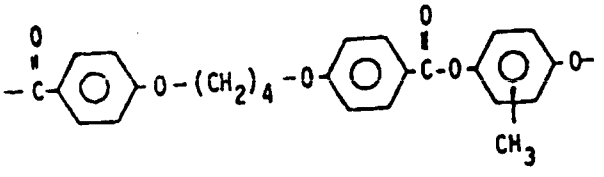
≈ 350

T (Melting) °C

Flexible Group

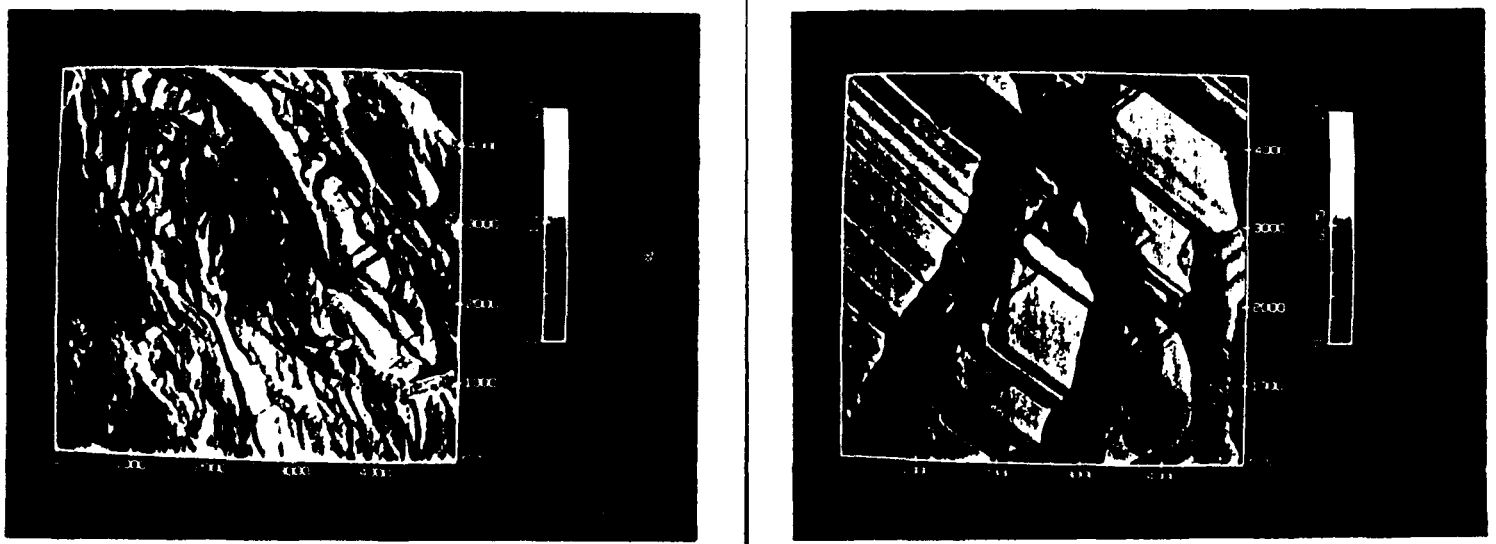


> 400

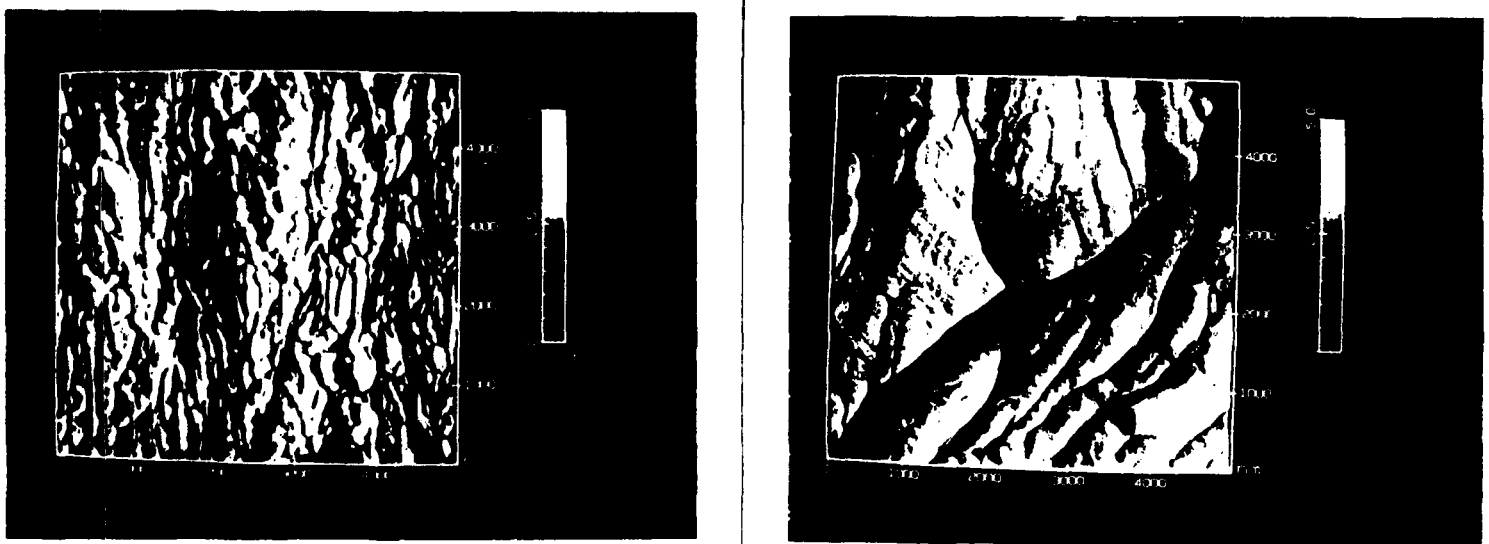


≈ 210

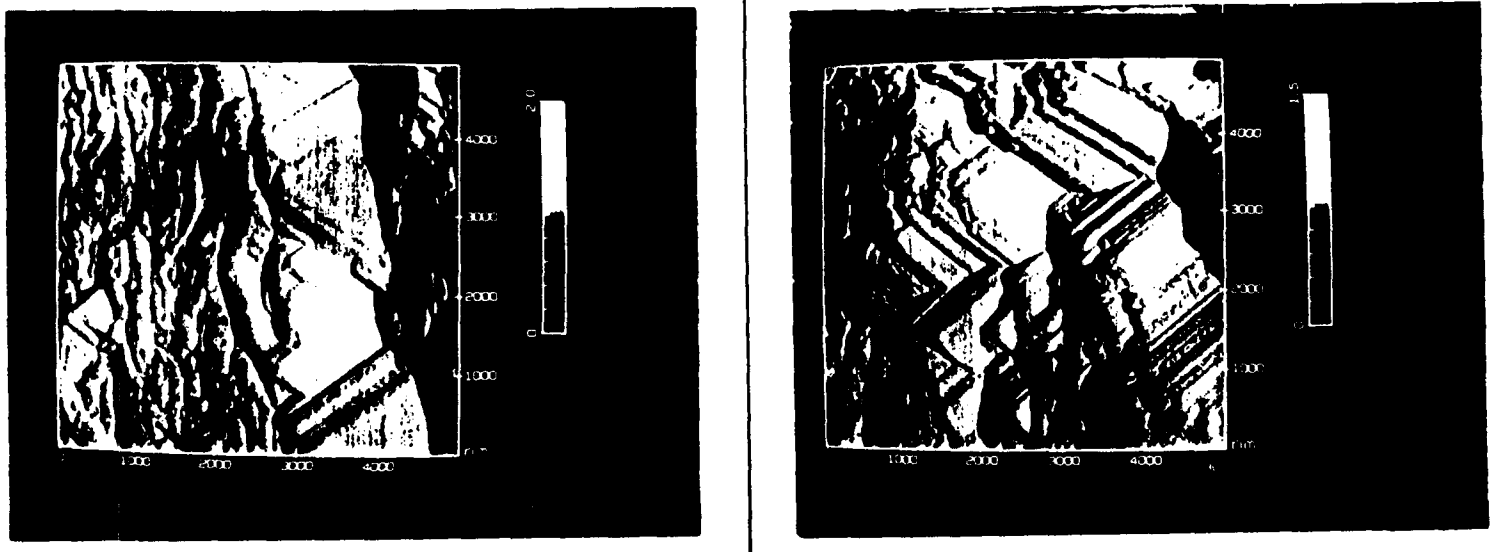
Melting Point vs Structure.



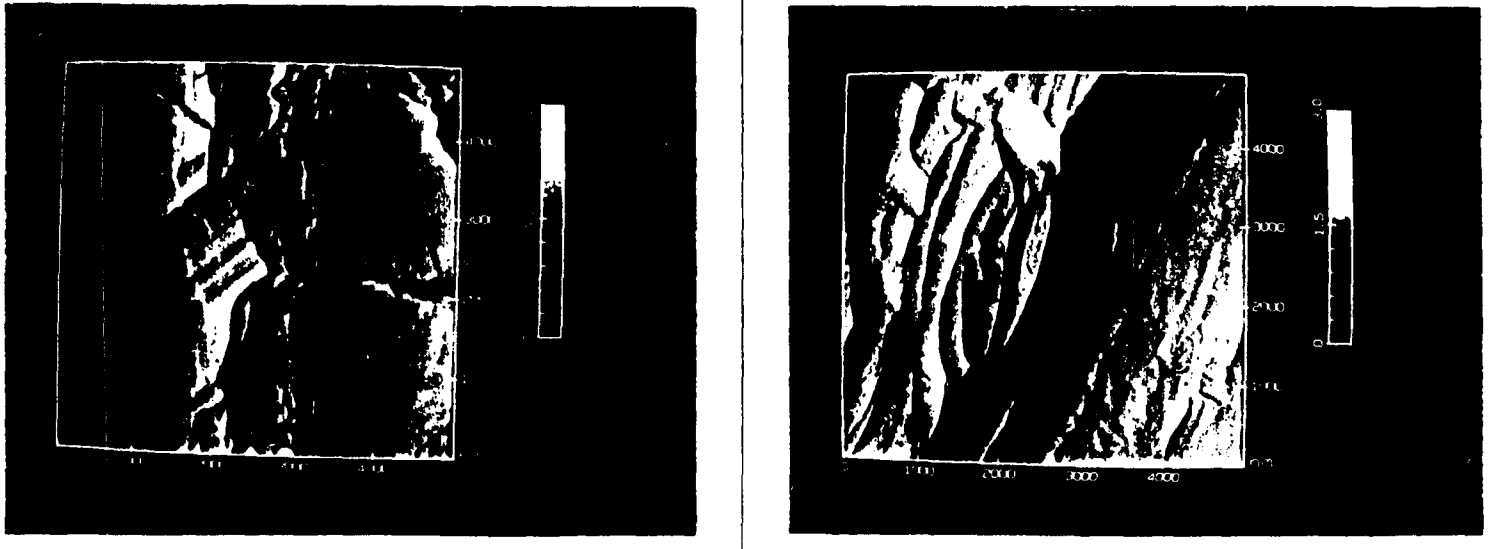
AFM images of CELANESE VECTRA A950 polymer taken of skin and core regions



AFM images of AMOCO XYDAR SRT-500 polymer taken of skin and core regions



AFM images of DUPONT HX-4000 polymer taken of skin and core regions



AFM images of AMOCO XYDAR SRT-300 polymer taken of skin and core regions

Surface Spectroscopy

J. Adin Mann, Jr.
Department of Chemical Engineering
Case Western Reserve University
Cleveland, OH 44106

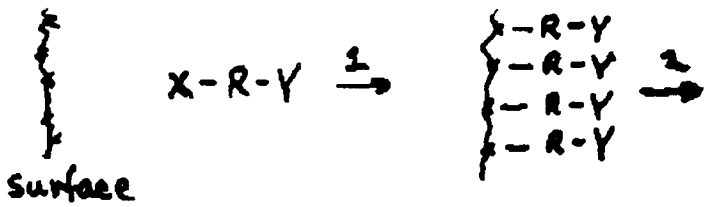
This project is just being funded so that work reported herein illustrates techniques rather than represents work done under contract. A major thrust is to use surface analysis techniques to study annealing effects in the surfaces of liquid crystal polymers.

The techniques discussed include the Raman spectroscopy of ultrathin films which in this case are monomolecular films on various substrates. These surfaces are also being studied by surface sensitive x-ray diffraction techniques. We are planning to develop various ellipsometry techniques for the project with a special focus on ellipsometric spectroscopy in the IR region of the spectrum.

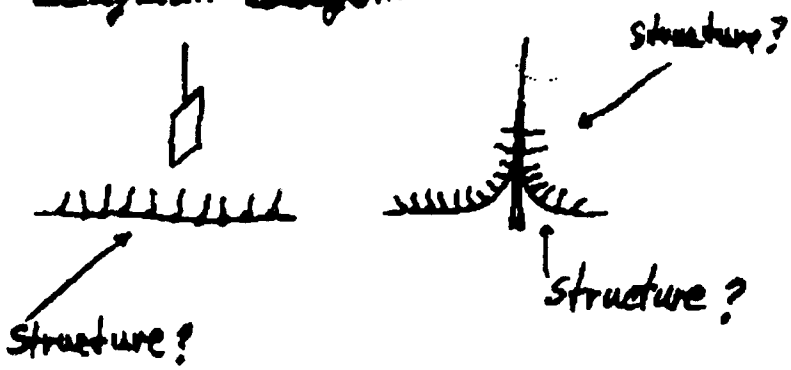
There follows a set of figures that are briefly annotated to show results obtained to date with several of these techniques.

Surface Modification

1. "Self assembly"

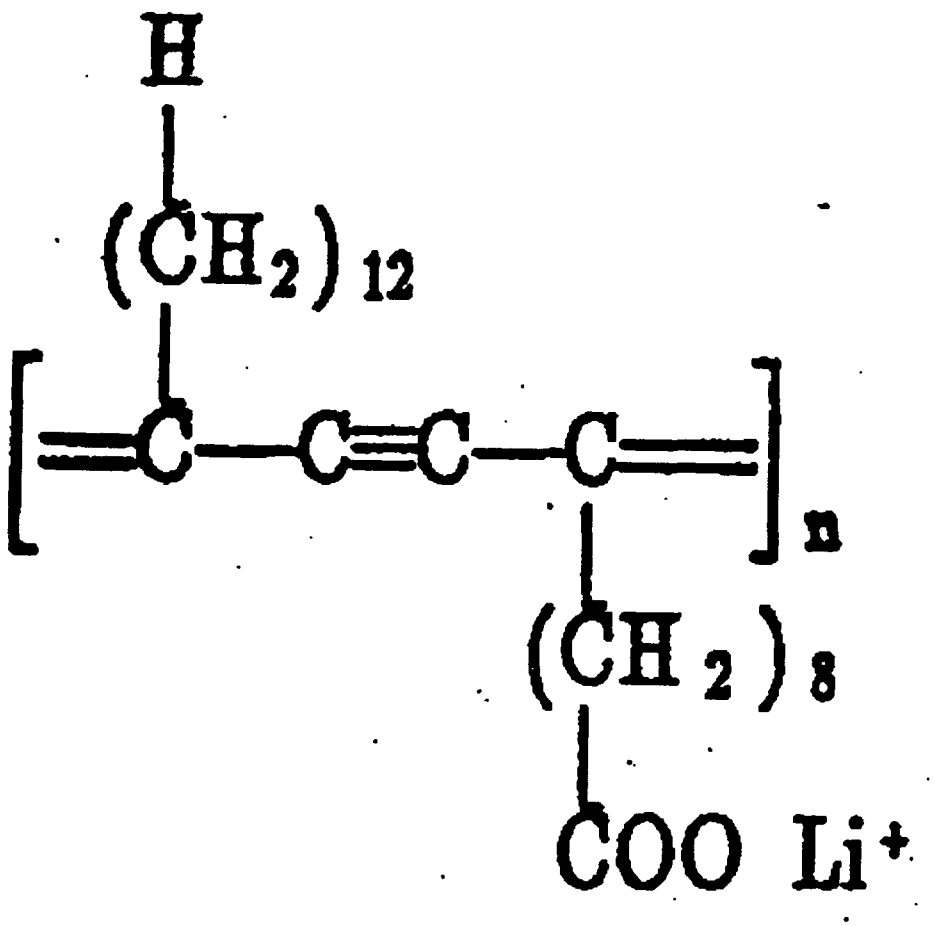


2. Langmuir Blodgett

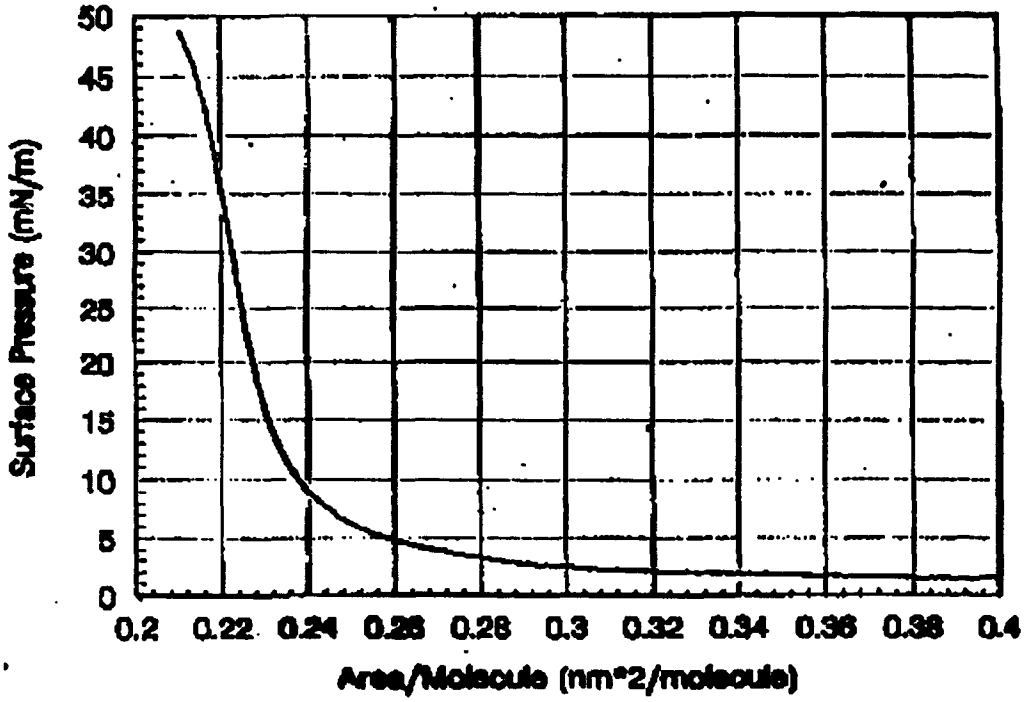


1. Surface Modification

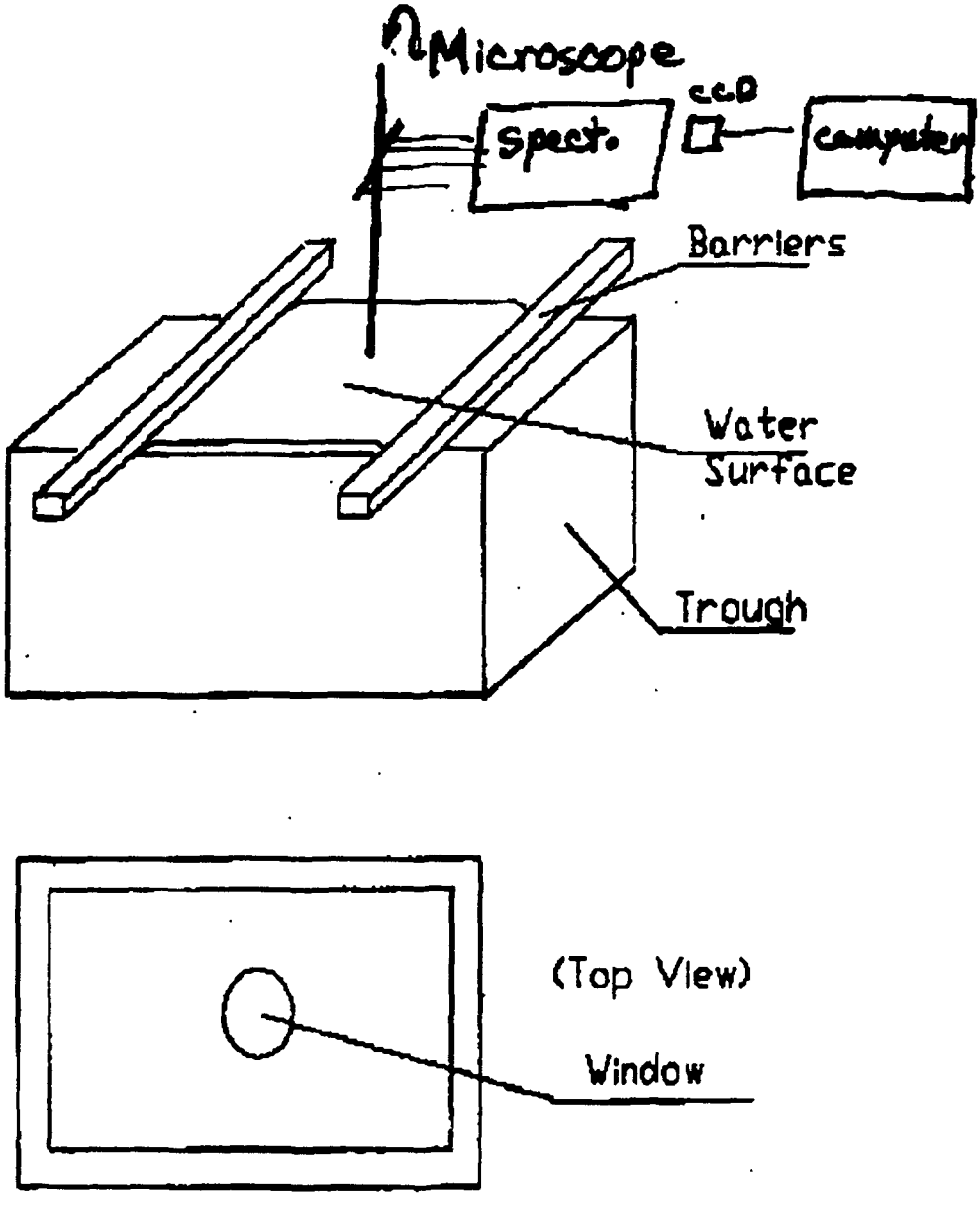
Surface modification by self-assembly of organic monolayers are shown for a detailed discussion of these methods see A. Ullman, "An Introduction to Ultrathin Organic Films . . .," Academic Press. ISBN 0-12-708230-1, QC176.9.073U44,1991.



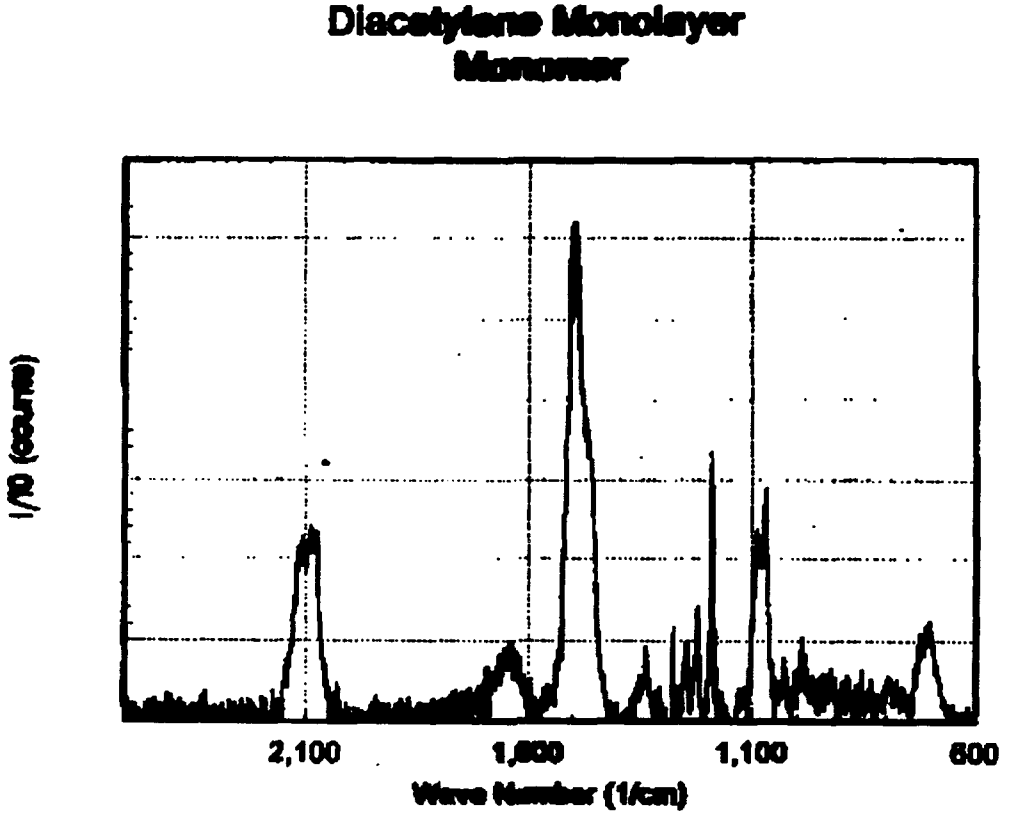
Before polymerization, the monomer inside [·] has two acetylene groups separated by one carbon-carbon bond. The monolayers of both form solid, two-dimensional crystals. Polymerization is done in situ using UV light. The structure is studied with the monolayer on the surface of the water, then it is transfered to a solid substrate using the Langmuir Blodgett technique (LB).



The isotherm of unpolymerized diacetylene. Polymerization is done with a dilute LiOH solution as the substrate and the film compressed to about 15 mN/m.

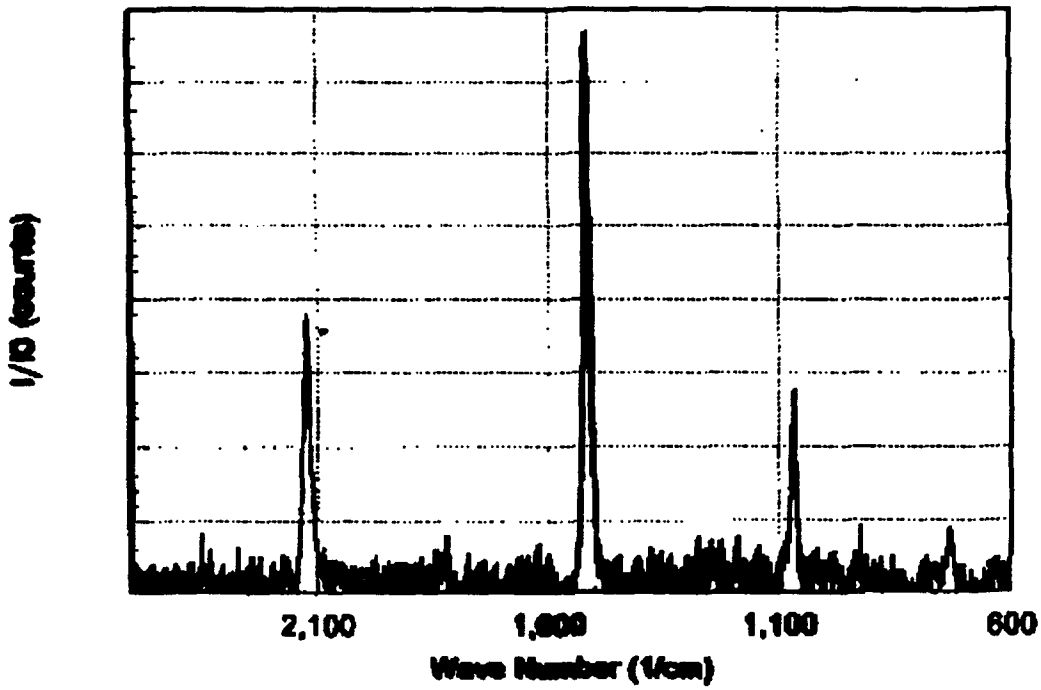


Rough diagram of the Langmuir through used to control the monolayer during the Raman scattering experiments. A Dilor x y Raman spectrometer was used; the trough fit on the microscope stage that is part of the instrument.



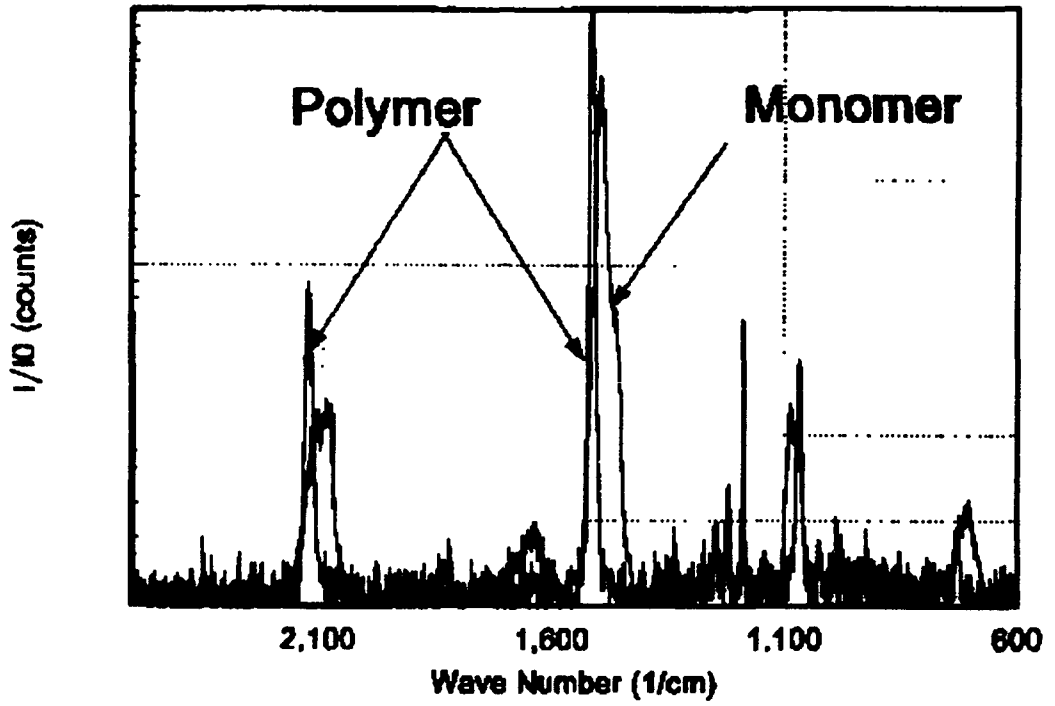
Raman Spectrum of the unpolymerized monolayer spread at the air water interface. The bands have been assigned based on the monomer structure. Note the quality of the spectrum even though the scattering crossection of a monolayer is small. So far as we know, spectra of this kind have not been reported before this work.

Diacetylene Monolayer Polymerized

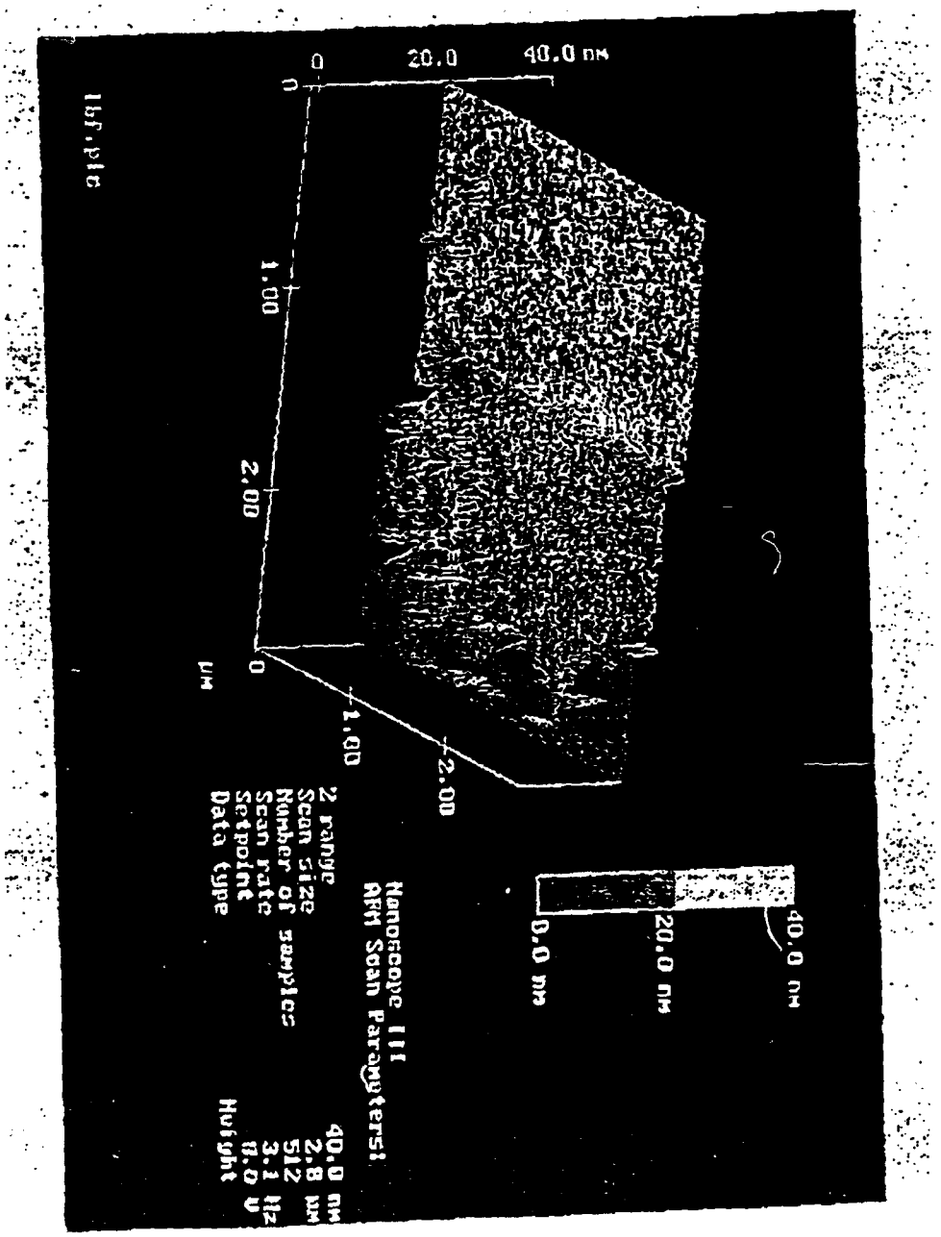


The polymerized diacetylene monolayer. Notice the simplification of the spectrum.

DIACETYLENE MONOLAYERS

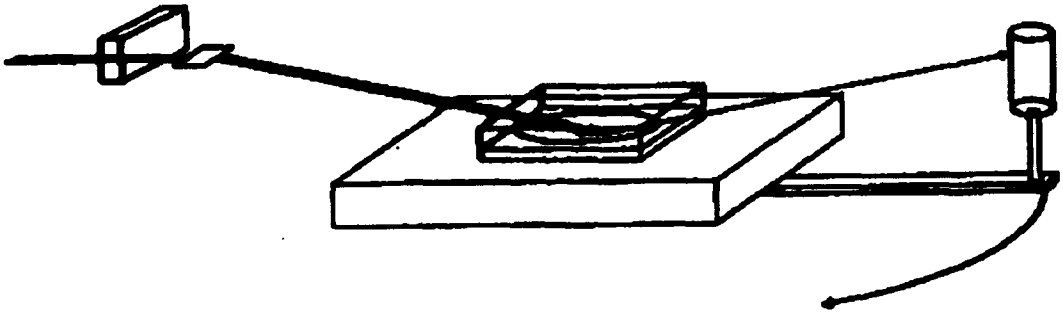


Notice the sharpness of the polymer bands. The monolayer is a two-dimension crystal and is probably of large size (> 1 mm).

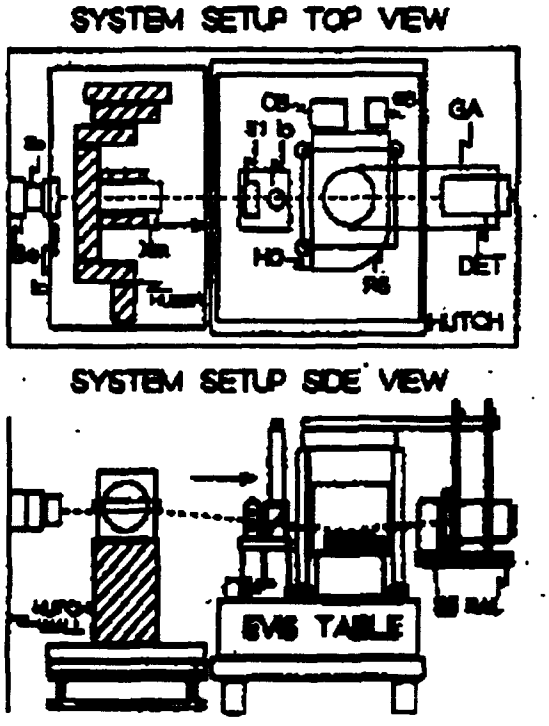


LB film of a three step disposition of a condensed monolayer. (Shih, Johnson, Mann - unpublished) AFM microscopy of LB films.

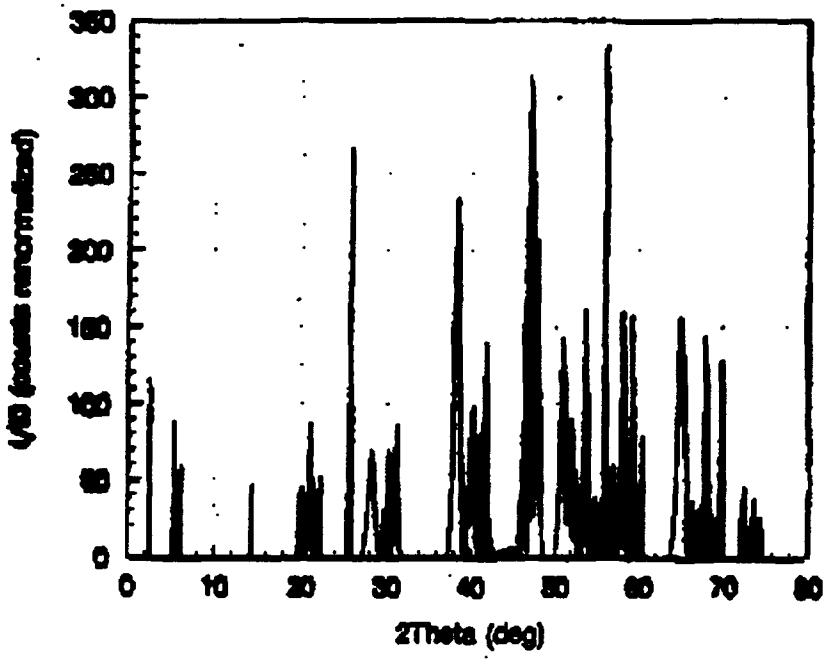
Glancing X-Ray Diffraction



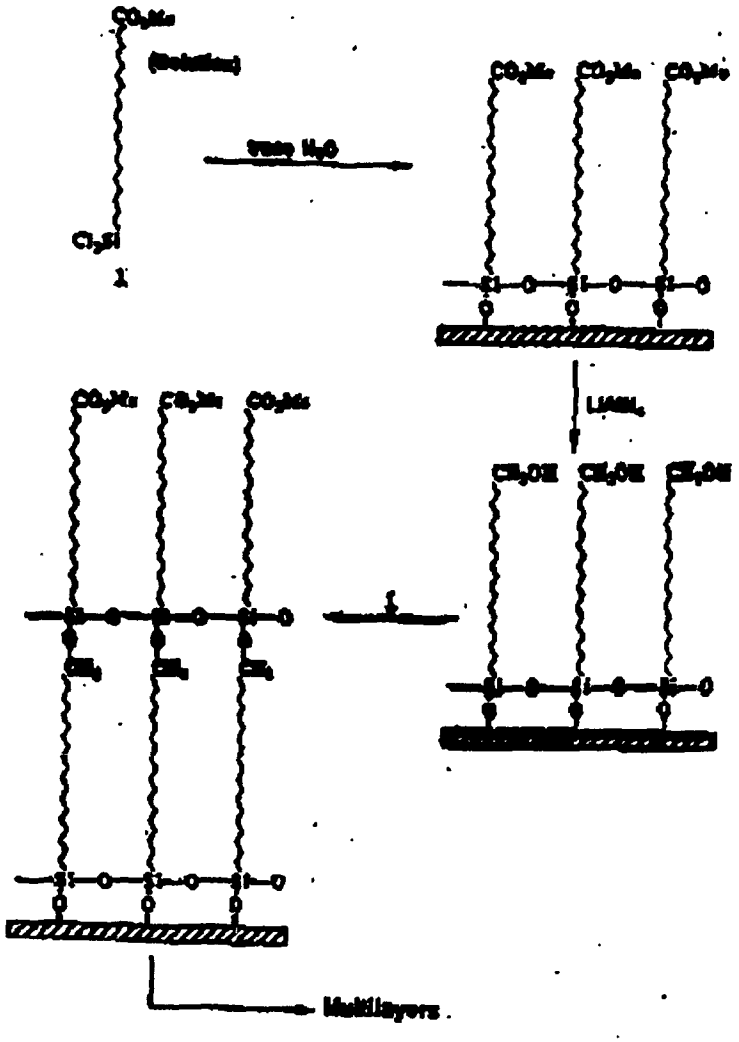
GLANCING X-RAY DIFFRACTION: Incident monochromatic synchrotron x-rays are reflected downward onto the surface at approximately 0.5° . Scattering is detected at various vertical and angular positions by a position sensitive detector.



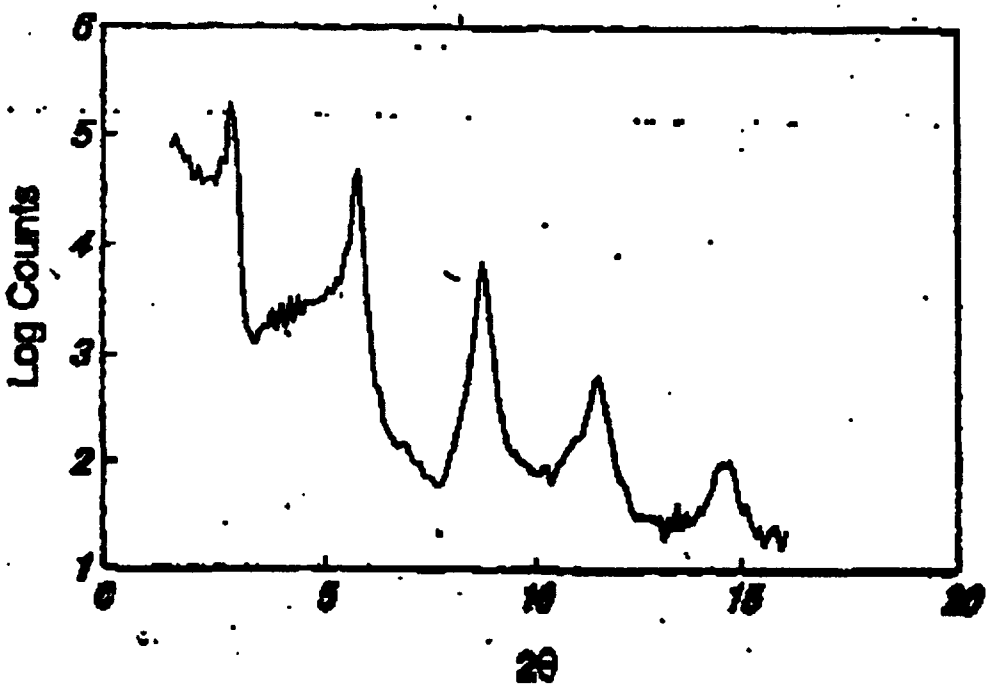
Setup used on x23B, Brookhaven. The beamline is run by NRL-ONR.



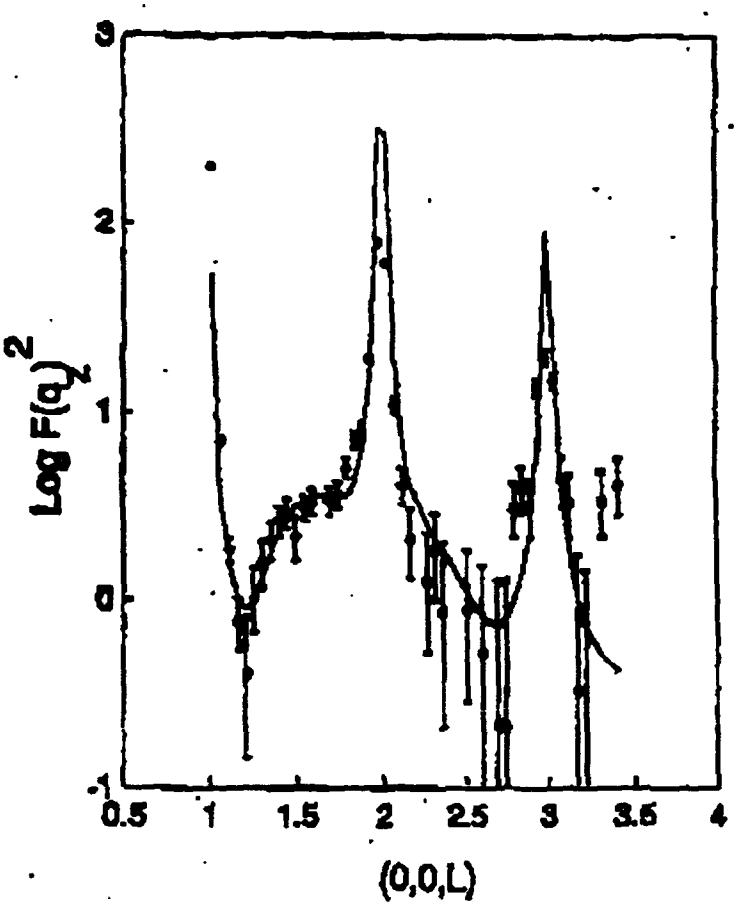
The 2Theta scan of polymerized dicetylene. The spread monolayer way polymerized in situ. The same technique was used as in the Raman studies.



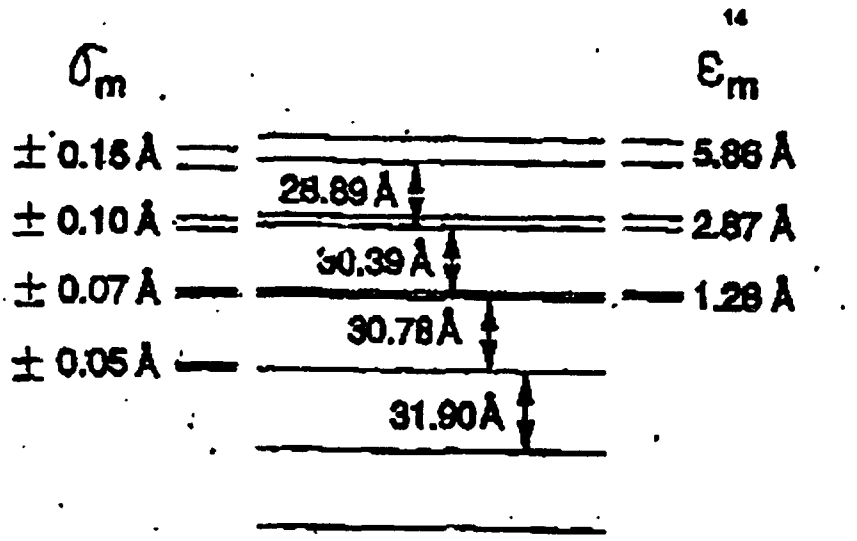
Surface x-ray scattering can be done on smooth solids of a wide variety. This monolayer is an example of a self-assembled monolayer built up on a Si substrate. The sample was provided by A. Ulman of Eastman Kodak.



A scan of the reflectivity as a function of the incident angle (and thereby the reflection angle). Notice the well formed peaks and the sholders on the 2nd and 4th peaks ($\approx$5 deg and $\approx$10 deg). The sholders are missing on the 3rd and 5th peaks. This can be modeled as shown next.



The scattering function for the layered structure was modeled and fit to the data. Notice in particular that not only are the peaks fit but the details of the sholder at $\vec{q}$ = (0,0,1.5)Å^{-1} corresponding ≈7 deq are reproduced.



This figure shows the spacings computed from the model by a least-squares computation.

LCP MEETING

Butler University, Indianapolis, IN

February, 1992

Chlorine Edge X-Ray Absorption Spectroscopy

R. W. Hoffman, *et al.*, Department of Physics, Case Western Reserve University, Cleveland, OH 44106-7079.

Chlorine Edge X-Ray Absorption Spectroscopy

ABSTRACT

Cl edge X-Ray Absorption Fine Structure (XAFS) spectra were successfully obtained for the first time in ammonium perchlorate (AP) pressed pellets during August and October, 1991 at Beamline X19-A at the National Synchrotron Light Source at Brookhaven National Laboratory. The research team consisted of Professors R. W. Hoffman and J. A. Mann and Mr. G. A. DeRose from CWRU and Drs. K. P. Chaffee and J. J. Rusek from Phillips Laboratory, Edwards AFB.

As is common, the Extended XAFS (EXAFS) spectra (greater than 50 eV above the Cl absorption edge at 2823 eV) were weak and damped rapidly, suggesting that the coordination was low-Z. A detailed phase and amplitude analysis of the EXAFS spectra is in progress and will be discussed later.

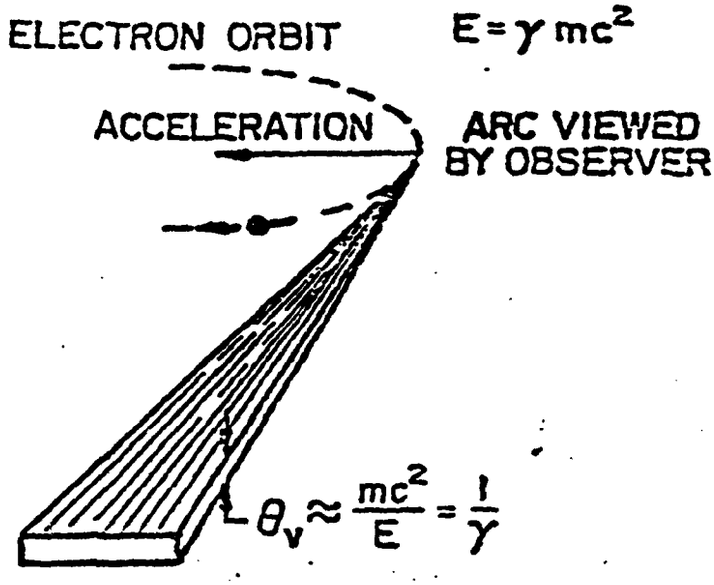
The near edge (XANES) spectra (within 50 eV of the absorption edge) were stronger and more intense. XANES expresses the Cl-local symmetry and multiple scattering and band structure effects. Unfortunately, analysis is difficult as no reliable computer codes are available. Our analysis is presently in the fingerprint stage.

Energy shift and spectral effects are presented for AP pellets with monolayer drops of various binders; we have completed and are testing program changes to use the inadvertent air Ar edge for energy calibration - a technique not readily available for the fluorescent x-ray detection used because of the very soft Cl edge energy.

We have also observed orientational differences from pressed pellets, and single crystal AP by taking advantage of the highly polarized x-rays from synchrotron radiation sources.

Copies of viewgraphs used in the presentation follow:

SYNCHROTRON RADIATION



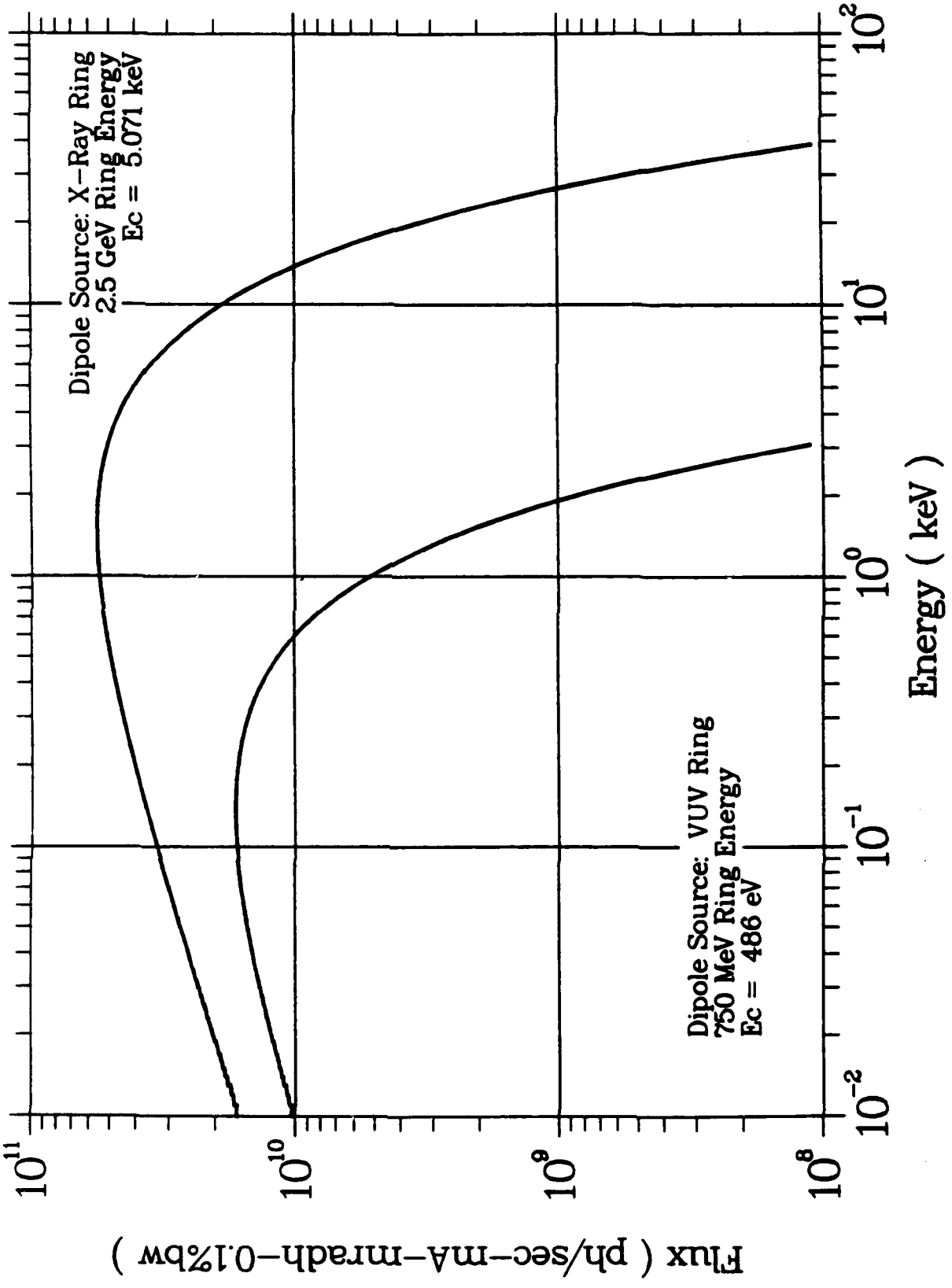
CASE II: $\frac{v}{c} \approx 1$

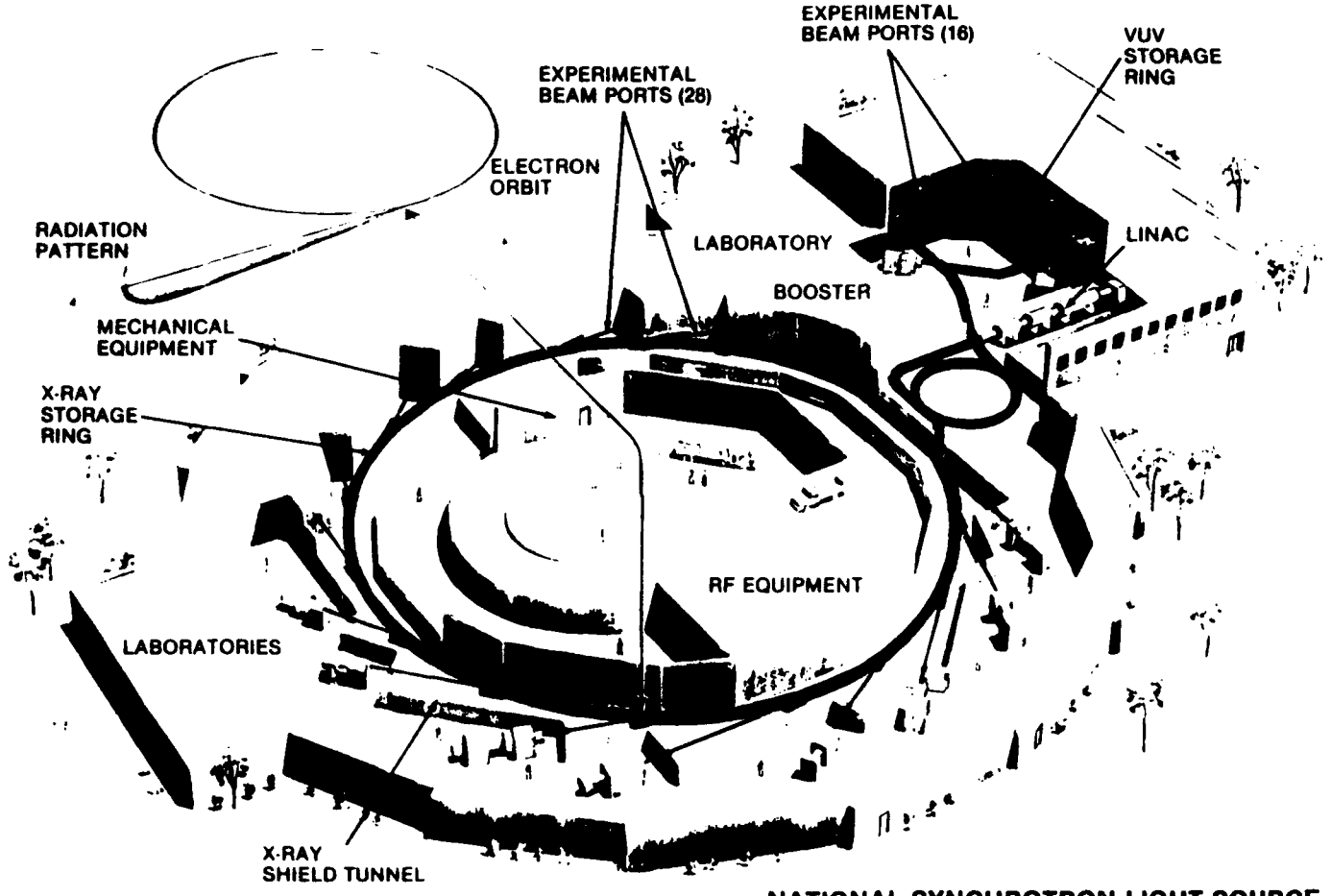
For 6-GeV Synchrotron:

$$\gamma = 11742$$

$$\theta_v \simeq mc^2/E_{GeV} = 1/\gamma \approx 85 \text{ microradians}$$

5. NSLS BENDING MAGNET SPECTRA





NATIONAL SYNCHROTRON LIGHT SOURCE
BROOKHAVEN NATIONAL LABORATORY

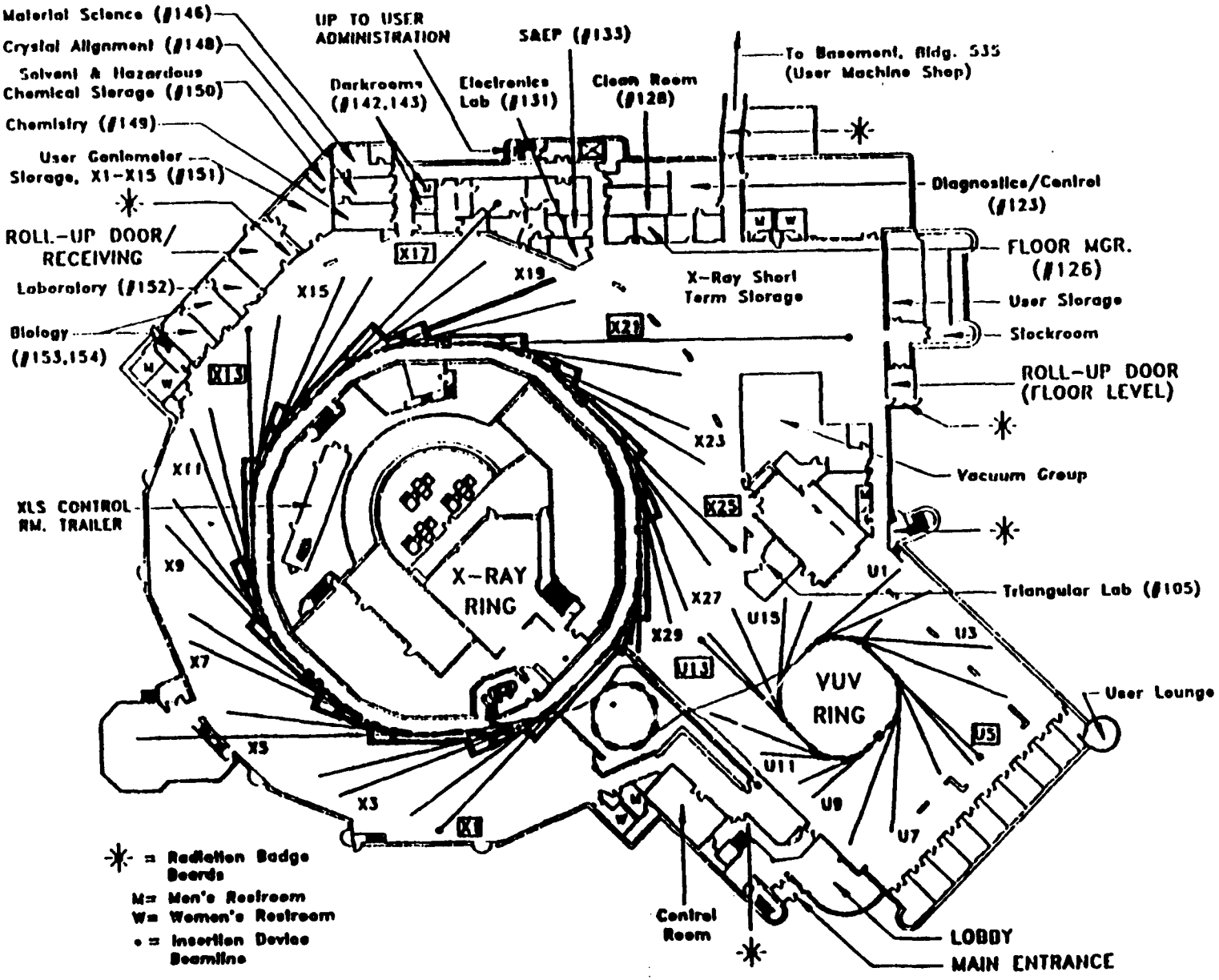


Figure 1 Floor plan of the National Synchrotron Light Source experimental area.

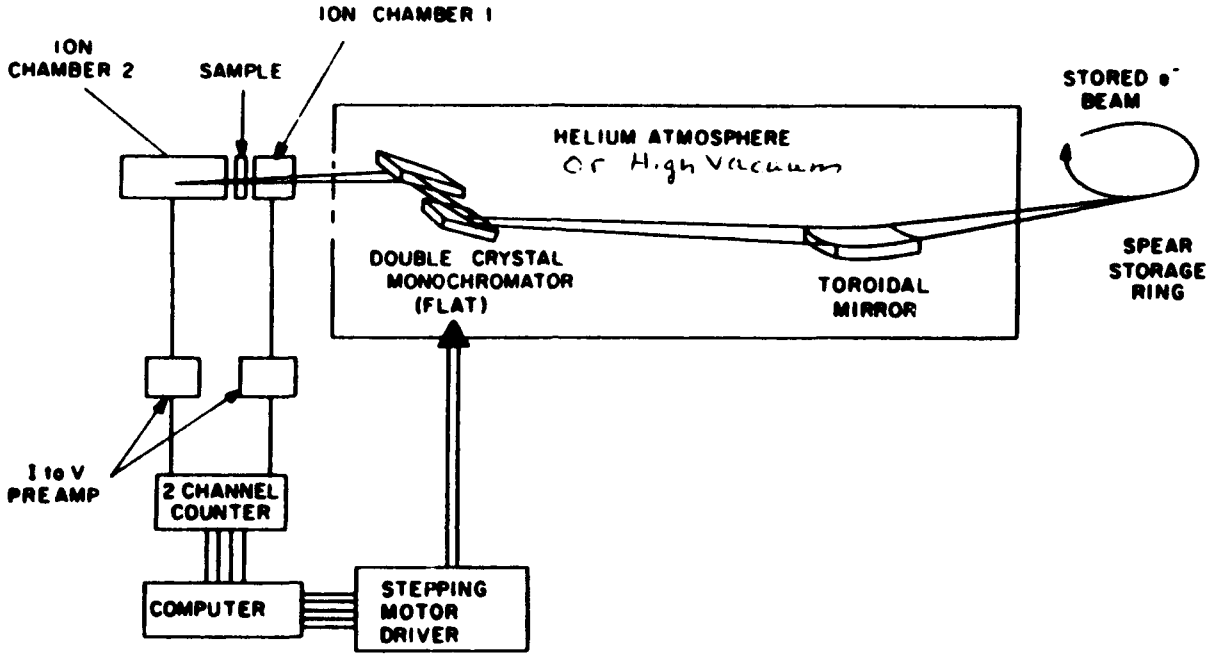


Fig. 13. Schematic diagram of the EXAFS spectrometer in transmission mode. The synchrotron radiation from the electron storage ring, represented disproportionately by a broken ellipse at the upper right corner, is collected by a toroidal mirror and monochromatized by a double crystal monochromator. The incident beam intensity is measured by the ionization chamber 1 and the transmitted beam intensity by the ionization chamber 2. The energy of the beam is changed by changing the angle between the monochromator crystal and the incident beam.

Characterization of the NSLS X-19A Beamline

A. Tunable Energy Range (keV)

Si(111)	(1)	2.19 - 7.93
	(2)	7.40 - 13.5
Si(220)	(1)	3.46 - 12.5
	(2)	12.08 - 22.1

B. Beam Spot Size

Unfocused: 4 mm (V) × 40 mm (H)
Focused: 1 mm (Diameter)

C. Photon Flux (Photons/Sec)

2.5 keV - $\sim 10^{10}$
5.0 keV - $\sim 10^{11}$
10.0 keV - $\sim 5 \times 10^{11}$
at I=100 mA, E_e=2.5 GeV, Si(111) crystal, unfocused beam.

D. Energy Resolution (eV)

1.1 eV [Si(111) with 4 mm slit at 2.5 keV]
✓ 0.5 eV [Si(111) with 2 mm slit at 2.5 keV]
1.4 eV [Si(111) with 0.1 mm slit at 7.0 keV]
0.8 eV [Si(220) with 0.1 mm slit at 7.0 keV]

E. Polarization

99% at 10.0 keV and ____ mm slit

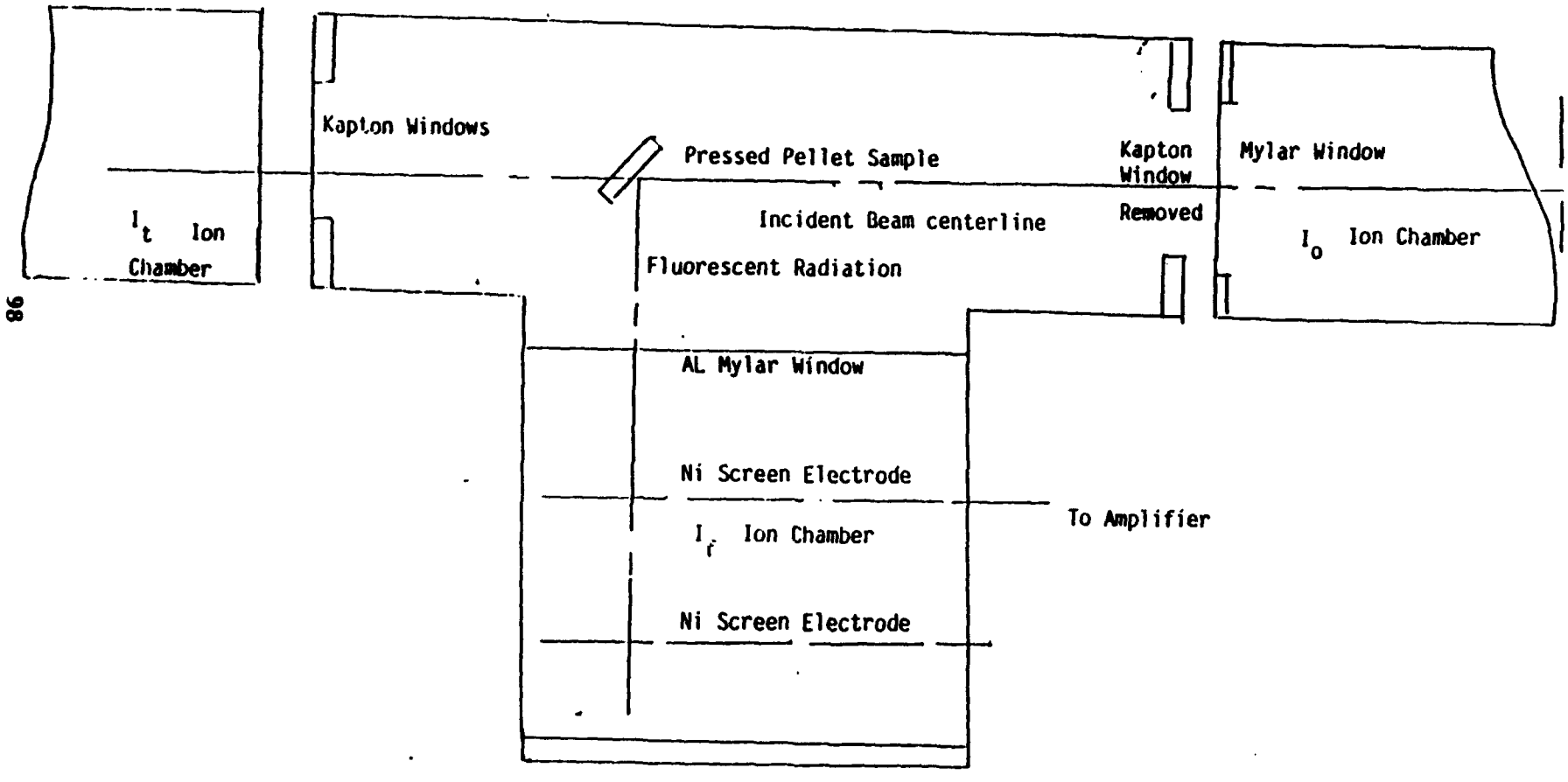
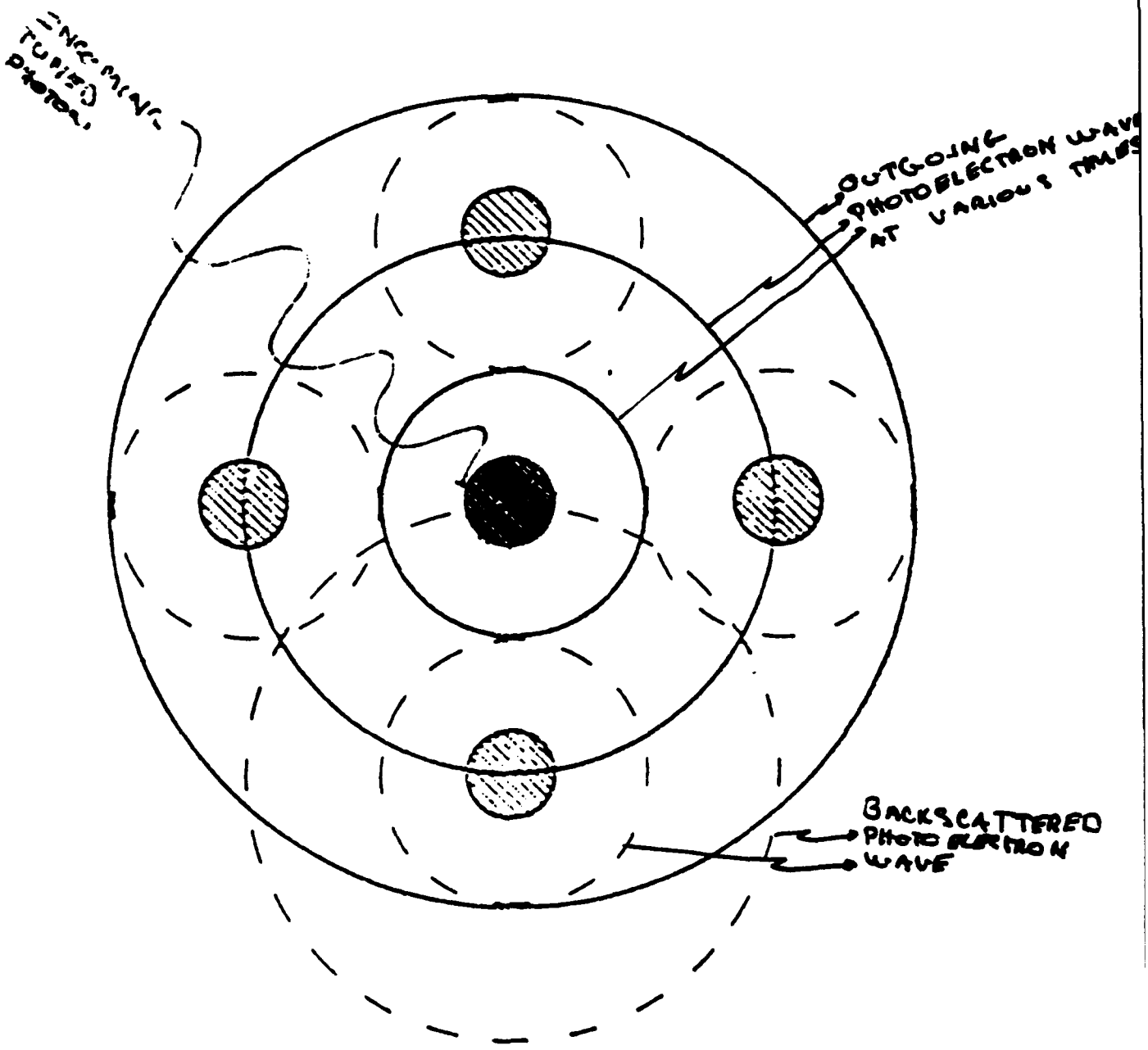


Figure 3 (CWRU) Lytle Detector for Fluorescence Detection of XANES and EXAFS



EXAFS

WEAK SINGLE SCATTERING CONCEPTS

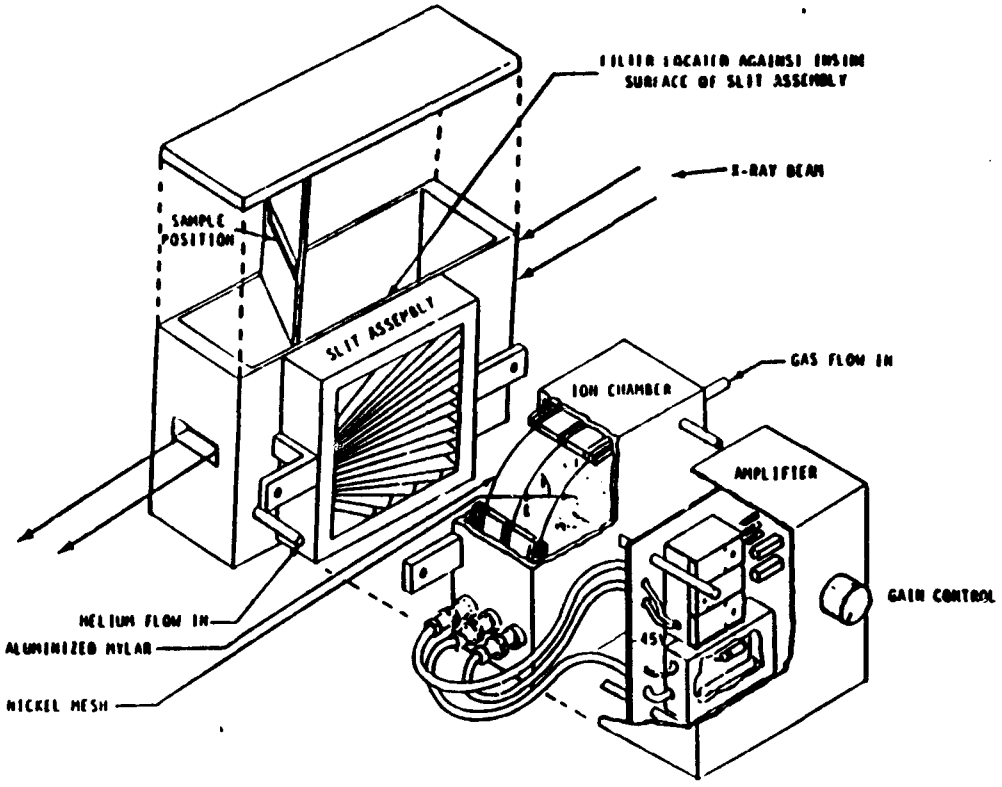


Fig. II.4.3 Fluorescent x-ray ion chamber detector.

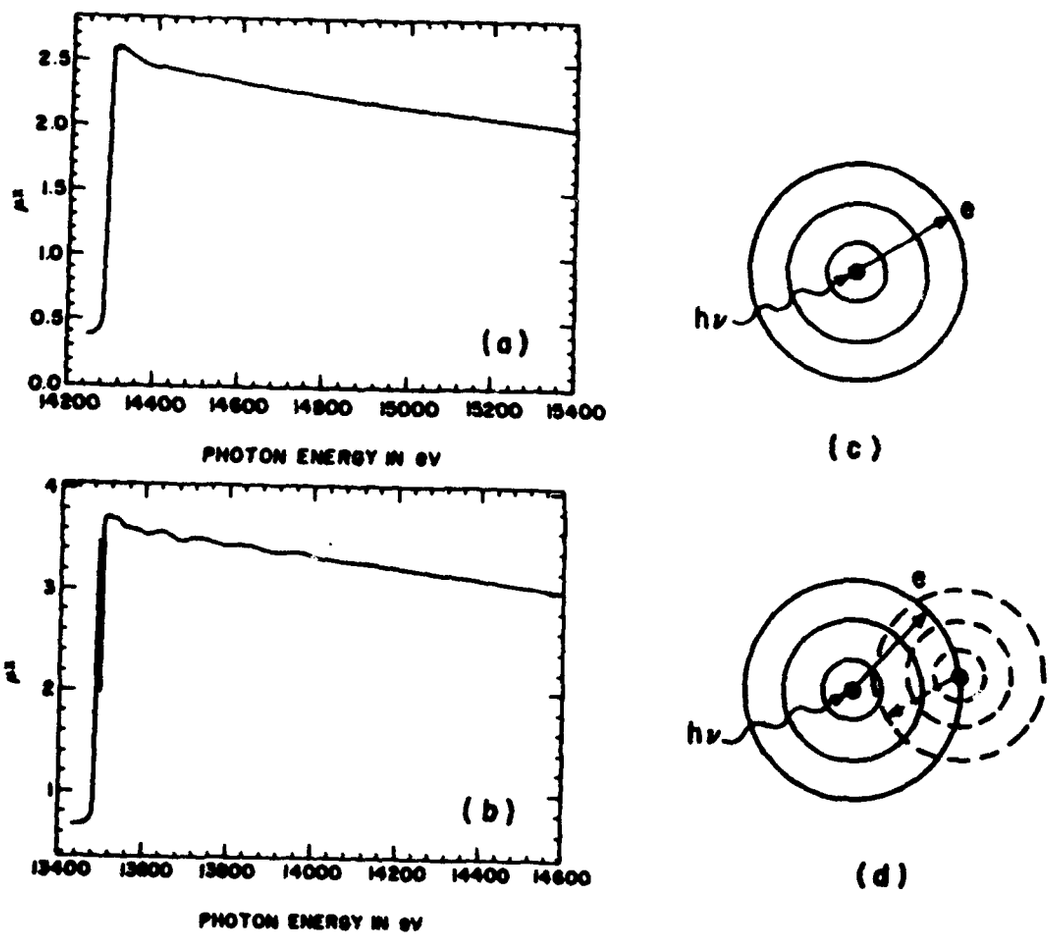
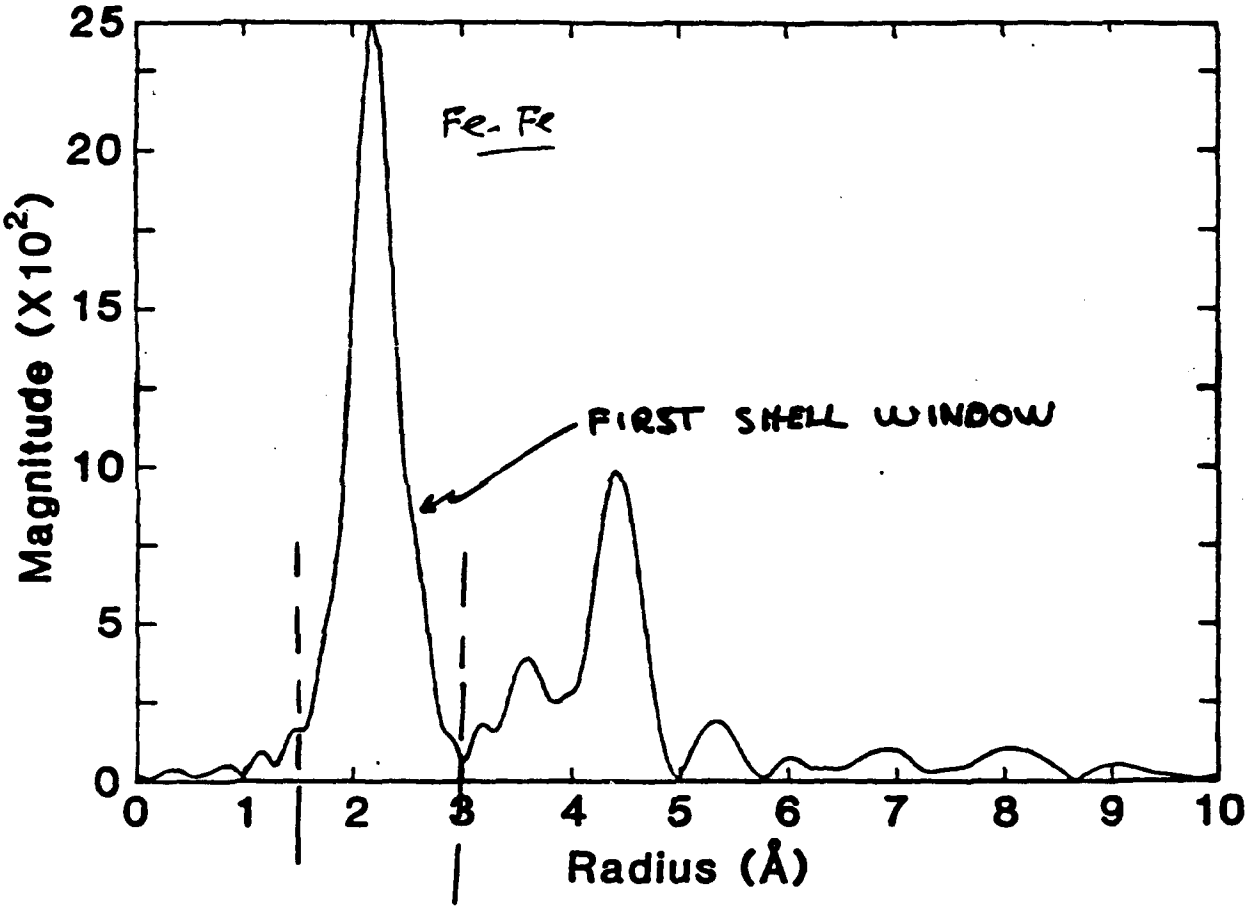


Fig. 2. Qualitative rationalization of the absence and presence, respectively, of EXAFS in a monatomic gas such as *Kr* (a and c) and a diatomic gas such as Br_2 (b and d).

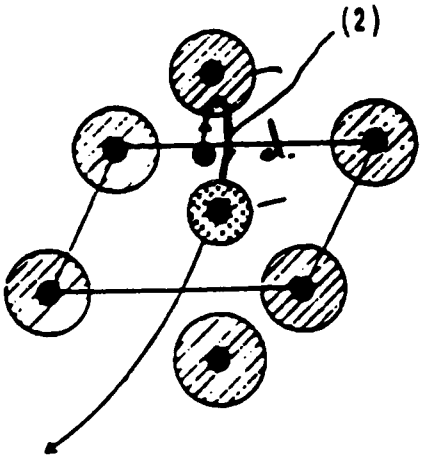


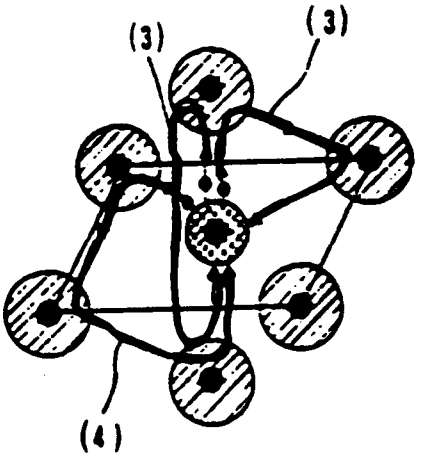
Fourier Transform For Iron Metal

		N	R Å
5 nm. First Shell	EXAFS	8.0	2.48
	XRD	8.0	2.48
6 nm Fe - Cathodically prot. In-situ	EXAFS	8.6	2.48

EXAFS

XANES





SINGLE SCATTERING

MULTIPLE SCATTERING

Absorbing atom

Photoelectron pathways

n = 2

Get "d"

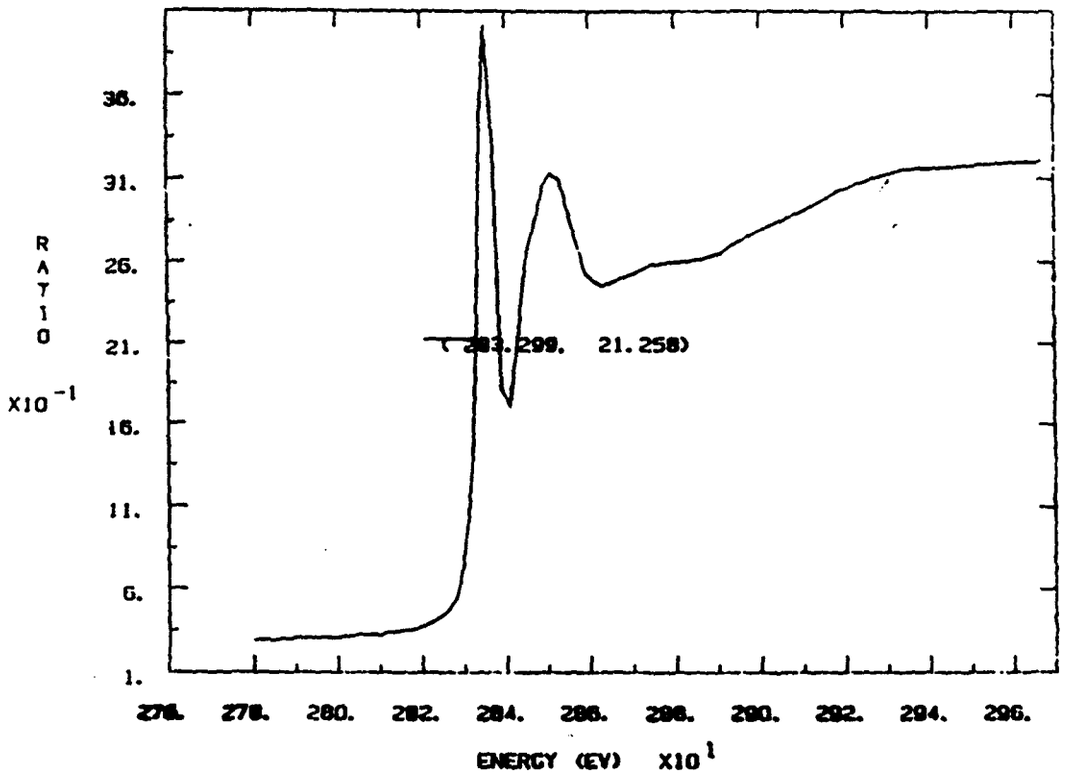
(first shell pair correlations)

n = ∞ in principle

Get high order pair correlations "bonding"

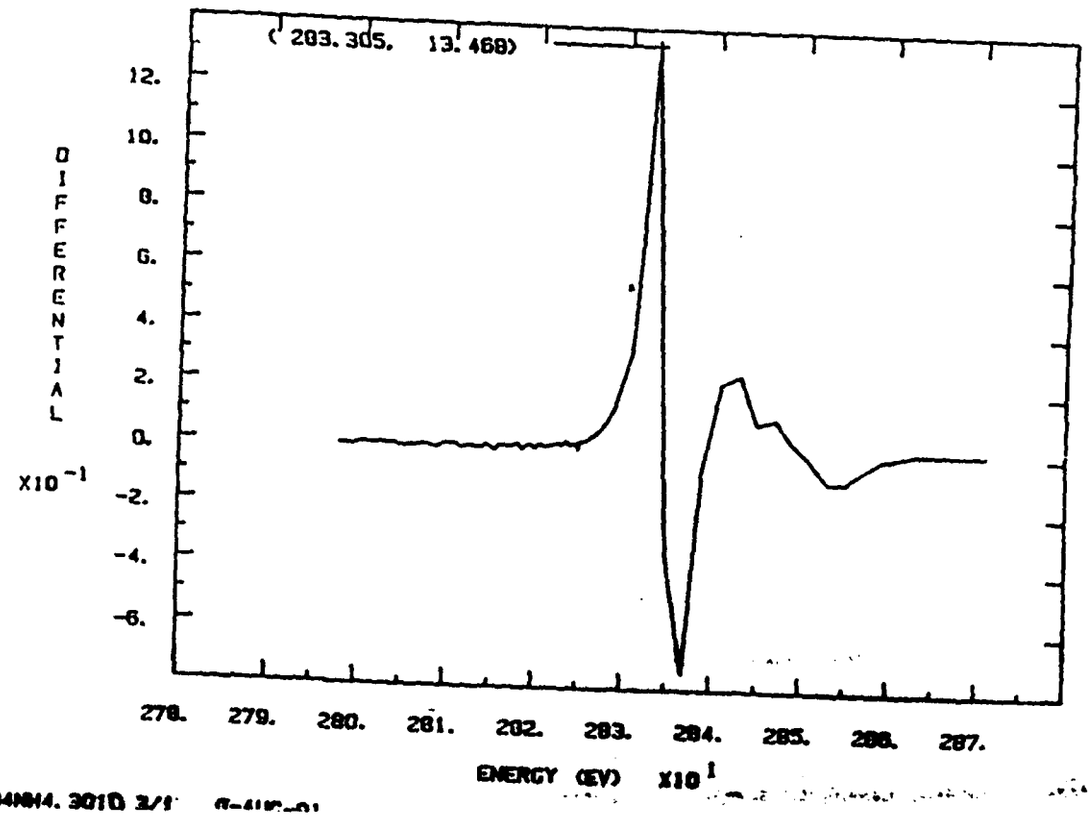
weak "simple"

Strong "complex"



CL04NH4.301W 3/1 8-AUG-91 Figure 4a CLedge scan for energy calibration

Cl Edge Energy Calibration



CL04NH4.301D 3/1

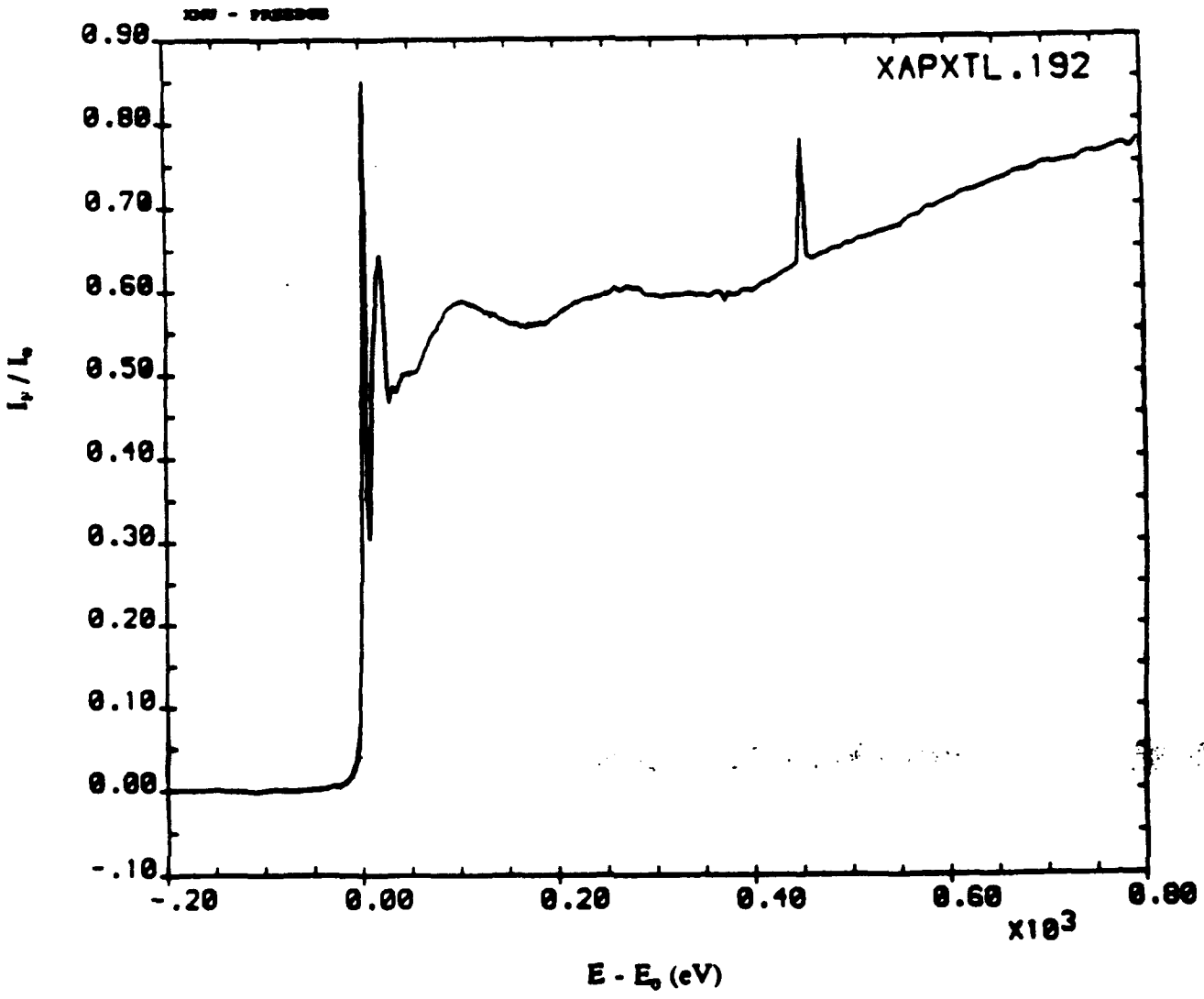


Figure 2: XAFS spectrum of NH_4ClO_4 single crystal with pre-edge removed relative to E_0 = 2722.7 eV.

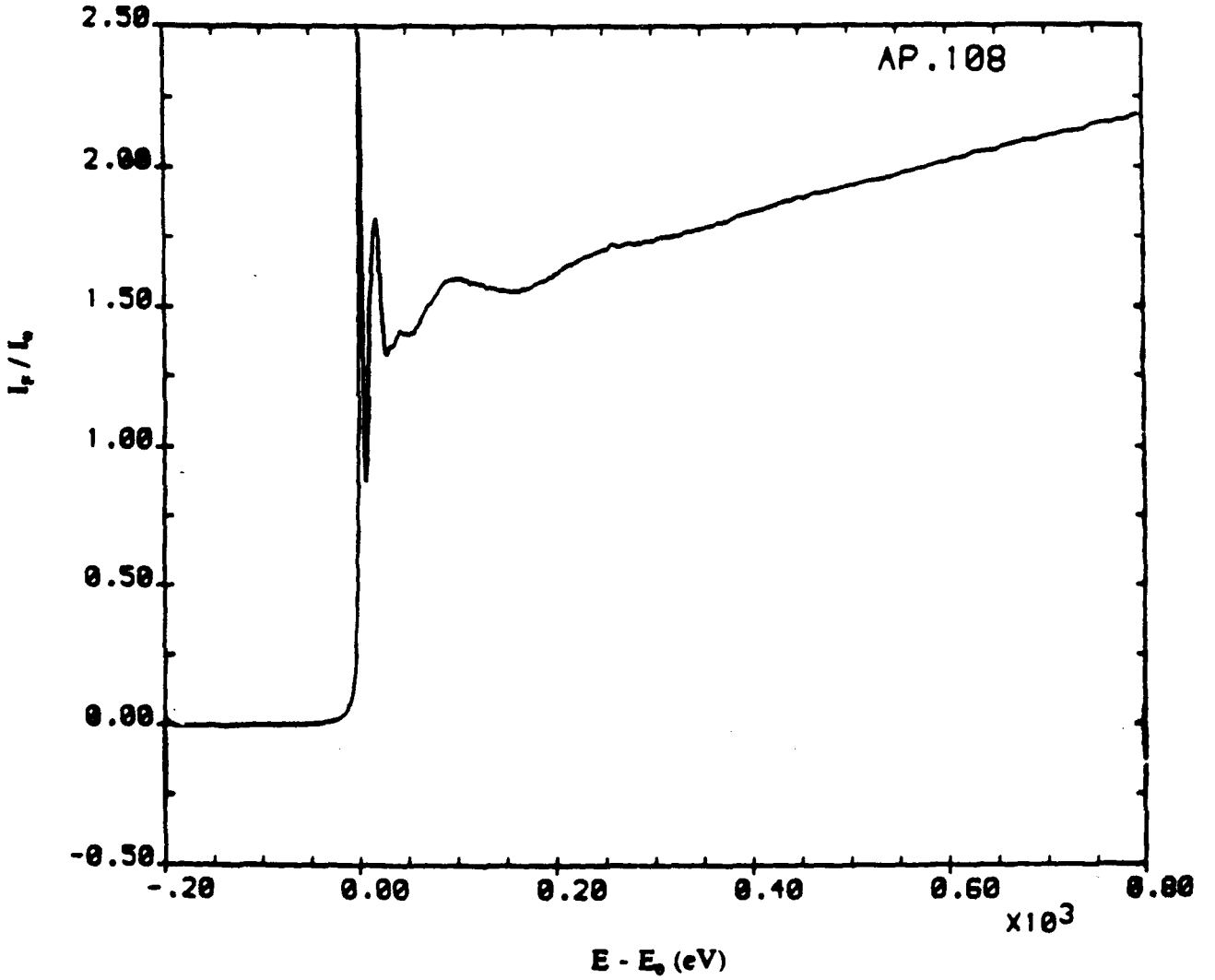
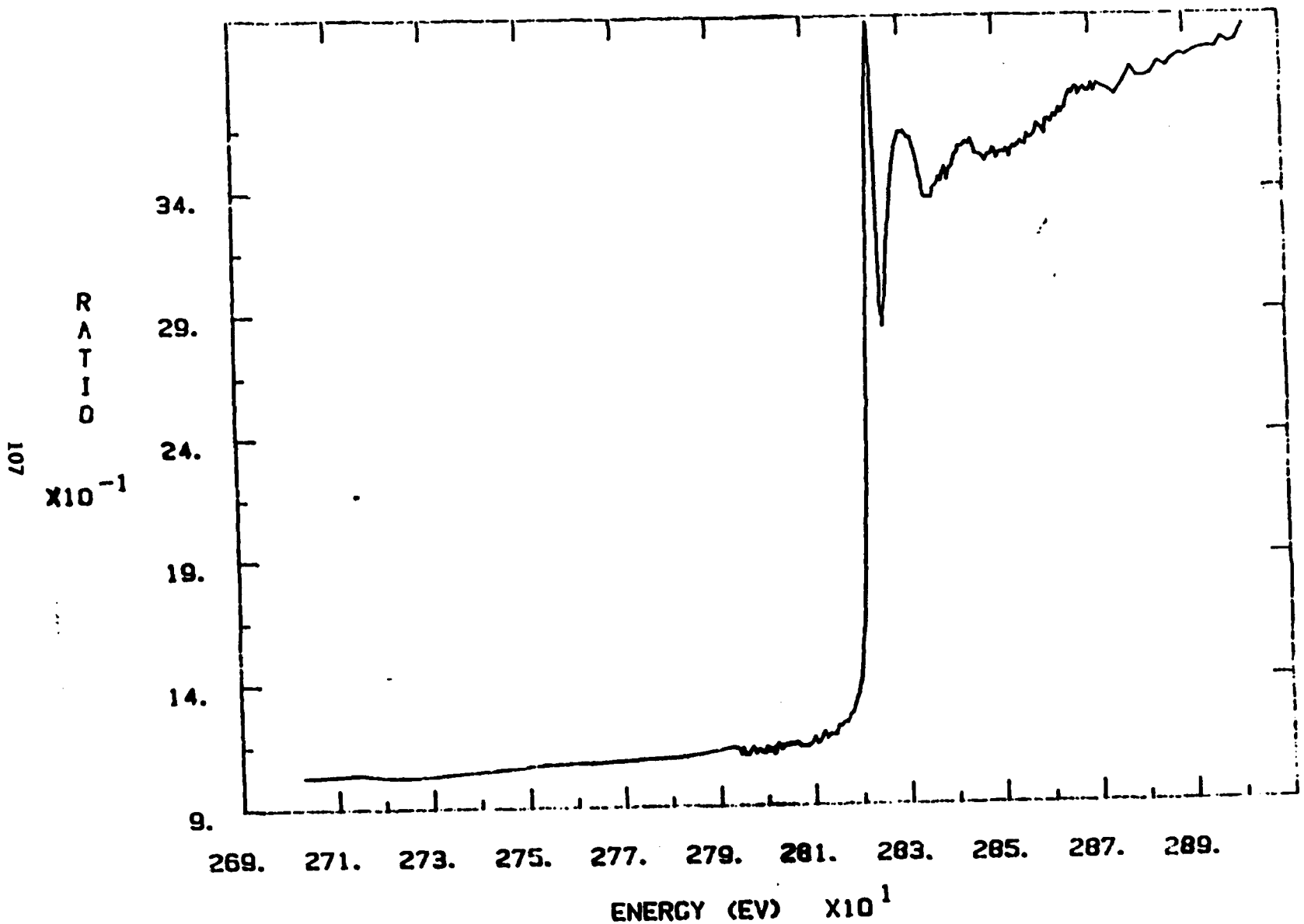
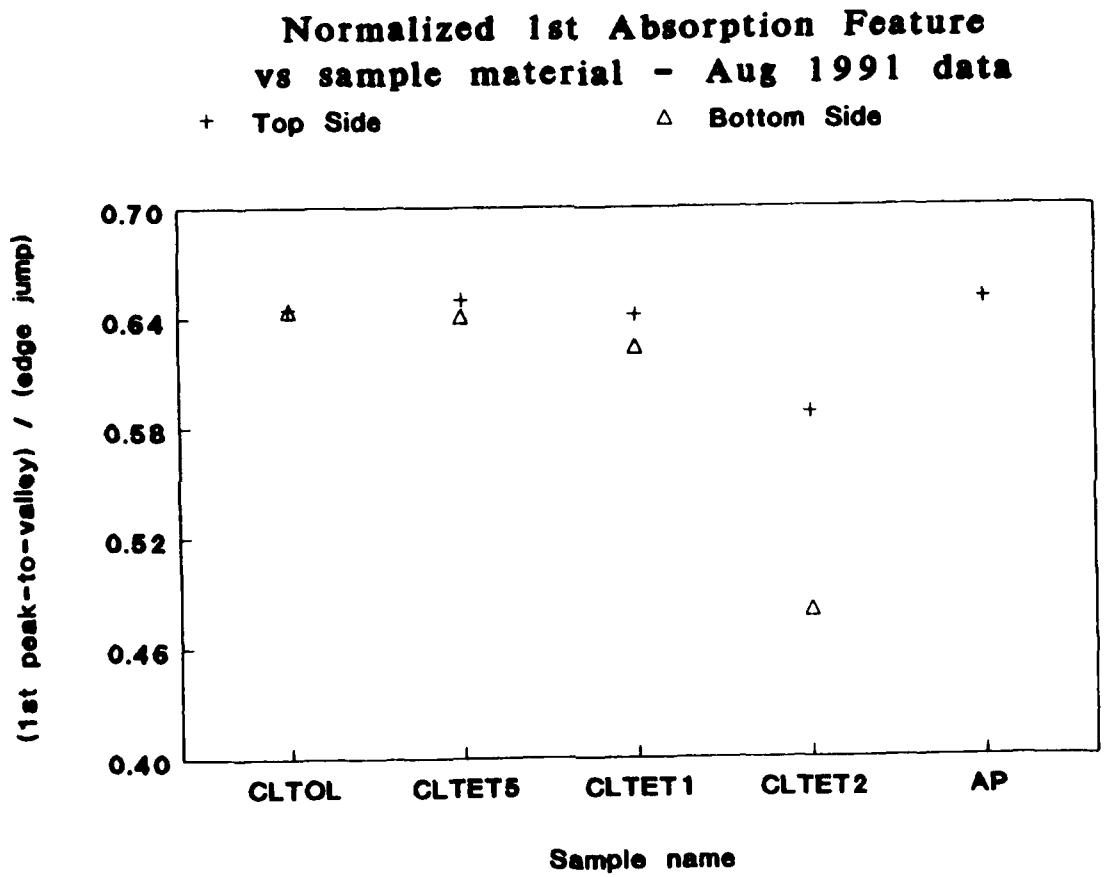


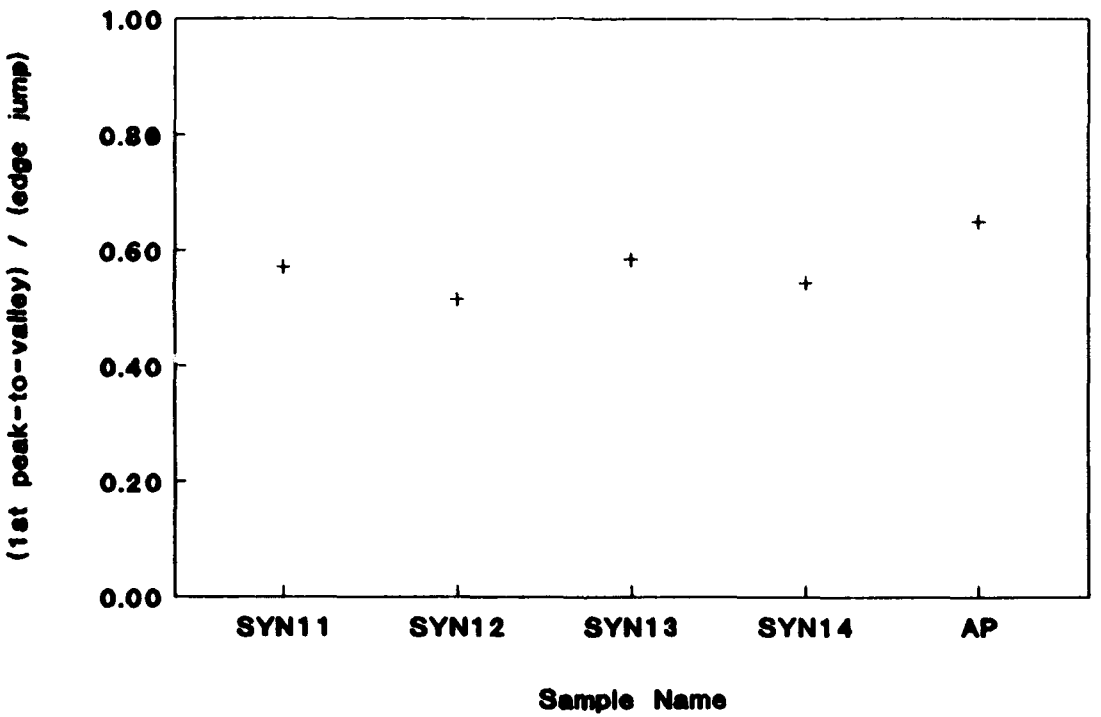
Figure 1: XAFS spectrum of NH_4ClO_4 pressed powder pellet with pre-edge removed relative to E_0 = 2722.7 eV.



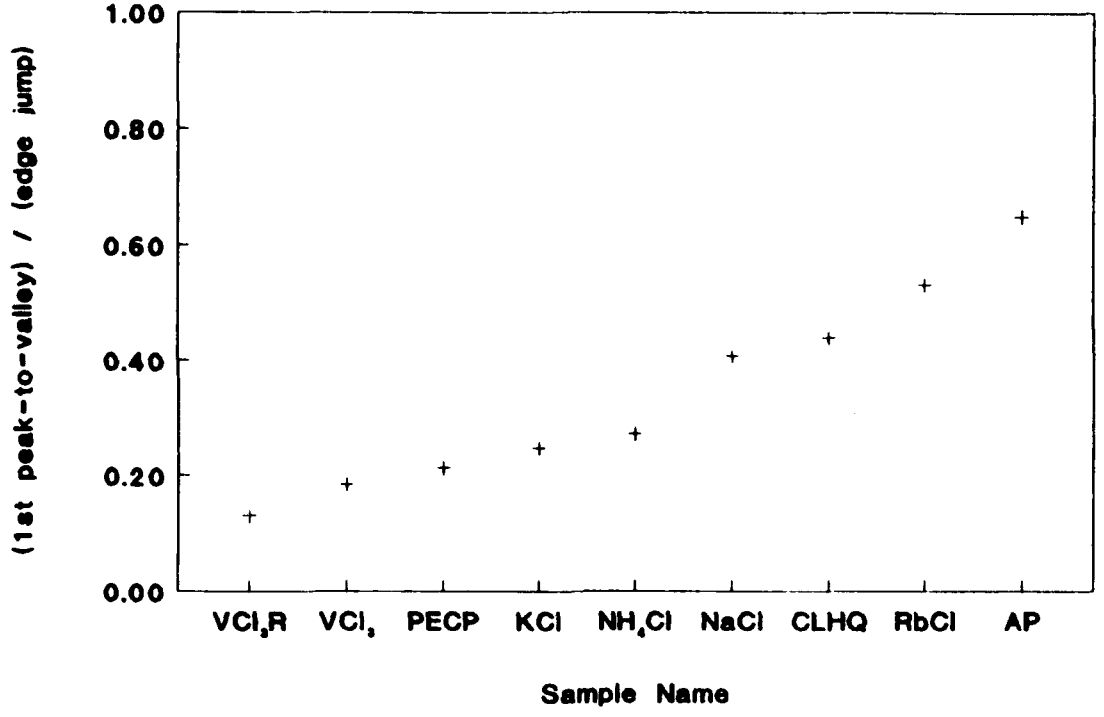
CLCLHQ.002 3/1 11-AUG-91 Figure 5 Cl XANES Scan of Chlorohydroquinone


Normalized 1st Absorption Feature
vs sample material - Aug 1991 data
+ Top Side
△ Bottom Side
(1st peak-to-valley) / (edge jump)
0.70
0.64
0.58
0.52
0.46
0.40
CLTOL
CLTET5
CLTET1
CLTET2
AP
Sample name

Normalized 1st Absorption Feature vs sample material - Oct 1991 data



Normalized 1st Absorption Feature vs sample material - Oct 1991 data

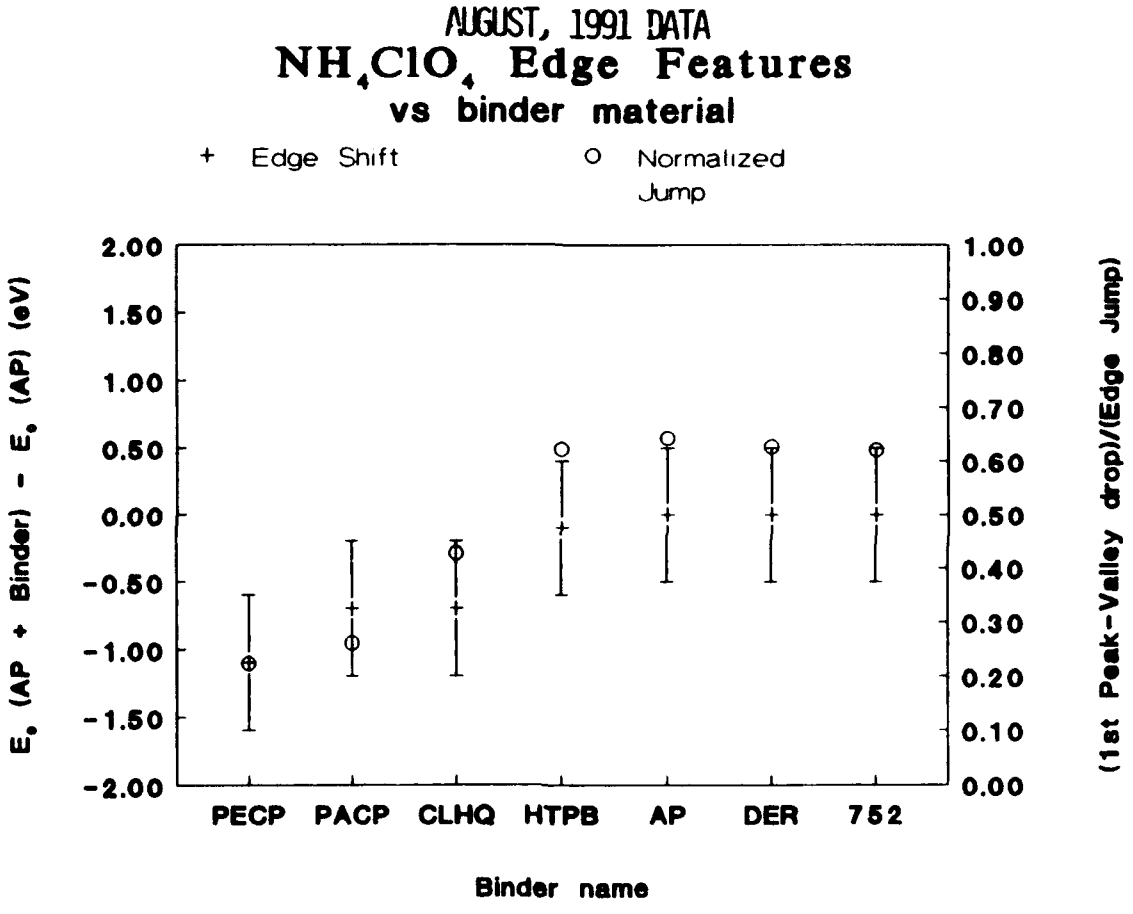


August, 1991 XANES Results: Sample Side Dependence

Sample	Normalized Jump	
	Top Towards Beam	Bottom Towards Beam
AP/Toluene	0.645	0.644
AP/TET 0.5 ML	0.650	0.641
AP/TET 1.0 ML	0.642	0.624
AP/TET 2.0 ML	0.588	0.480
AP/Blank	0.650	

October, 1991 XANES Results: Cl K-edge samples

Sample	Normalized Jump
AP	0.650
AP/CLHQ	0.440
AP/PECP	0.213
VCl_3R	0.131
VCl_3	0.185
KCl	0.248
NH_4Cl	0.272
NaCl	0.408
RbCl	0.532
SYN11	0.572
SYN12	0.516
SYN13	0.585
SYN14	0.544


AUGUST, 1991 DATA
NH4ClO4 Edge Features
vs binder material
+ Edge Shift
O Normalized Jump
E0 (AP + Binder) - E0 (AP) (eV)
(1st Peak-Valley drop)/(Edge Jump)
2.00
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
-2.00
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
PECP
PACP
CLHQ
HTPB
AP
DER
752
Binder name

INTERNAL REFLECTION FLUORESCENCE OF POLYMERIC SURFACES.

P. B. Oldham, Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762.

The characteristics and dynamics of materials in the liquid-crystalline state have intrigued both scientists and engineers for a number of years. A considerable amount of work has been done to characterize the bulk properties of liquid crystalline materials but there are significant questions concerning interfacial microenvironments which remain largely unanswered. The goal of this work is to combine the capabilities of site-selective fluorescence probes with the surface selectivity of total internal reflection fluorescence (TIRF). Through the use of optical waveguides, TIRF can selectively probe the first few hundred nanometers of a surface interface. This technique will thus be employed to investigate liquid crystal polymer (LCP) materials at a surface interface over a range of temperatures. Probe molecules sensitive to both the physical and chemical environment will be used. The data obtained should provide considerable insight into surface interactions involving liquid crystals.

The major thrust in this research effort is to determine the feasibility of TIRF spectroscopy to monitor LCP deposition onto a solid surface from a solvated environment. This entails an overall effort including the following tasks: 1) investigation of solvent systems and solubility determinations for commercial LCPs, 2) chemical attachment of fluorescence probe molecules either directly to the reflection element surface or to the polymer itself, 3) optimization of optics and investigation of surface growth kinetics of the select LCPs using TIRF.

INTERNAL REFLECTION FLUORESCENCE of POLYMERIC SURFACES

P.I.: Dr. PHILIP B. OLDHAM
DEPARTMENT of CHEMISTRY
MISSISSIPPI STATE UNIVERSITY

GRAD: Mrs. DEBBIE BEARD SAEBO

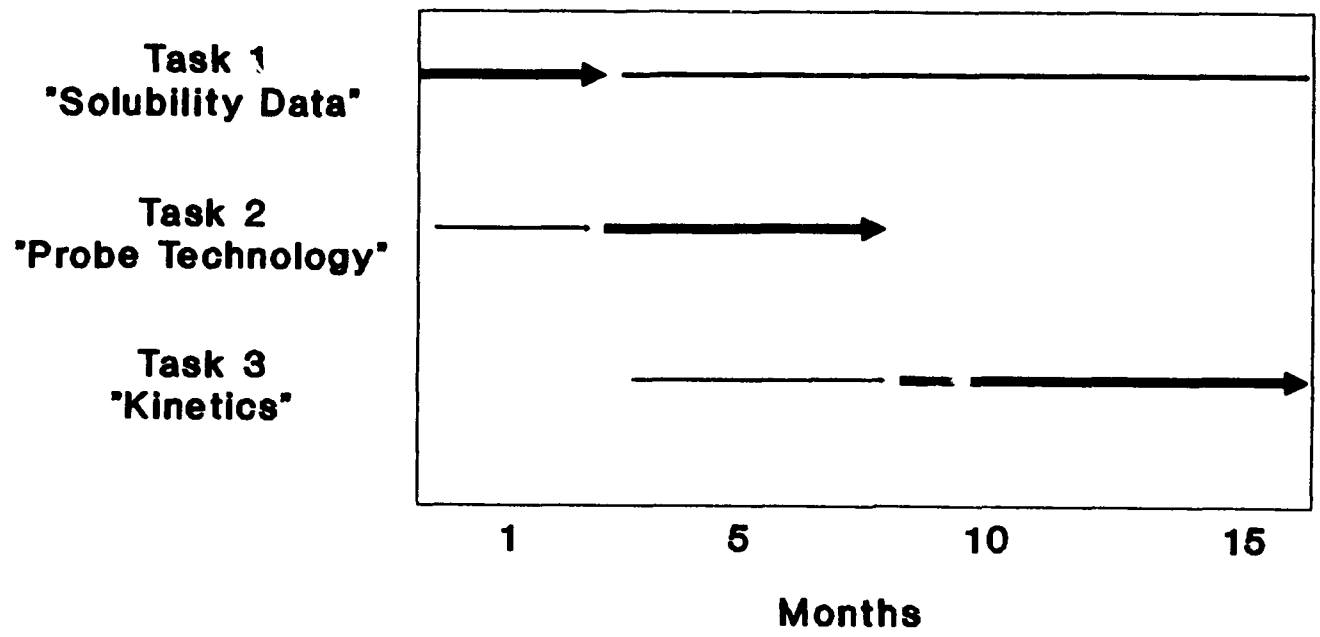
PROJECT OBJECTIVES

(1) POLYMER SOLUBILITY

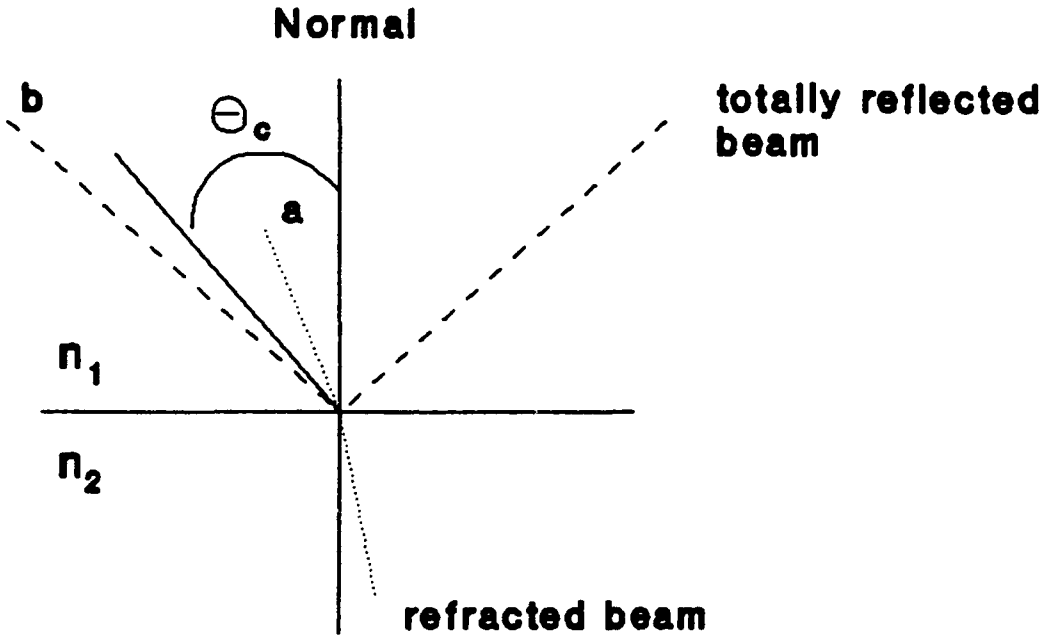
(2) CHEMICAL DERIVATIZATION of POLYMER SURFACE

(3) MONITOR KINETICS of POLYMER DEPOSITION

Schedule of Technical Effort



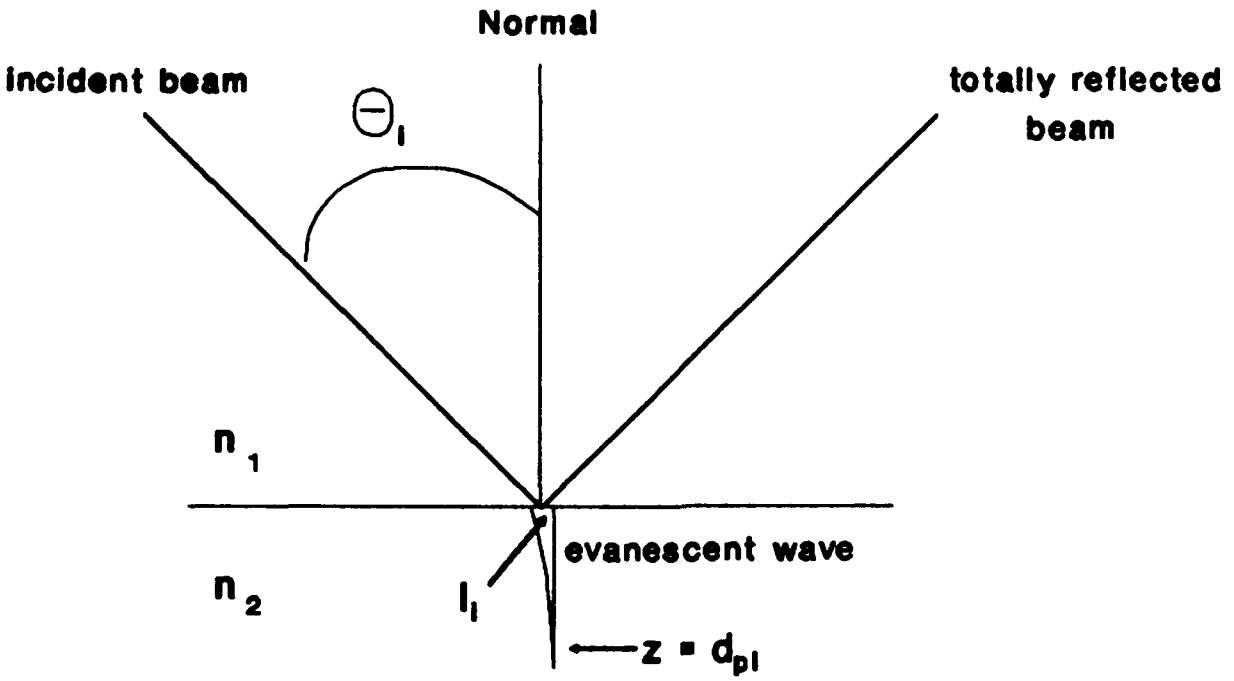
$$\theta_c = \mathrm{Sin}^{-1}(n_2/n_1)$$



$n_1 > n_2$

a = incidence angle < critical angle

b = incidence angle > critical angle


Normal
incident beam
totally reflected beam
Θ_i
n_1
n_2
evanescent wave
I_i
$z = d_{pi}$

$$d(\theta_1) = \frac{\lambda_1}{4\pi}\sqrt{(n_1 \sin\theta_1)^2 - n_2^2}$$

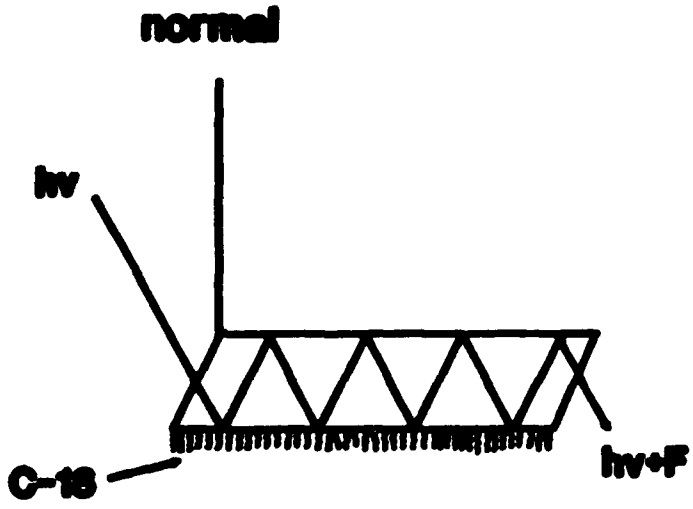
$\theta i \equiv$ incidence angle
$\lambda i \equiv$ incident light wavelength
n_1 and $n_2 \equiv$ refractive indices $(n_1 > n_2)$

$$I_{ex} = k_{ex} \varepsilon \phi_f I_1 \int_0^\infty C_z e^{(-z/d_{p1})} dz$$

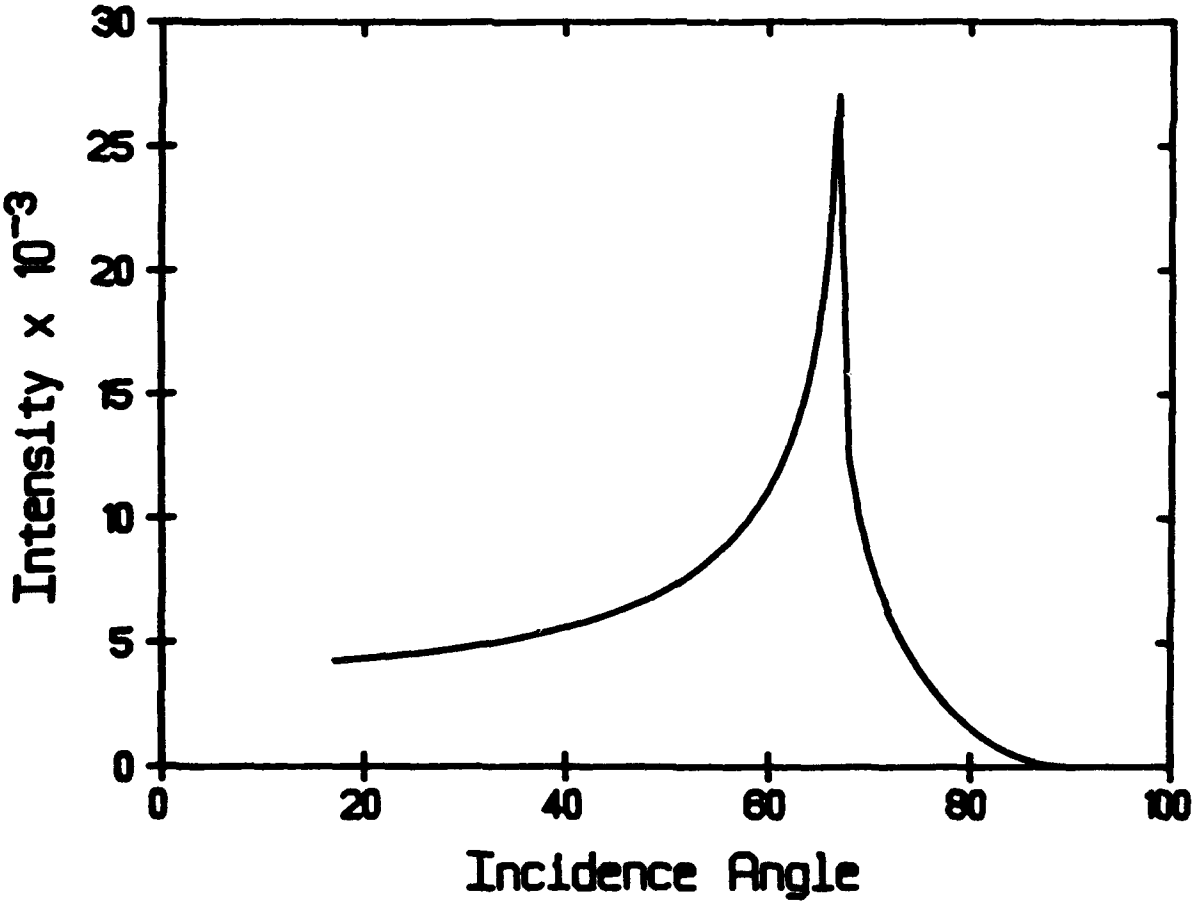
$$I_{em} = k_{em} \int_0^\infty e^{(-z/d_{p0})} dz$$

$$I_f = k_{ex} k_{em} \varepsilon \phi I_1 \int_0^\infty C_z e^{-\frac{z}{d_{p1} + d_{p0}}} dz$$

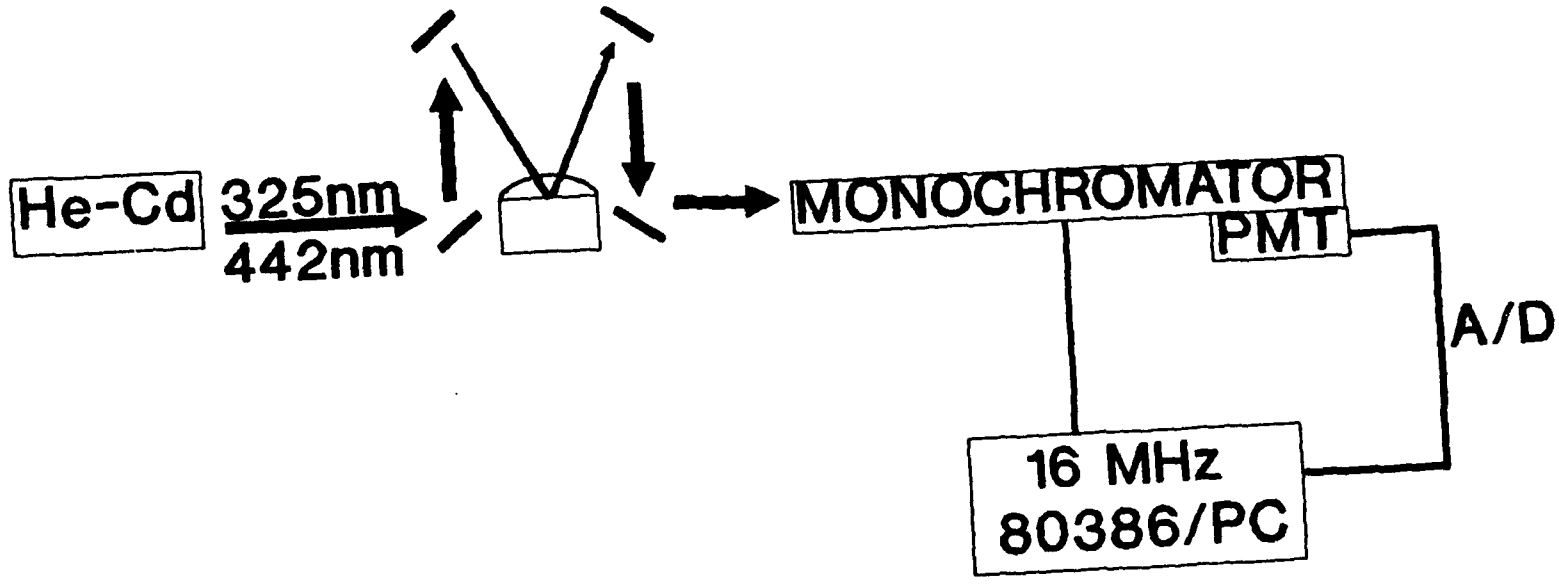
Total Internal Reflection Fluorescence



Fluorescent probe/solvent



OPTICAL DIAGRAM



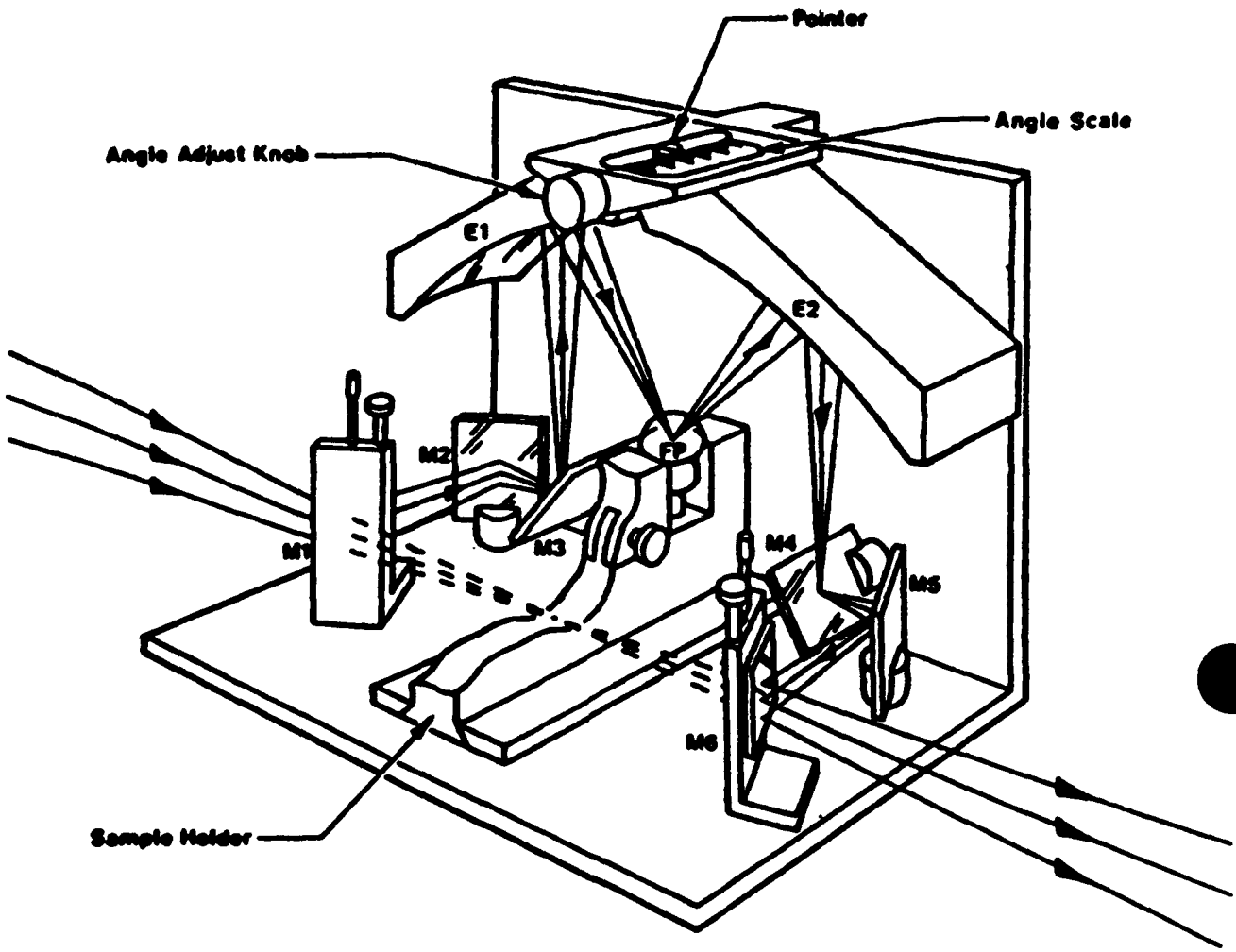
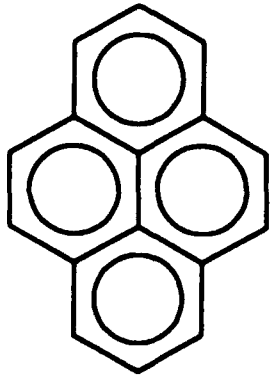


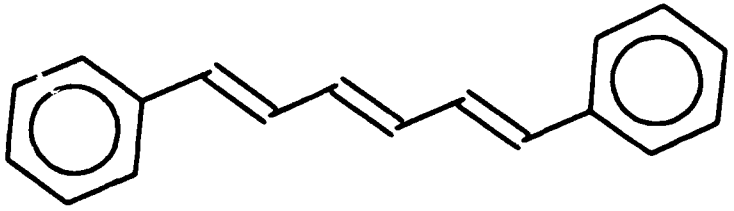
FIG. 1A. The Seagull® variable-angle reflection accessory.

Possible TIRF Experiments

1. Fixed Angle Surface Polarity
2. Variable Angle Depth Profile
3. TIRF - Anisotropy for Microviscosity



Pyrene



1,6-diphenylhexatriene

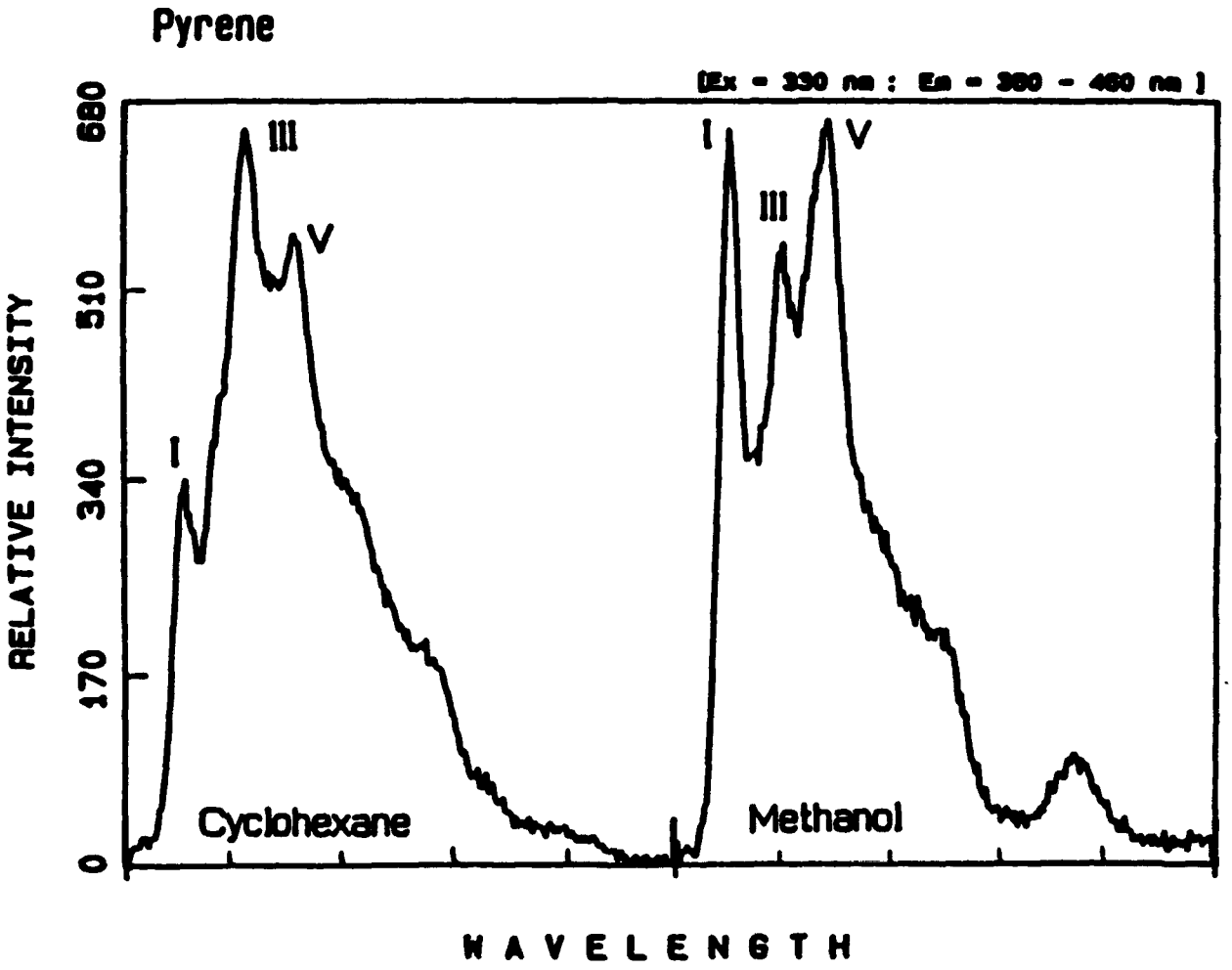
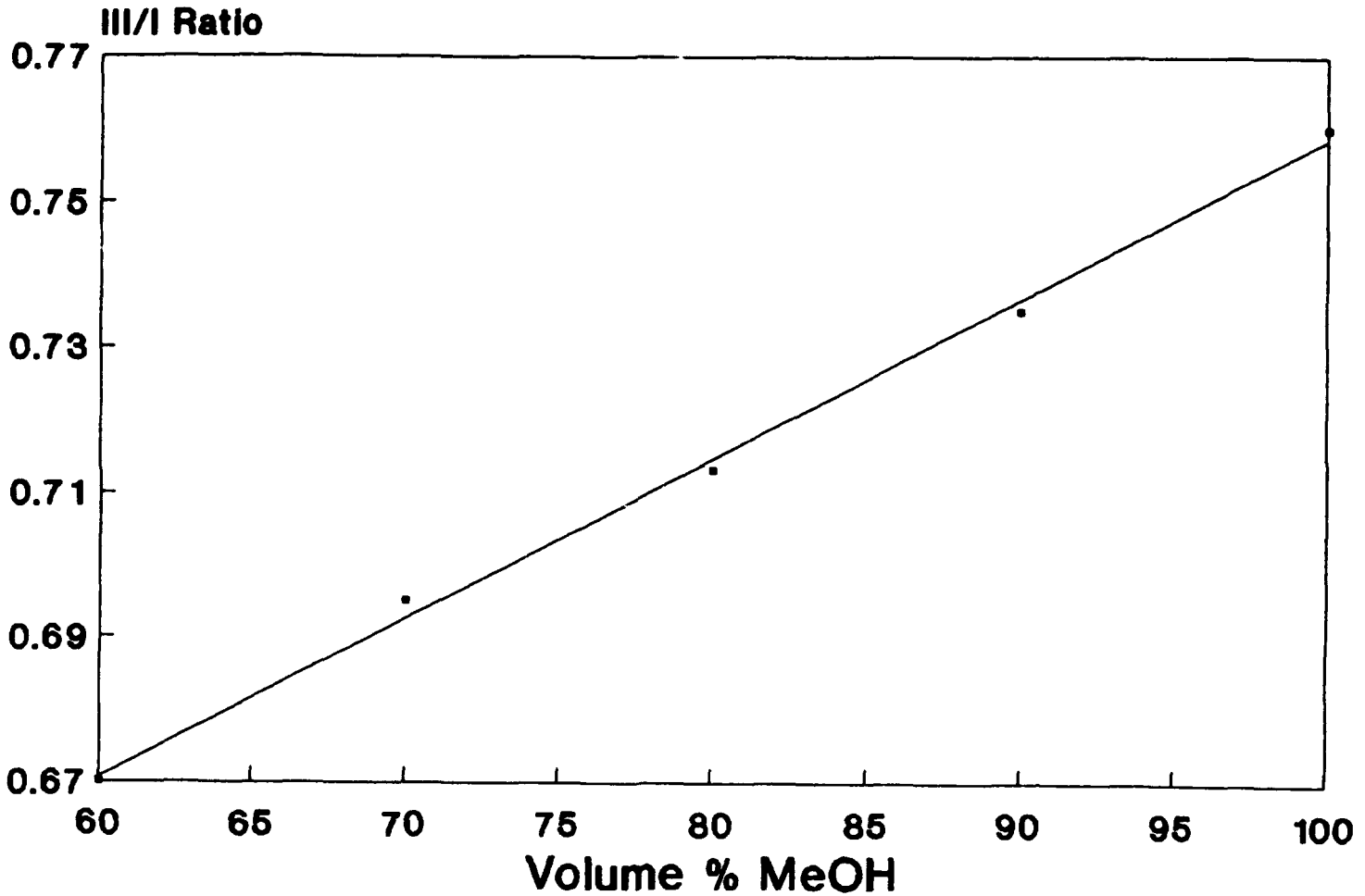
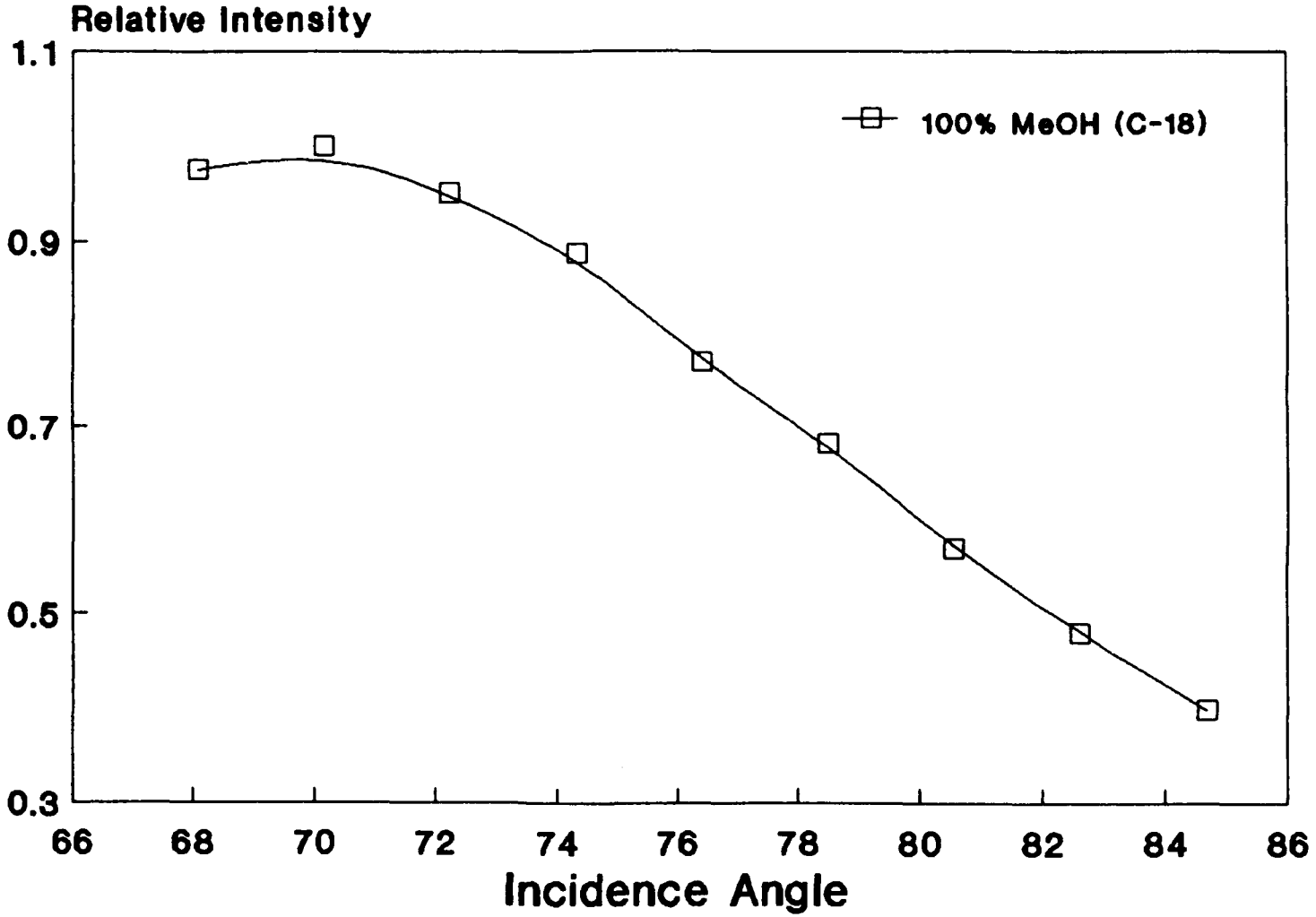


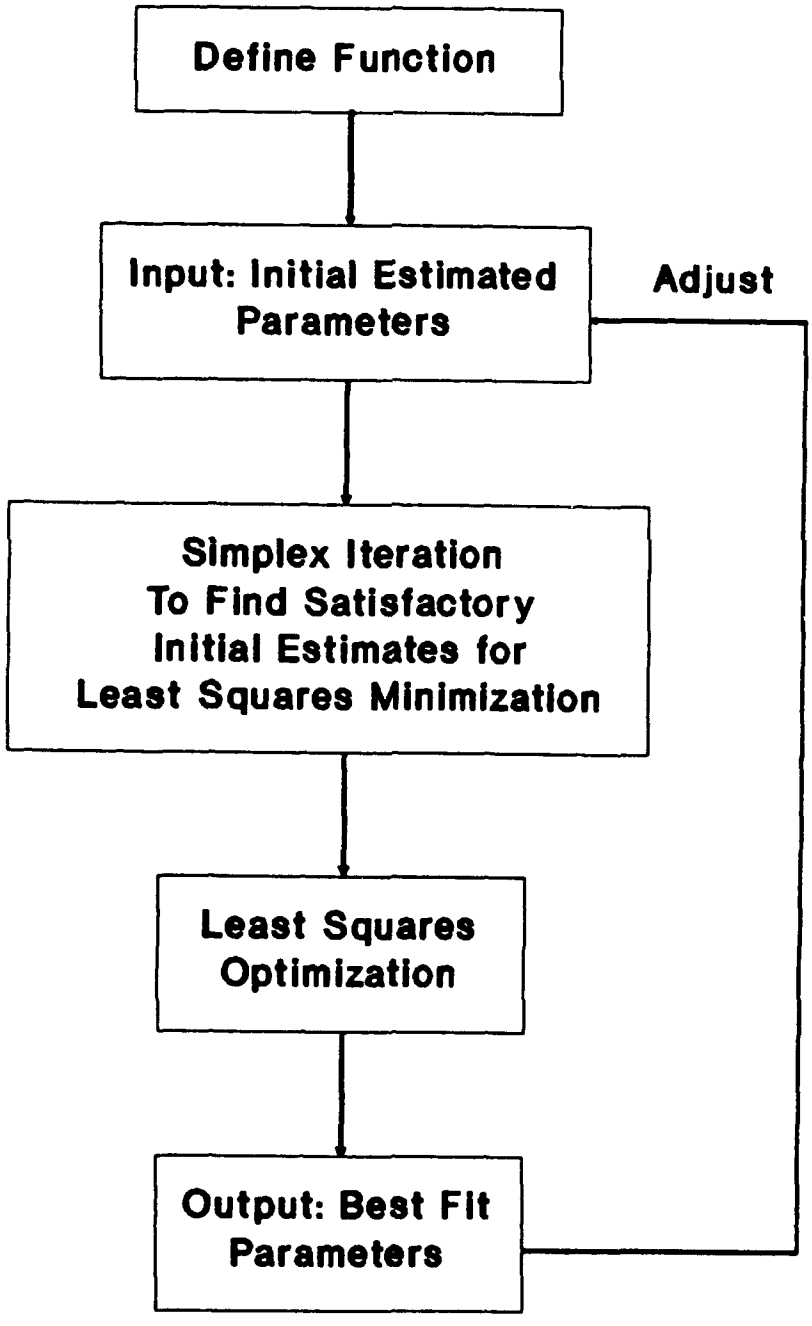
Figure IV-11. TIRF spectra of pyrene in cyclohexane and in methanol. (Emission wavelength : 360-460 nm). (X-axis : 1 unit = 20 nm).


III/I Ratio
0.77
0.75
0.73
0.71
0.69
0.67
60
65
70
75
80
85
90
95
100
Volume % MeOH

VA-TIRF C-18/PYRENE STUDIES

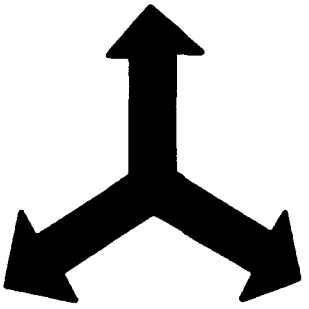


Analysis of VA-TIRF Data



Fluorescence Anisotropy

(r)



(ϕ) Rotational Correlation Time

(η) Viscosity

$$r = \frac{r_0}{1 + (\tau/\phi)}$$

$$\phi = \frac{\eta V}{RT}$$

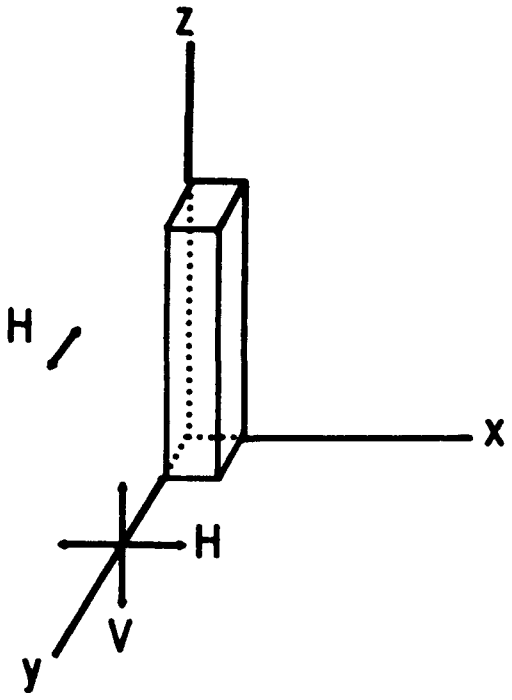
r_0 = limiting anisotropy

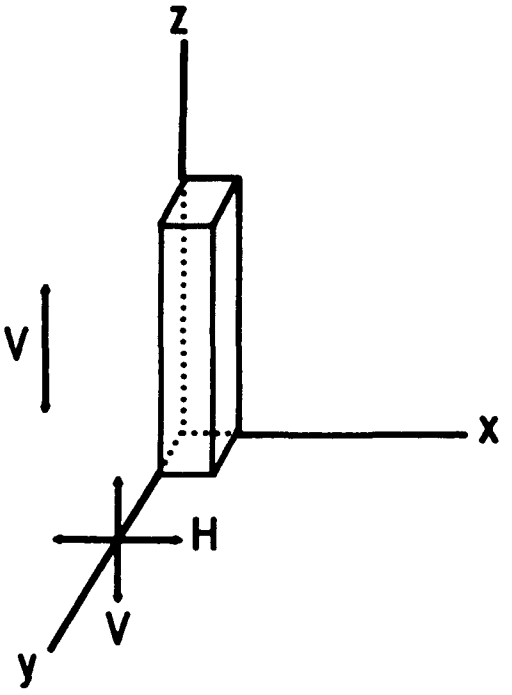
τ = fluorescence lifetime

R = gas constant

T = temperature

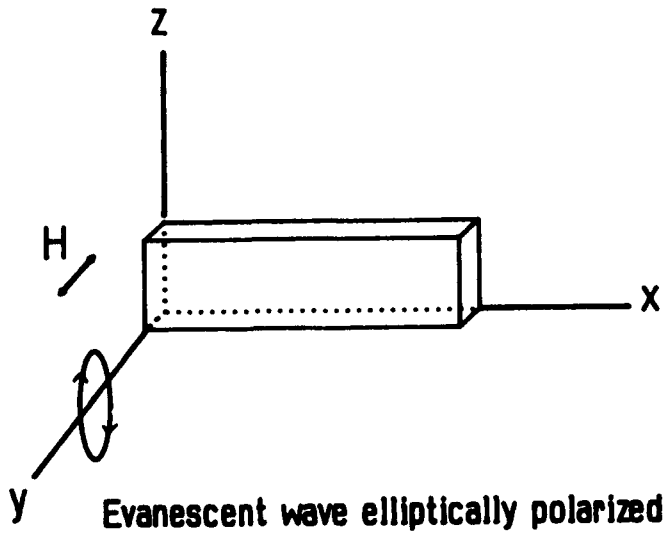
V = molecular volume



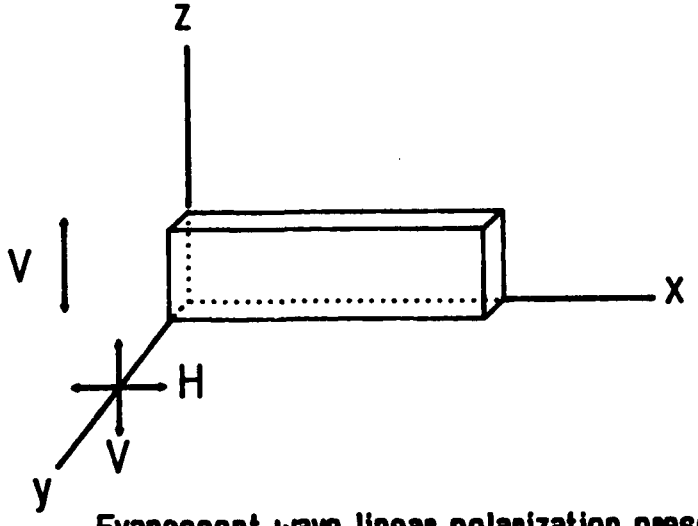


$$G = \frac{I_{HV}}{I_{HH}}$$

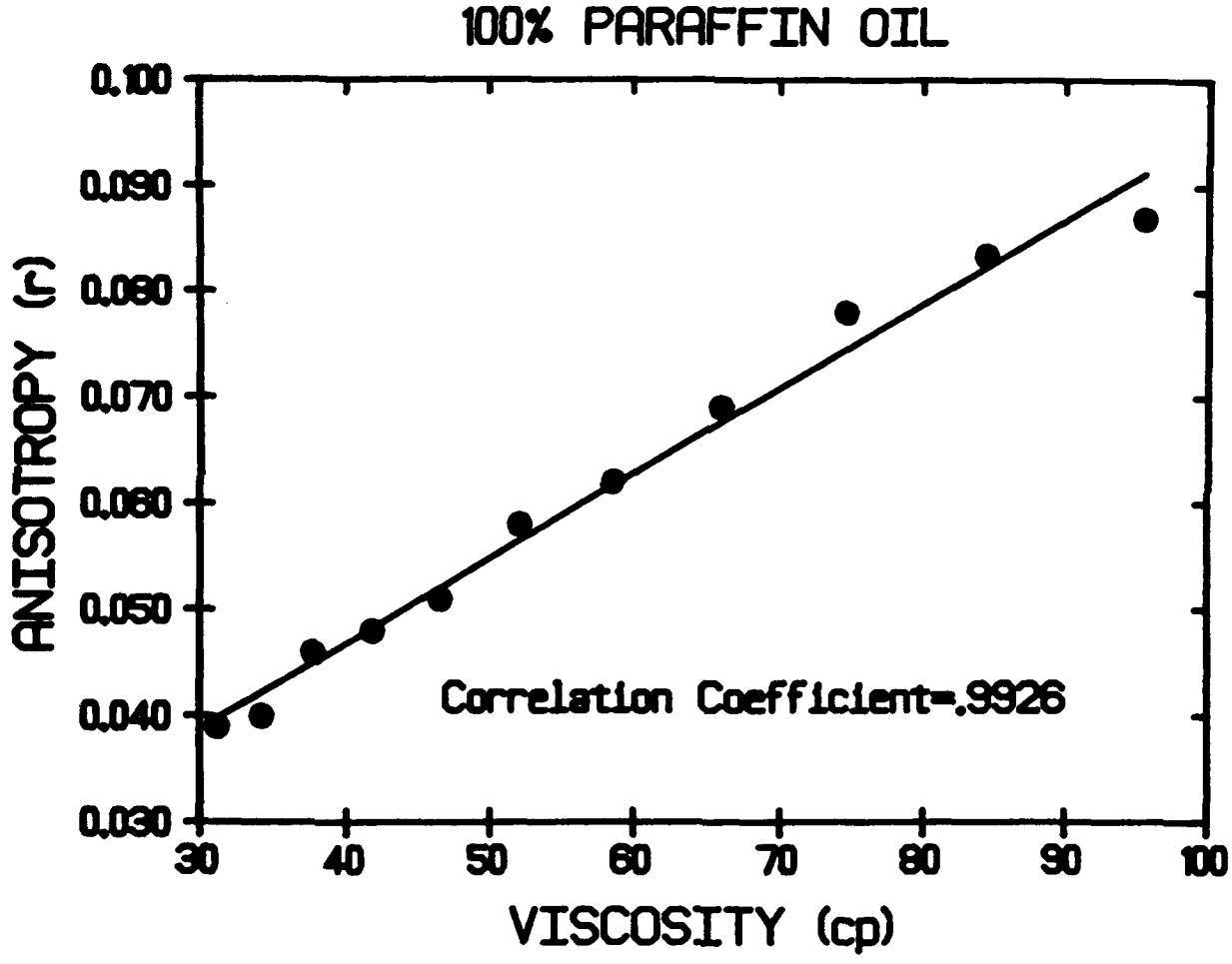
$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}}$$

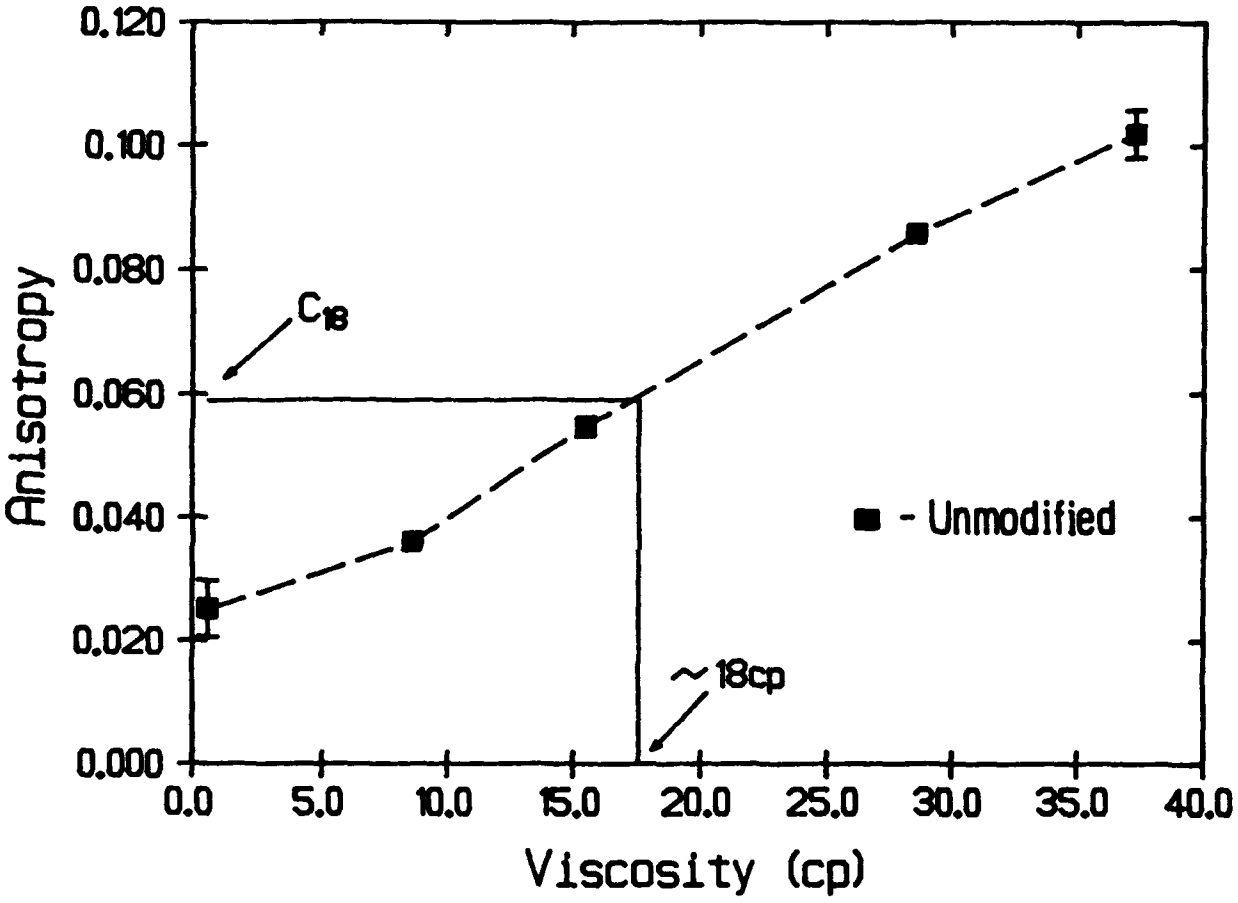


Evanescent wave elliptically polarized



Evanescent wave linear polarization preserved


100% PARAFFIN OIL
ANISOTROPY (r)
0.100
0.090
0.080
0.070
0.060
0.050
0.040
0.030
30
40
50
60
70
80
90
100
VISCOSITY (cp)
Correlation Coefficient=.9926


0.120
0.100
0.080
0.060
0.040
0.020
0.000
Anisotropy
C_{18}
■ - Unmodified
~18cp
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
Viscosity (cp)

SOLVENT REQUIREMENTS

(1) REASONABLE POLYMER SOLUBILITY (few mg/ml)

(2) RELATIVELY SAFE AND EASILY HANDLED

(3) OPTICALLY COMPATIBLE WITH TIRF

SOLUBILITY PROCEDURE

GRIND POLYMER

DRY POLYMER ~36 HOURS

WEIGH ~5mg POLYMER & PLACE IN VIAL

ADD 10ml OF TEST SOLVENT TO VIAL

COVER VIAL OPENING WITH ALUMINUM FOIL

LEAVE IN DARK AREA UNDER FUME HOOD

SHAKE VIAL FOR ~2 MINUTES 10 TIMES/DAY FOR 18 DAYS

ALLOW UNDISSOLVED POLYMER TO SETTLE TO VIAL BOTTOM OVER 24 HOUR PERIOD

PIPETTE SOLVENT AWAY FROM SOLID LEAVING ~2ml

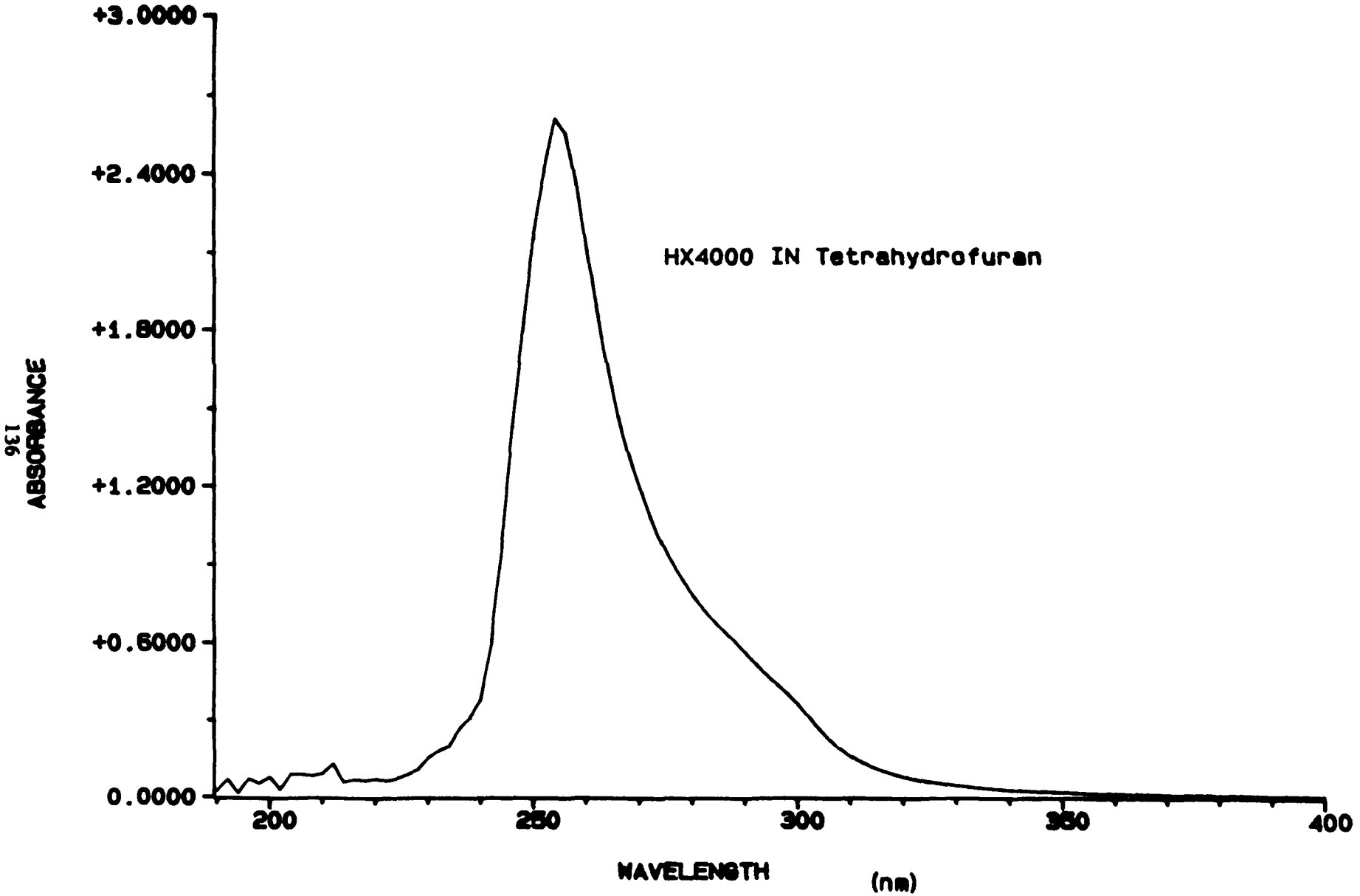
EVAPORATE REMAINING 2ml OF SOLVENT LEAVING UNDISSOLVED POLYMER

DRY POLYMER FOR 2 DAYS AT ~130°C

WEIGH POLYMER

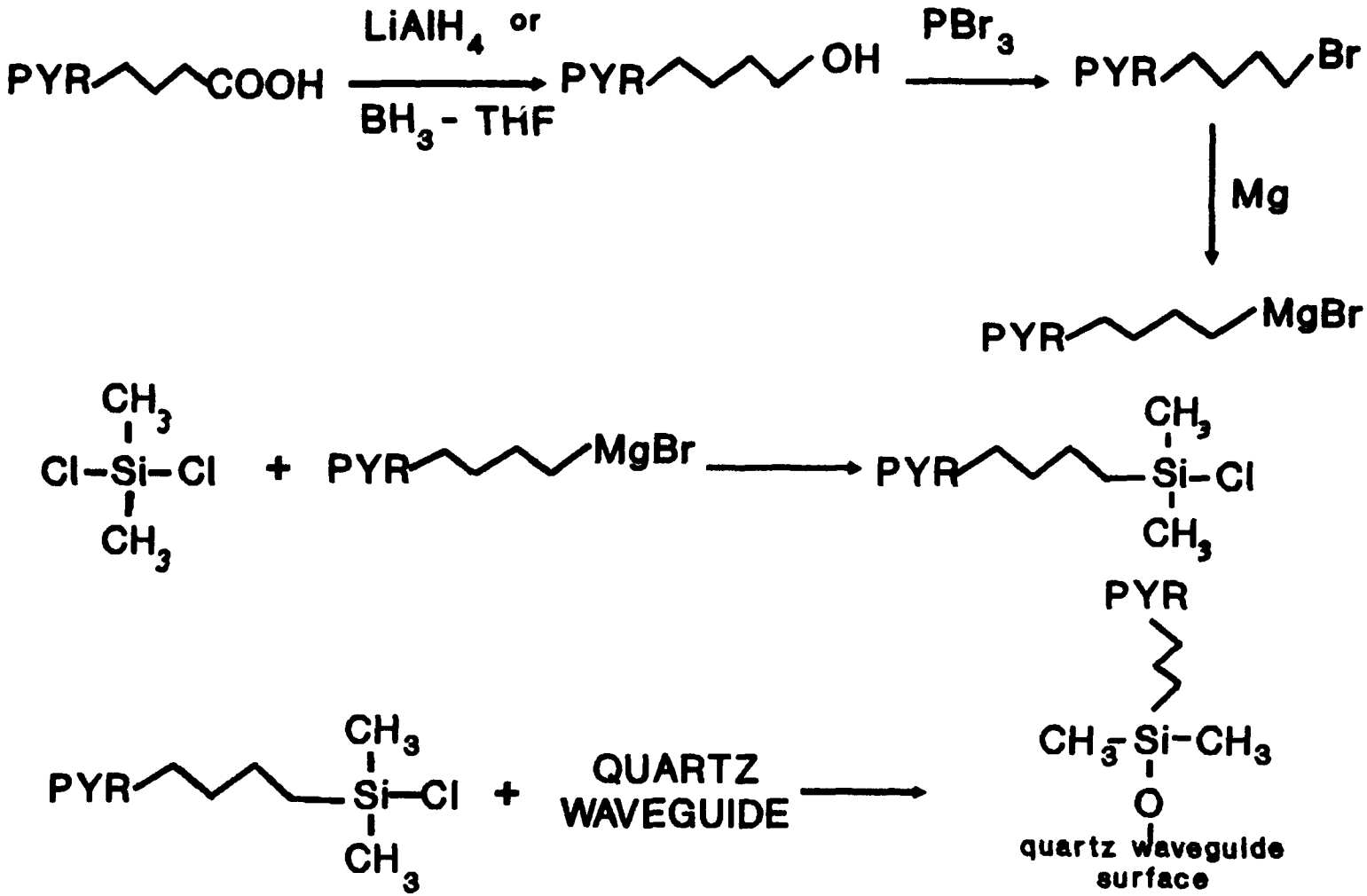
SOLUBILITY CALCULATION:

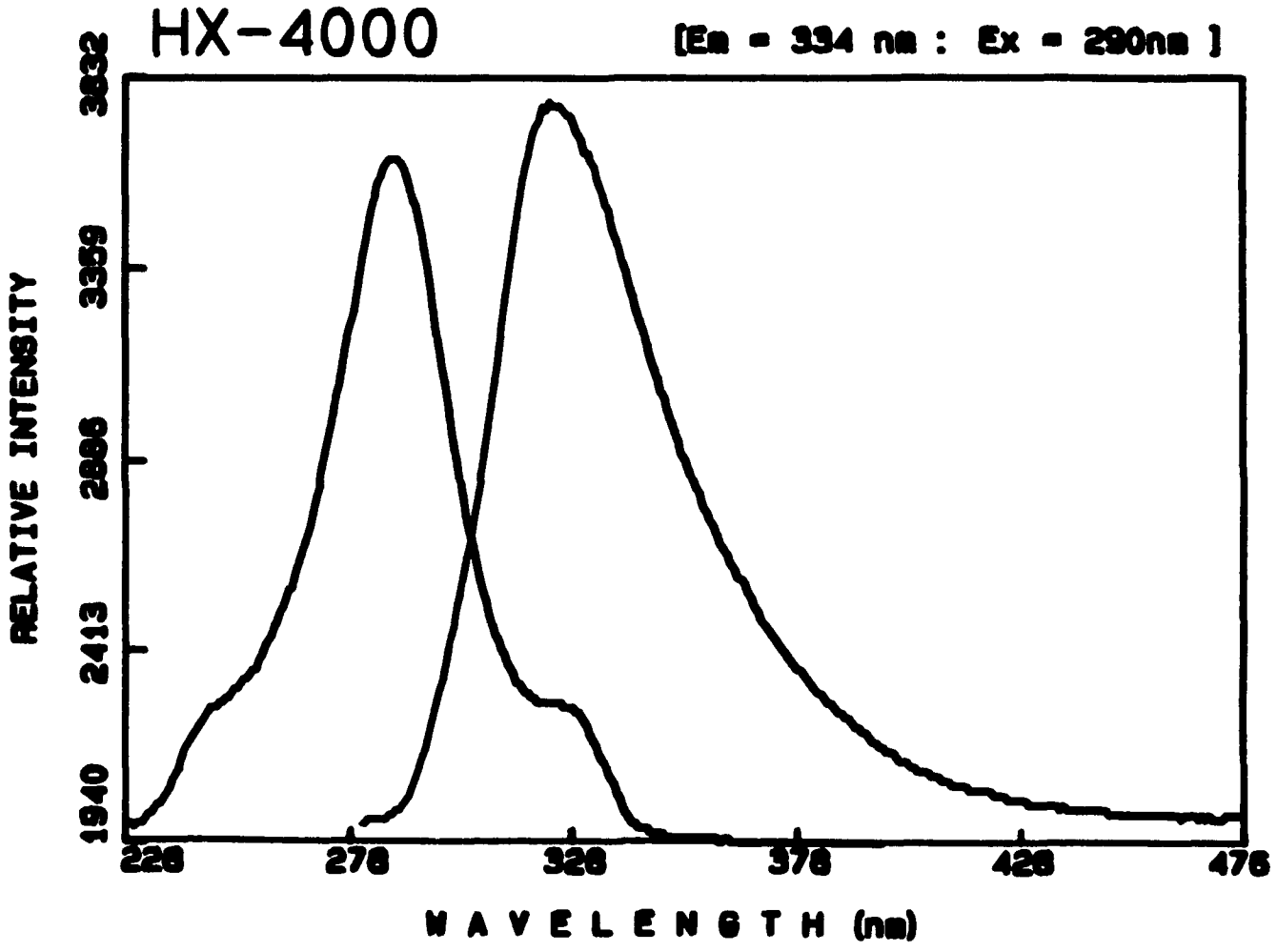
$$\frac{\text{(INITIAL WEIGHT - FINAL WEIGHT) mg}}{\text{TOTAL VOLUME OF SOLVENT IN ml}}$$


+3.0000
+2.4000
+1.8000
+1.2000
+0.6000
0.0000
ABSORBANCE
136
HX4000 IN Tetrahydrofuran
200
250
300
350
400
WAVELENGTH
(nm)

Room Temperature Solubility of HX4000 in different solvents.

SOLVENT	SOLUBILITY(mg/ml)	ABSORBANCE	λ(nm)
Acetone	0.070	----------	----
Acetonitrile	0.100	0.12328	244
Benzene	0.100	0.01759	282
sec-Butanol	0.100	0.00703	328
		0.32249	280
		0.34500	271
		0.36200	260
tertiary-Butanol	0.060	0.00580	262
		0.00642	256
Cyclohexane	0.110	0.47130	312
		1.34530	276
		1.53490	268
		1.50040	260
		3.22840	224
Ethyl Acetate	0.080	0.05356	360
		0.35486	252
Hexane	0.080	----------	----
Methanol	0.100	0.01796	244
		----------	----
Methylene Chloride	0.180	1.44060	246
Tetrahydrofuran	0.130	2.61060	254
Toluene	0.050	0.05203	284
o-Xylene	0.150	0.02919	288
m-Xylene	0.100	0.03366	326
		0.22304	288
Ultra pure Water	0.120	0.01949	244


PYR COOH
LiAlH4 or
BH3 - THF
PYR OH
PBr3
PYR Br
Mg
PYR MgBr
CH3
Cl–Si–Cl
CH3
+
PYR MgBr
PYR
CH3
Si–Cl
CH3
PYR
CH3
PYR
Si–Cl
CH3
+
QUARTZ
WAVEGUIDE
PYR
CH3–Si–CH3
O
quartz waveguide
surface


HX-4000
[Em = 334 nm : Ex = 290nm]
RELATIVE INTENSITY
3832
3359
2886
2413
1940
226
276
326
376
426
476
WAVELENGTH (nm)

Abstract

The simple and reliable single filament test methods for predicting the compressive properties of fibers are a must for development activities of fibers in laboratories because of difficulties in composite compression test methods. Therefore, in this study, two single filament compression test methods, the elastic loop and bending beam tests, are conducted for several polymeric fibers including Kevlars, PBO and PBZT and a few carbon fibers such as T-50 and P-75S, in order to obtain their compressive properties. Also the compressive failure modes of fibers, which occur as a kink band formation in polymeric fibers and as a fracture in carbon fibers are investigated. In addition, a FORTRAN program is written for numerical analysis of non-linear geometry elastica problems such as bending of a single fiber considering large displacements.

A comparison of the results obtained in this study is made with previous studies. It is found that, generally,the compressive strengths of the fibers obtained from elastica loop and bending beam tests,are higher than the composite compression test results. The kink band formation in polymeric fibers were investigated and it can be concluded that the critical kink band formation represents the buckling of separated microfibrils due to

elastic instability. Also the FORTRAN program is applied to measure the fiber compressive properties as a new potential single filament test method.

Dr. Anthony N. Palazotto
Professor
Aeronautics and Astronautics Dept

Air Force Institute Of Technology
Wright Patterson Air Force Base,Ohio

EXPERIMENTATION AND ANALYSIS

OF COMPRESSION TEST METHODS FOR SINGLE FILAMENT POLYMER FIBERS

1Lt. Sukru FIDAN

POLYMERS

- Long,covalently bonded molecular chains along fiber axis

  High tensile strength and modulus

- Chains, intermolecularly bonded by weak van der Walls or hydrogen bonding

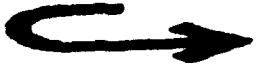
  Low compressive strength and shear modulus

  Highly anisotropic fibers

PROBLEM

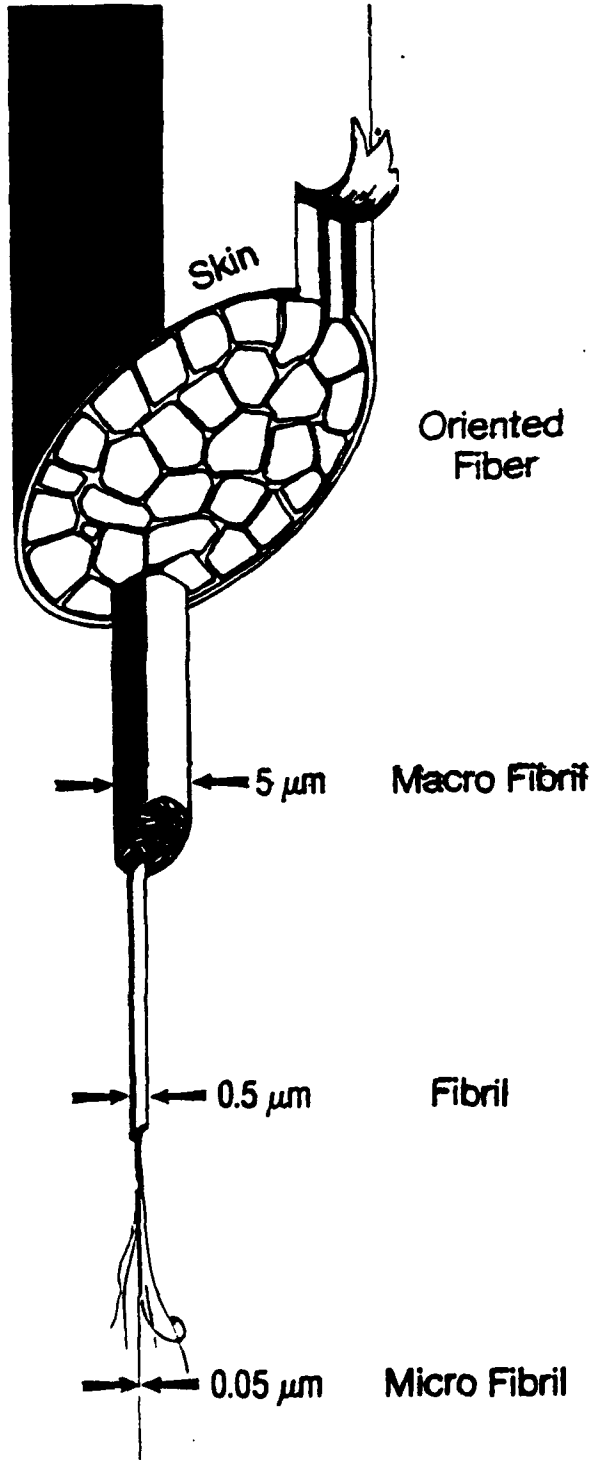
- Need to improve the compressive properties of polymeric fibers
- No clear explanation of compressive failure mechanisms
- Small quantity fibers produced in development programs
- Composite compression testing is not feasible

Solution



PURPOSE

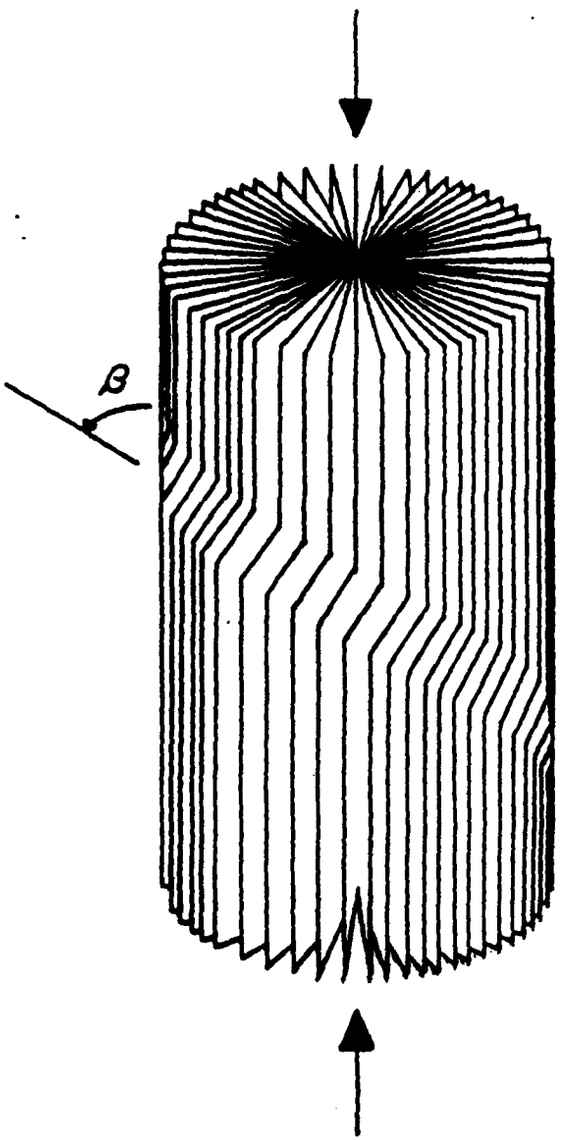
- Single filament compression test methods
  - Elastica loop test
  - Bending beam test
- Compressive properties of fibers
- Compressive failure mechanisms
- Numerical analysis of elastica problems

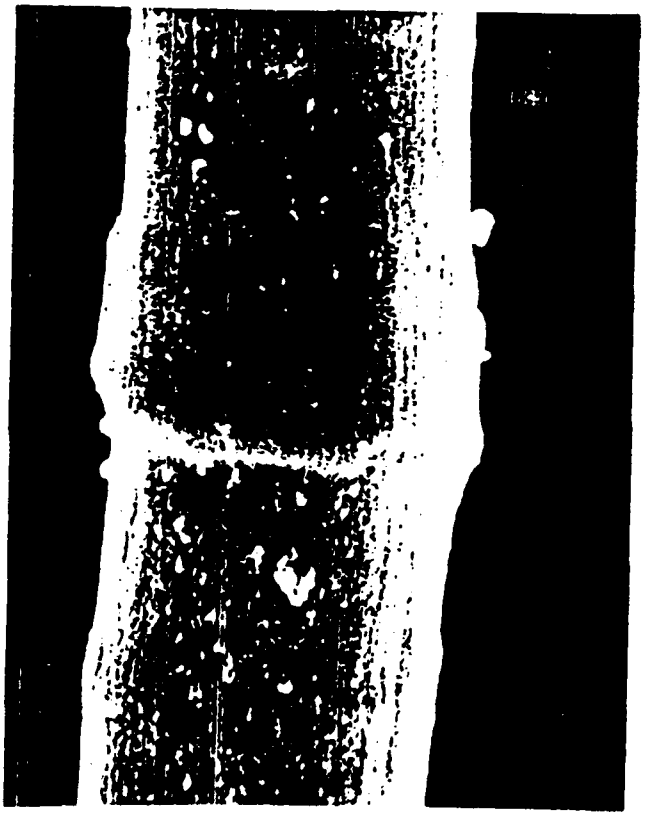

Skin
Oriented
Fiber
5 μm
Macro Fibril
0.5 μm
Fibril
0.05 μm
Micro Fibril
L C Sawyer

COMPRESSIVE FAILURE MODES

- Shear failure
  - •High modulus carbon fibers
- Kink band formation
  - •Polymer fibers
- Bending failure
  - •Glass fibers

KINK BAND FORMATION





THEORY

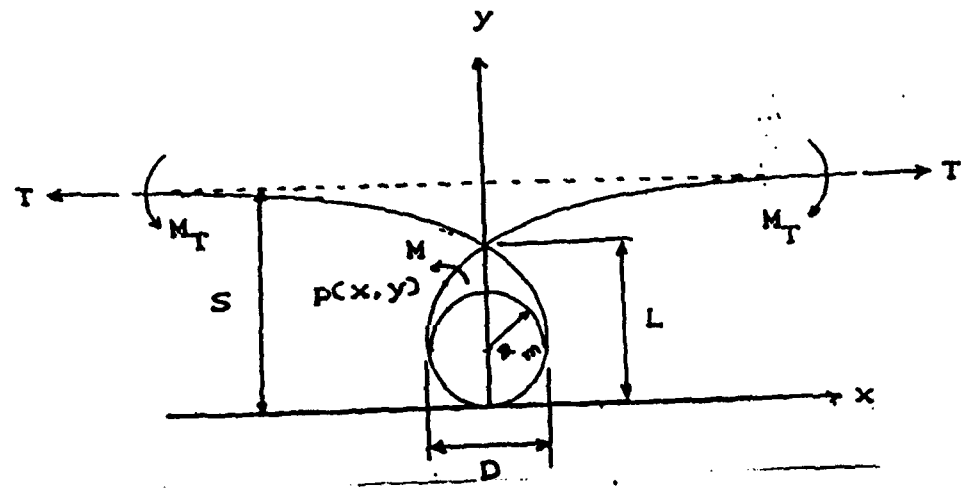
- Elastica loop test
- Bending beam test
- Numerical analysis of elastica problems

FIRST LET'S CONSIDER THE ELASTICA LOOP PROBLEM.

ELASTICA LOOP TEST

- A fiber is twisted into a loop
- Loop size is reduced gradually by pulling on the loop ends
- Fiber deformation was observed by optical microscope
- Also scanning electron microscope is used for this purpose

ELASTICA LOOP TEST



Geometry of Elastica Loop

$$x = \pm S \left[\frac{2y}{S} - \frac{y^2}{S^2} \right]^{1/2} \mp \frac{S}{4} \ln \left[\frac{1+(2y/S - y^2/S^2)^{1/2}}{1-(2y/S - y^2/S^2)^{1/2}} \right]$$

ELASTICA LOOP TEST

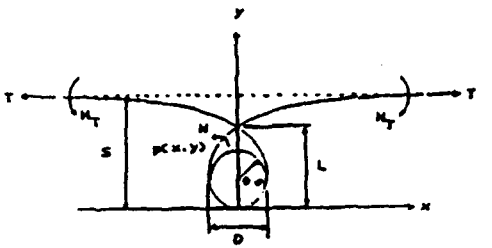
- Linear elastic material
- Shear stress and material anisotropy neglected
- Bending moment at the arms neglected
- Fiber is an infinite bar

ELASTICA FORMULATION

$$M = M_T + T\,(S-y)$$

$$M = \frac{E\,I}{R_m}$$

$$\frac{1}{R_m} = \frac{d^2y\,/\,dx^2}{[1+(dy/dx)^2]^{3/2}}$$



$$x = \pm\, S\left[\frac{2y}{S} - \frac{y^2}{S^2}\right]^{1/2} \mp \frac{S}{4}\,\mathrm{Ln}\left[\frac{1+(2y/S - y^2/S^2)^{1/2}}{1-(2y/S - y^2/S^2)^{1/2}}\right]$$

This analysis yields very important results:

$$S^2 = \frac{4\,E\,I}{T}$$

$$D = 0.5328\,S$$

$$L = 0.7136\,S$$

$$R_m = S/4$$

ELASTICA LOOP TEST

- Compressive strain is calculated by

$$\varepsilon_{cr} = \frac{r}{R_m}$$

where ε_{cr} = critical compressive strain

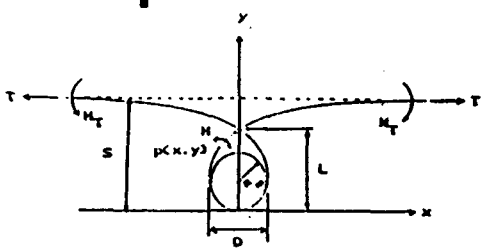
r = fiber radius

R_m = minimum radius of curvature of the location where the last kink band is seen.

ELASTICA LOOP TEST

- Measurements are taken at the critical loop where the first kink bands seen

- Two methods are applied to find the minumum radius of curvature:
  - Elastica formulation
  - Circle drawing in the loop graphically

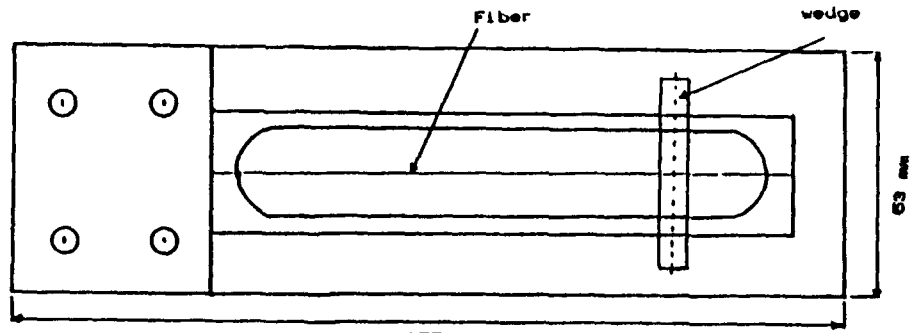


ELASTICA LOOP TEST

Two methods are applied:

1. Optical microscopy method
2. Scanning electron microscopy method

BENDING BEAM TEST



$$\varepsilon(x) = \frac{3\,t\,d}{3\,L^2}\left(1 - \frac{x}{L}\right)$$

Schematic Drawing of Bending Beam Test
Apparatus and Strain Distribution in the fiber

BENDING BEAM TEST

Criteria

- Last kink band is observed
- Assumed that the fiber is perfectly bonded to the beam
- The strain at any point in the fiber equals the strain at the surface of the beam

BENDING BEAM TEST

Measurement

- Distance ℓ is measured by travelling stage
- The ℓ value is substituted into strain formula below

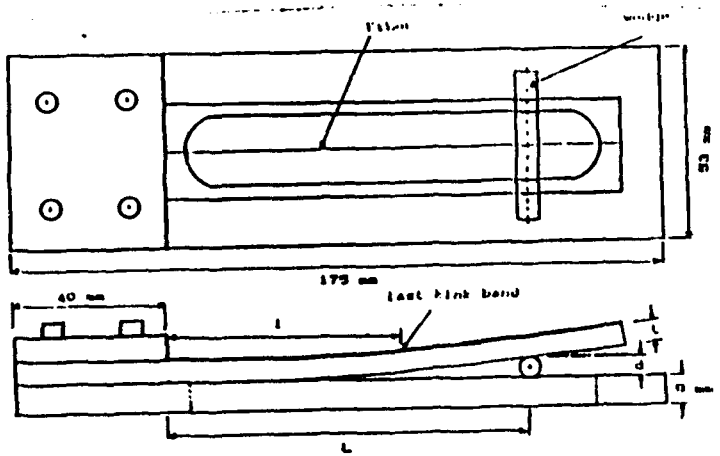
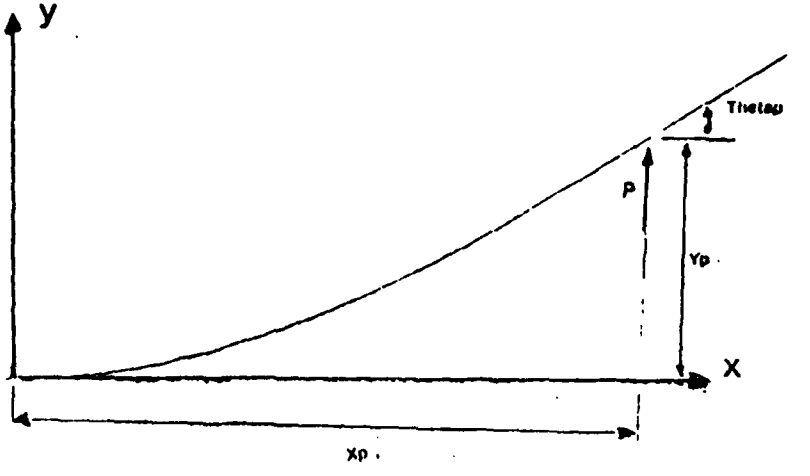


Figure 7. Schematic Drawing of Bending Beam Test Apparatus and Strain Distribution in the Fiber

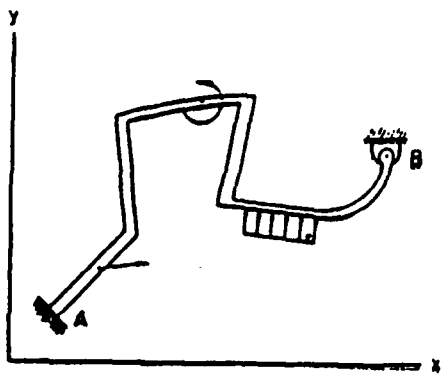
ELASTICA SHOOTING TECHNIQUE

- Xp ,Yp and Thetap are measured
- The FORTRAN program is run to analyse the experiment
- Iteration for above values is done by increment of P values



ELASTICA PROBLEMS
SHOOTING TECHNIQUE

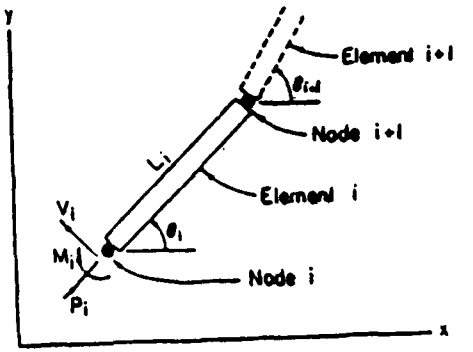
- Arbitrary shape and loading
- Non-uniform member
- Cross-sectional dimensions small compared to the length
- Displacements are large but strains are small
- Linear elastic material



SHOOTING TECHNIQUE

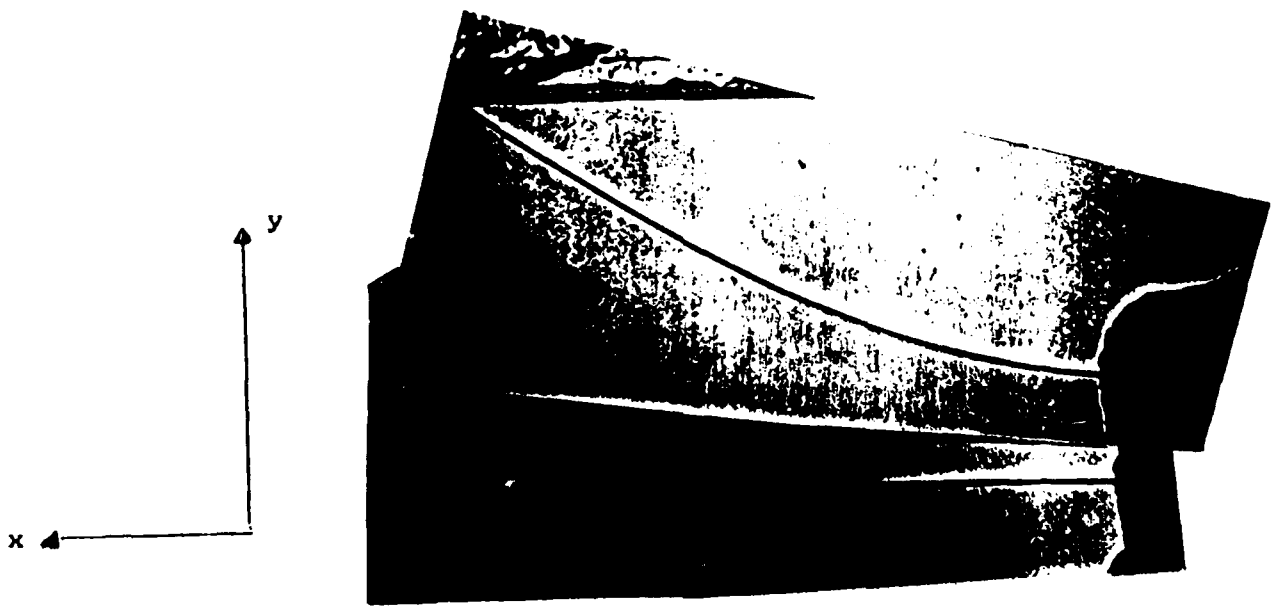
Problem Formulation

- Initial geometry and material properties
- Division into elements of the fiber
- Applied external forces and moments at node points
- Three boundary conditions at each end



ELASTICA SHOOTING TECHNIQUE

- One end of the fiber is fixed, the other end is bent in y-direction
- The first kink bands are observed near the fixed end



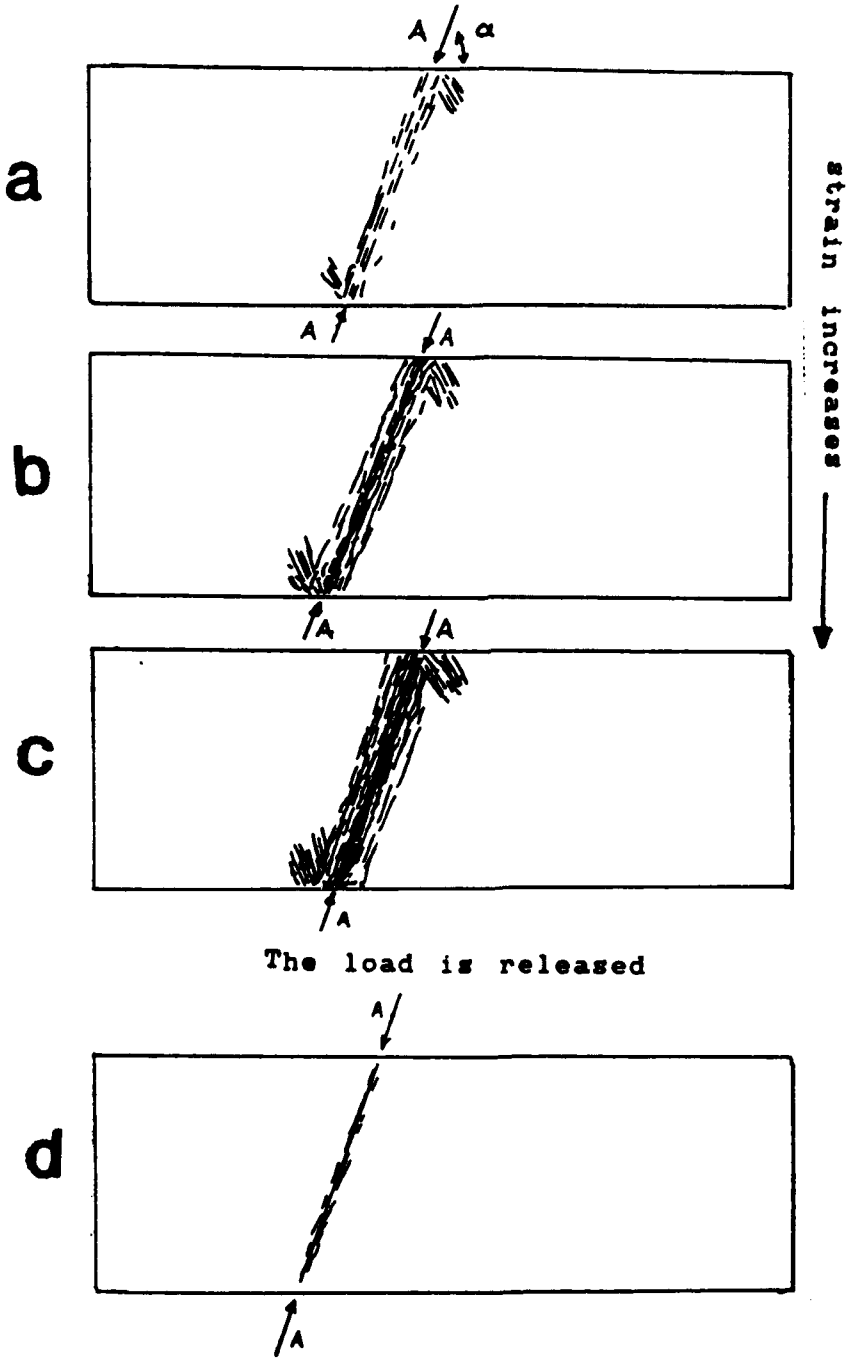
BASIC CRITERIA

For all three experiments:

- Observation of the critical kink bands
- The assumptions made:
  - Fiber behaves linear elastic until the first kink band forms
  - The compressive stress which initiates the critical kink band formation are the compressive strength of the fiber

EXPERIMENT

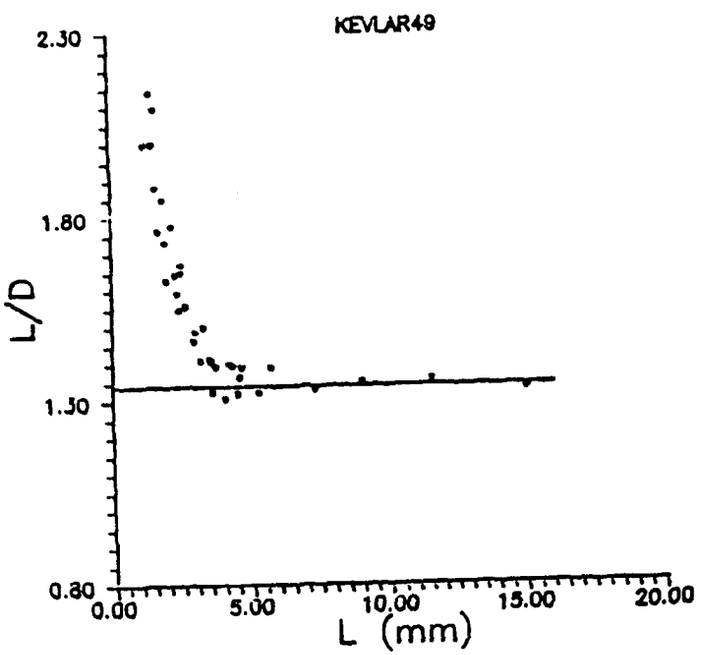
- Elastica loop test
- Bending beam test
- Elastica shooting test

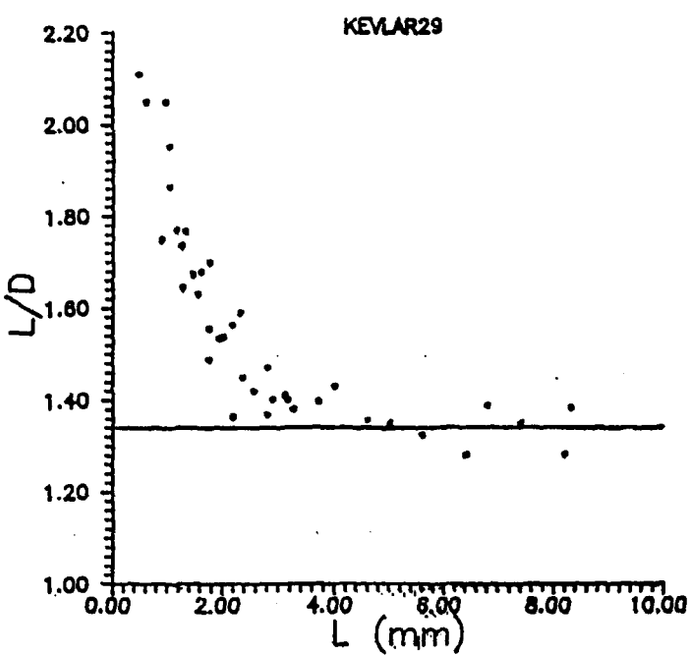


The load is released

RESULTS AND OBSERVATIONS

Fiber Compressive Behavior Plots obtained from the Elastica Loop Tests





RESULTS AND OBSERVATIONS

Critical Strains and Compressive Strengths of the Fibers

FIBER	d (mm)	E (GPa) [1]	ELASTICA LOOP TEST εcr(%) Optical radius	ELASTICA LOOP TEST εcr(%) Micro elastic	ELASTICA LOOP TEST εcr(%) SEM radius	BEAM TEST εcr(%) [2]	COMPRESSIVE SRENGTH, σc [4] (GPa) Beam Test	COMPRESSIVE SRENGTH, σc [4] (GPa) Elastica Loop
KEVLAR 29	0.012	78.6	.75 ∓.12	.68 ∓.02		.75 ∓.10	.59	.50
KEVLAR 49	0.012	110.3	.61 ∓.12	.61 ∓.08		.68 ∓.04	.69	.67
KEVLAR 149	0.012	113.8	1.05 ∓0.12	1.09 ∓0.09		- [8]	-	1.24
HT PBO [6]	0.030	183.0		.91 ∓.02		.18 ∓.08	.27	.47
HT PBO [7]	0.045	166.0		.26 ∓.02		.19 ∓.01	.53	.48
HT PBZT	0.017	308.0		.15 ∓.01	.11 ∓.02	.10 ∓.05	.30	.39
AS PBZT	0.020	110.0		.15 ∓.01	.18 ∓.01	- [8]	-	.17
T-50	0.007	398.0				1.04 ∓0.08	4.09	-
P-75S	0.010	517.0				.52 ∓.07	2.09	-

1 Composite compressive modulus for Kevlar fibers; Tensile modulus for the rest of the fibers
2 Corrected for tensile prestrain applied during mounting to beam.
3 Not able to see kink band formation.
4 Calculated by $\sigma c = E \times \varepsilon cr$
5 Calculated by using εcr in fifth column.
6 Treated by 5 % NH_4OH } Produced in Materials Laboratory.
7 Steam 1 type }
8 Not able to get this value because of fiber surface irregularities.
∓ values are standart deviations.

RESULTS AND OBSERVATIONS

Elastica Shooting Test Results

Critical strain obtained from elastica shooting test: 0.29 %

Critical strain obtained from elastica loop test : 0.26 %

ELASTICA LOOP TEST

Advantages and Disadvantages

- Advantages:
  1. Simple in nature
  2. Easy to take measurement
  3. Surface irregularities is not a problem
  4. In-situ observation of the fiber deformation gives more information about fiber compressive behavior

- Disadvantages:
  1. Special care must be taken to apply in-plane forces

BENDING BEAM TEST

Advantages and Disadvantages

- Advantages:
  1. Simple test in nature
  2. Easy to take measurements
  3. In-situ observations of the fiber is very useful
  4. The axial stress gradient created along the fiber is very advantageous
  5. No shrinkage problem observed

- Disadvantages:
  1. Fiber surface imperfections

CONCLUSIONS

- This study tries to model a concept of a growing kink band formation
  - Critical kink band
  - Molecular level deformation
- Only bending beam test was applied for carbon fibers. The compressive failure mode in carbon fibers were observed as a shear fracture.

CONCLUSIONS

- The elastica loop tests and bending beam tests were conducted successfully to predict fiber properties and their compressive behaviors
- It can be concluded that the critical compressive failure mode in polymeric fibers, kink band formation, results from the buckling and seperation of microfibrils due to elastic instabilities under compression stresses

CONCLUSIONS

- The compressive strength values obtained from this study are slightly higher than those obtained from the composite compression test method
- The axial stress gradient created along the fiber is very advantageous in observing the fiber compressive behavior at different stress levels

CONCLUSIONS

- In-situ observation of fiber deformation is very useful in examining the fiber compressive behaviors
- Experimentally concluded that the deviation slightly from elastic (L/D) ratio of 1.34 at critical loop stages in the elastica loop tests, doesn't change the final compressive values drastically

CONCLUSIONS

- The elastica shooting test as a potentially new, single filament compression test method, developed in this study.
- Motivation was:
- Apply numerical analysis on the elastica problems to get more sensitive results from the compression tests.

CONCLUSIONS

- Being open for further developments such as

  Computer interaction

  Sensitive test apparatus

  Visual display of deformed fiber

  Inclusion of non-linear material properties

RECOMMENDATIONS

- The elastica shooting test can be developed further for more simple and sensitive measurements of fiber compression or tensile properties.

RECOMMENDATIONS

- Kink band formation can be analysed further by combining the bending beam test and x-ray diffraction technique
- Need to investigate the fact that the critical kink bands are in the region close to the fiber surface

Abstract

Characterizing the time-temperature dependence of the macroscopic states, the phase transitions and the molecular/morphological structure is essential to the development of high temperature thermotropic resins for low cost fabrication of high performance primary structures. Frequency dependent electromagnetic/dielectric sensing techniques (FDEMS) provide a sensitive automated means for measuring the time-temperature dependence of resin properties and changes in state continuously throughout the entire cure cycle. FDEMS has the potential added advantage of measuring these properties in-situ in the mold during fabrication, thereby monitoring the particular time-temperature heat transfer affects of individual molds and fabrication processes.

In this feasibility study, using DuPont's thermotropic liquid crystal polymer HX-4000, FDEMS were shown to be a sensitive in-situ means for monitoring the effect of time and temperature on the physical state and properties of the HX-4000 resin. The sensor results were correlated with differential scanning calorimetry DSC measurements which also was demonstrated to be a useful laboratory technique for characterizing these changes. The successful use of sensors in-situ in the mold in a high temperature press demonstrated the potential capability of using the technique, both in a laboratory and a production environment.

The sensor measurements monitored the changing fluidity of the HX-4000 resin and the mobility of the polar liquid crystal moieties in the amorphous resin state. The FDEMS measurements indicated that in HX-4000 the resin anneals at temperatures around 300°C over a period of hours and that the resin undergoes further reactivity at temperatures near 380°C with time . The DSC results support and enhance these correlations as does the work on the effects of annealing on the mechanical softening temperatures which is reported on at this symposium. Overall, the results of this FDEMS feasibility study on HX-4000 strongly support the importance of detecting the changing properties of thermotropic resins and the ability of FDEMS sensors, corroborated with DSC and mechanical work as a means of monitoring these changes in-situ in the processing tool, both in the laboratory and production environment.

Frequency Dependent Dielectric Sensor Measurements: An Insitu Technique for Characterization, Cure Monitoring and Process Control

David Kranbuehl
Sean Hart
Yunfei Wang
Christina Short

Department of Chemistry and Applied Science
The College of William and Mary
Williamsburg, Virginia 23187 – 8795
(804) 221-2542

Immediate Objective

This year's immediate objectives are:

- Characterize through DSC, RDA, and FDEMS sensing, the time–temperature dependence of the macroscopic states, phase transitions, and molecular/morphological structure of high temperature thermotropic resins.

- Demonstrate the ability of FDEMS sensing to provide a means for insitu monitoring of these changes during processsing.

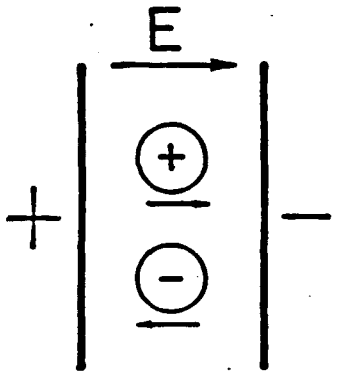
Overall Objective

To use embedded wafer thin frequency dependent electromagnetic sensors (FDEMS) for continuous, online, insitu measurement of thermotropic properties, in the laboratory, in the fabrication tool during processing and during use in the operating environment.

- Cure process design and optimization
- Closed loop intelligent process control
- Life monitoring, smart materials

Two Molecular Probes

Ionic - free charge σ

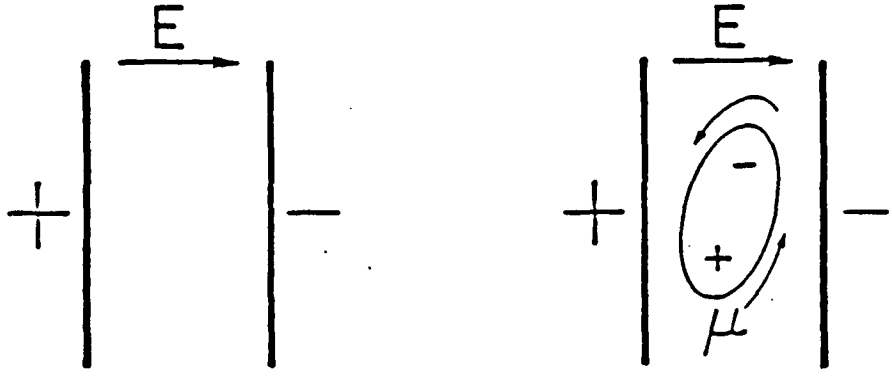


translational diffusion of ions

$$\rho_T \frac{dx}{dt} = \text{force}$$

sphere: $\rho_T = 6\pi\eta r$

Dipolar - bound charge τ



rotational diffusion of dipoles

$$\rho_R \frac{d\theta}{dt} = \text{torque}$$

sphere: $\rho_R = 8\pi\eta r^3$

FREQUENCY DEPENDENCE

$$\varepsilon' = \frac{C_{material}}{C_o} = \varepsilon' = \varepsilon'_{ionic} + \varepsilon'_{dipolar}$$

$$\varepsilon'' = \frac{G_{material}}{C_o 2\pi f} = \varepsilon'' = \varepsilon''_{ionic} + \varepsilon''_{dipolar}$$

IONIC · Translational Diffusion

$$\varepsilon'_i = Z_o \sin\frac{(n\pi)}{2}\frac{(G^2)}{C_o}\omega^{-(n+1)}$$

$$Z^* = Z_o(i\omega)^{-n}$$

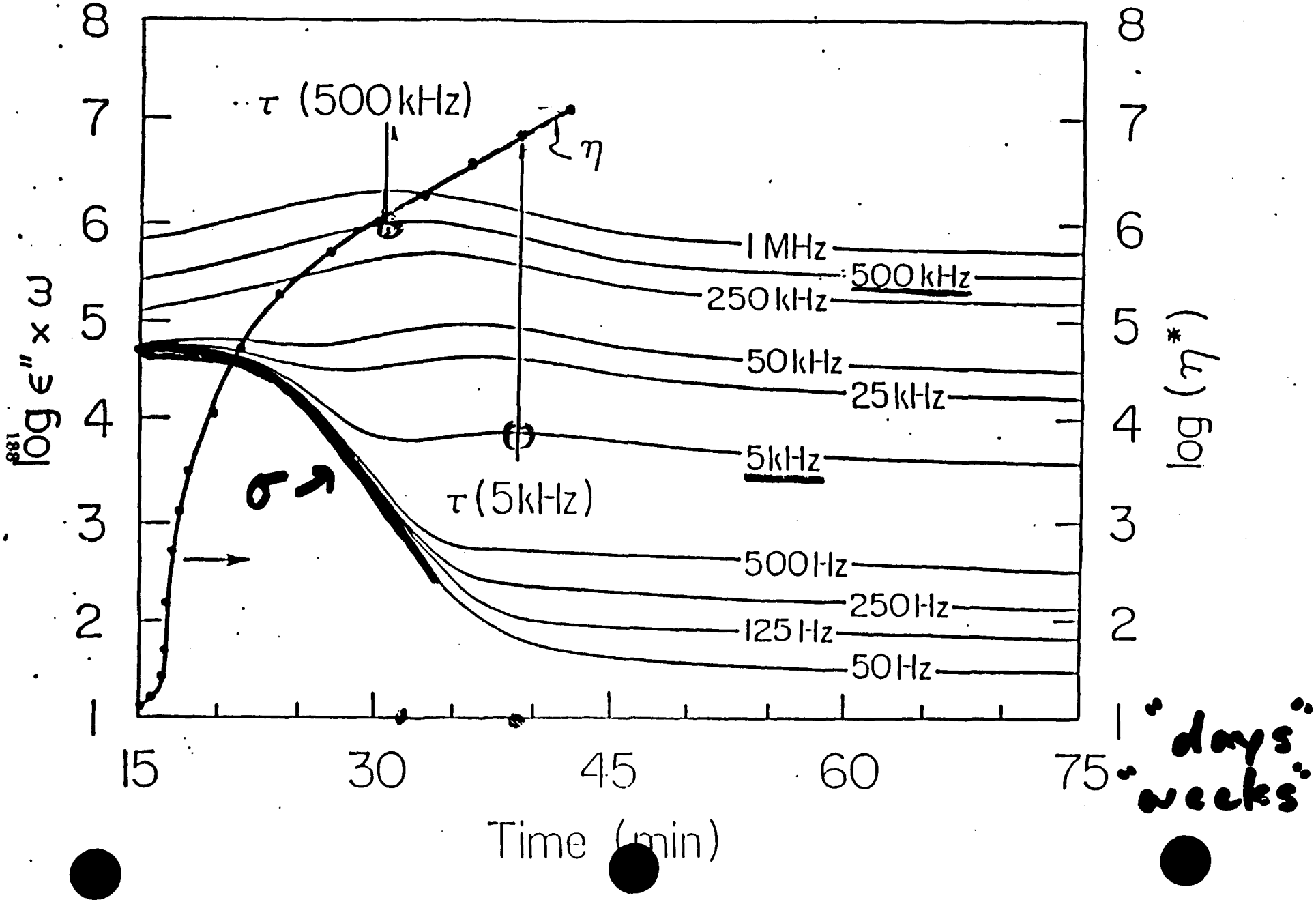
$$\varepsilon''_i = 1.8 \times 10^{14}\frac{\sigma}{f}$$

DIPOLAR · Rotational Diffusion

$$\varepsilon'_d - \varepsilon_\infty = \frac{\varepsilon_o - \varepsilon_\infty}{(1+\omega^2\tau^2)^\alpha}$$

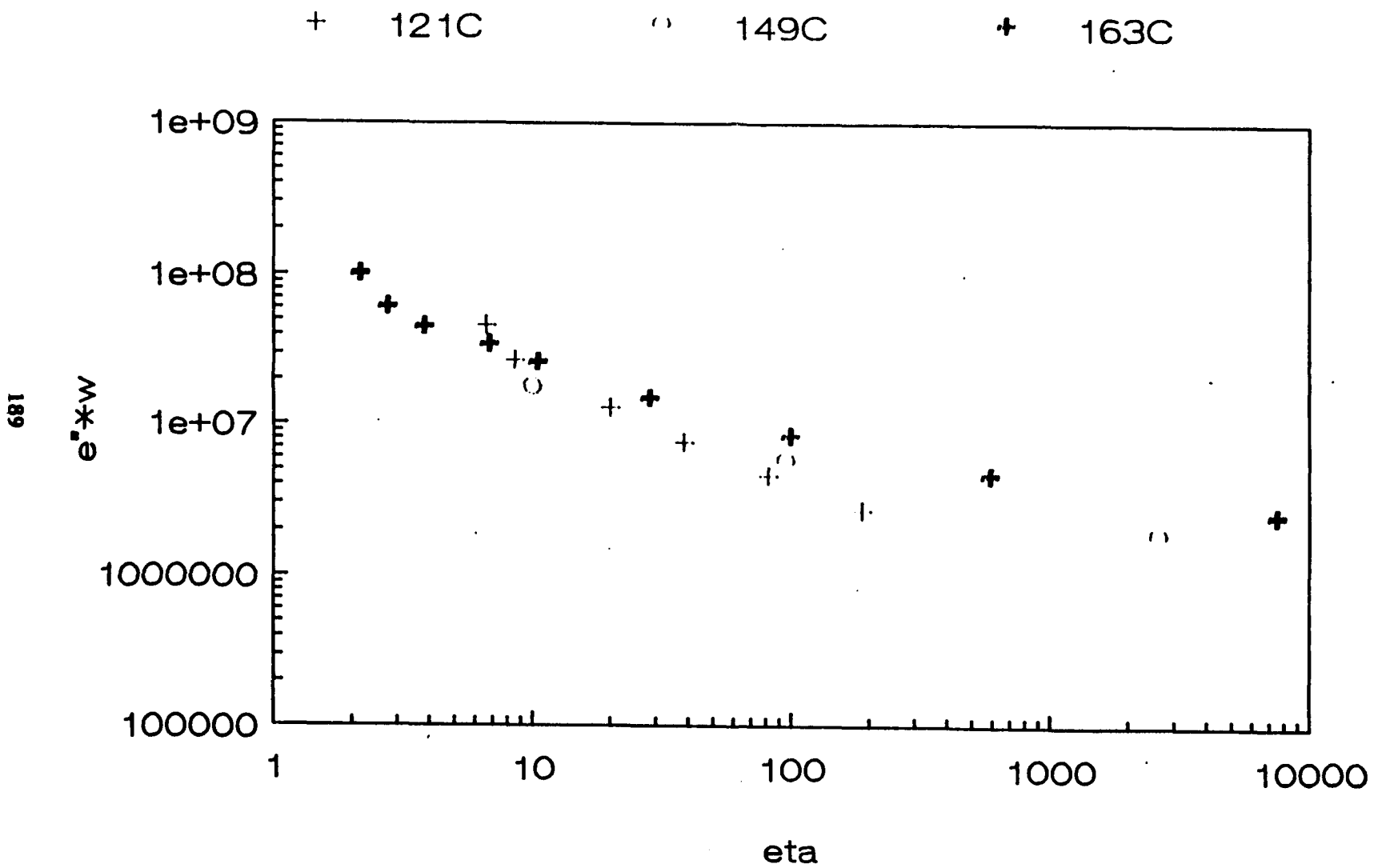
$$\varepsilon''_d = \frac{(\varepsilon_o - \varepsilon_\infty)(\omega\tau)^\alpha}{(1+\omega^2\tau^2)^\alpha}$$

Sensor Output

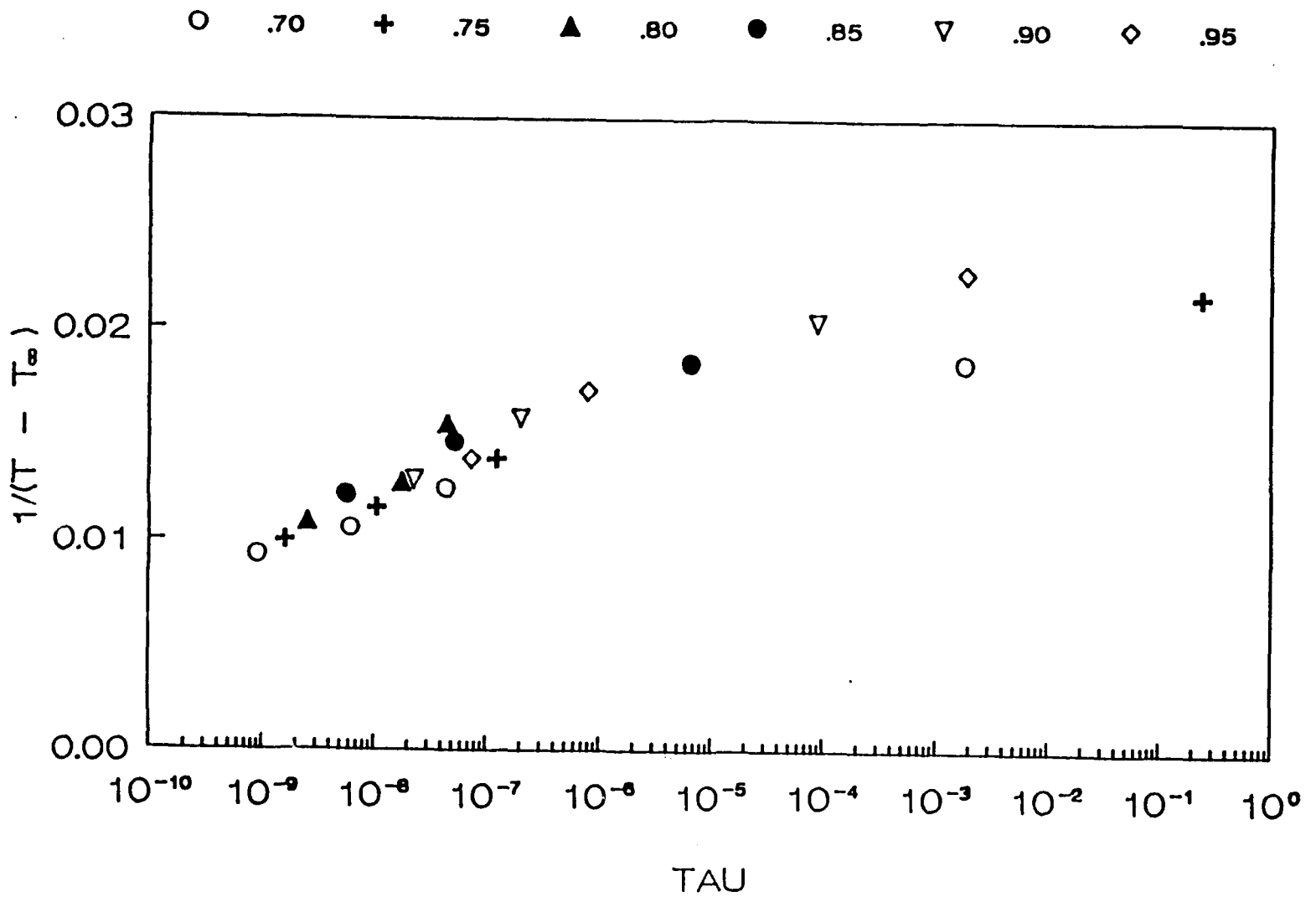


3501-6

e"*w vs. eta

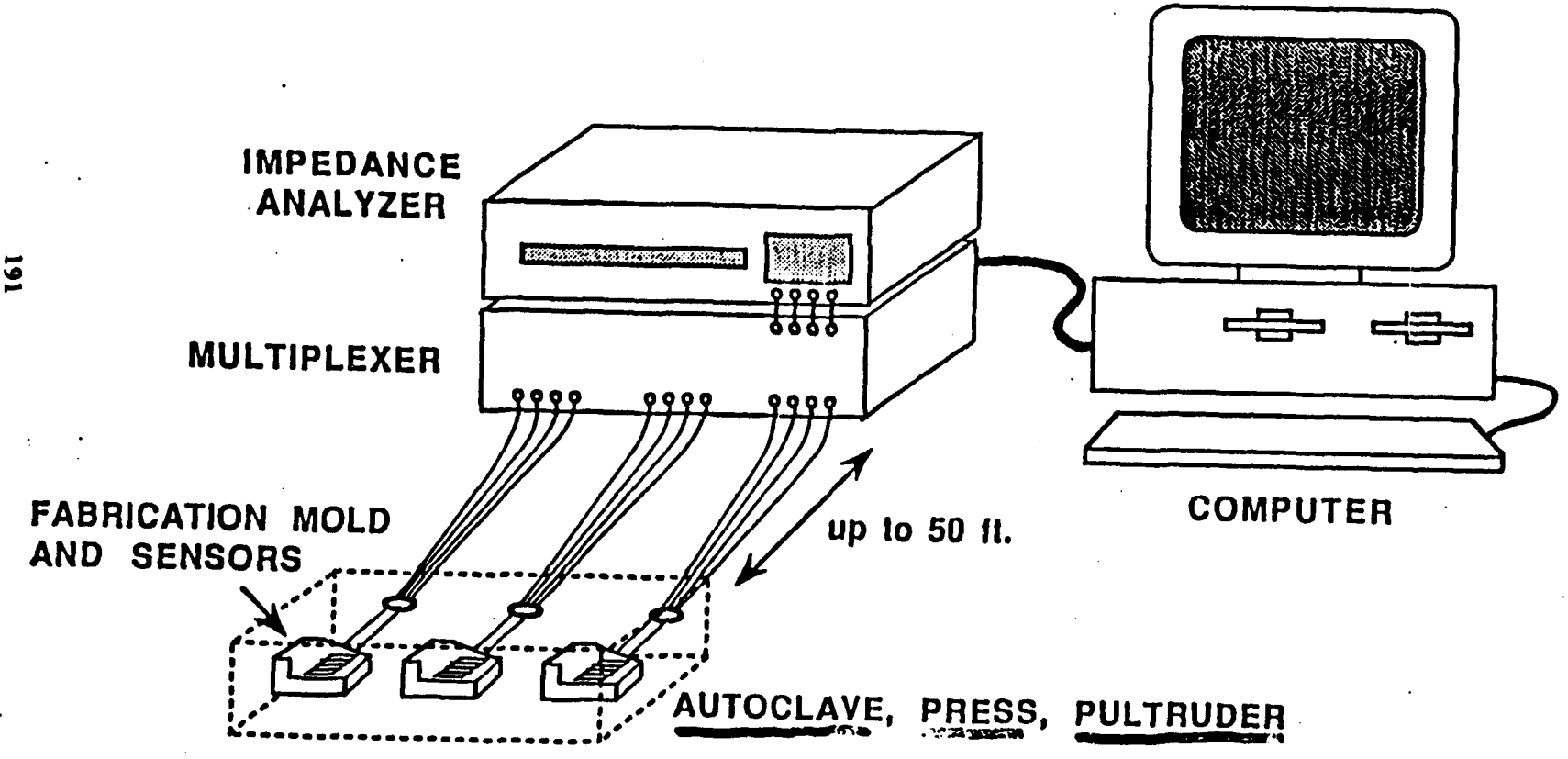


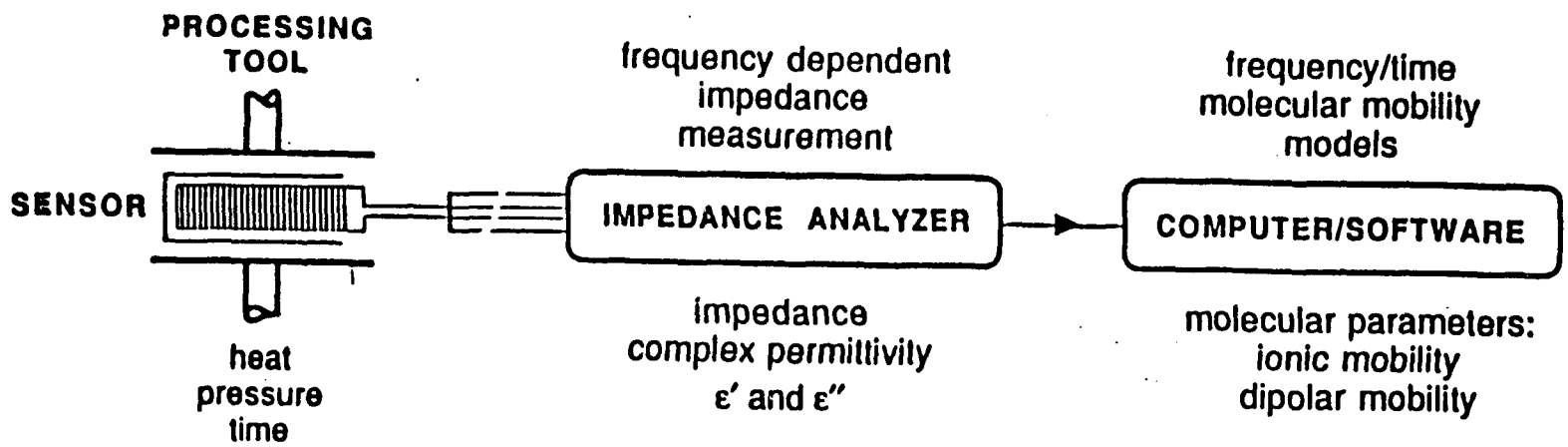
$1/(T-T_\infty)$ vs. Tau



Instrumentation

Physical Arrangement of Remote Sensors and Measuring System





- viscosity
- degree of cure
- buildup in modulus
- reaction completion
- T_g, T_m, T_c
- solvent content
- moisture uptake
- degradation, thermal, atomic O_2 , UV-high energy radiation
- age, batch variation

Advantages

- single inert sensor
- temperatures to >800 °F
- continuous uninterrupted simultaneous measurement of both ε' and ε''
- 4 place sensitivity in ε'
- 3 place sensitivity in ε''
- permittivity range 10^{-3} to 10^{7}
- frequency range 10^{-5} to 10^{7} Hz
- low cost multiplexing – multiple sensor measurements

AWARD

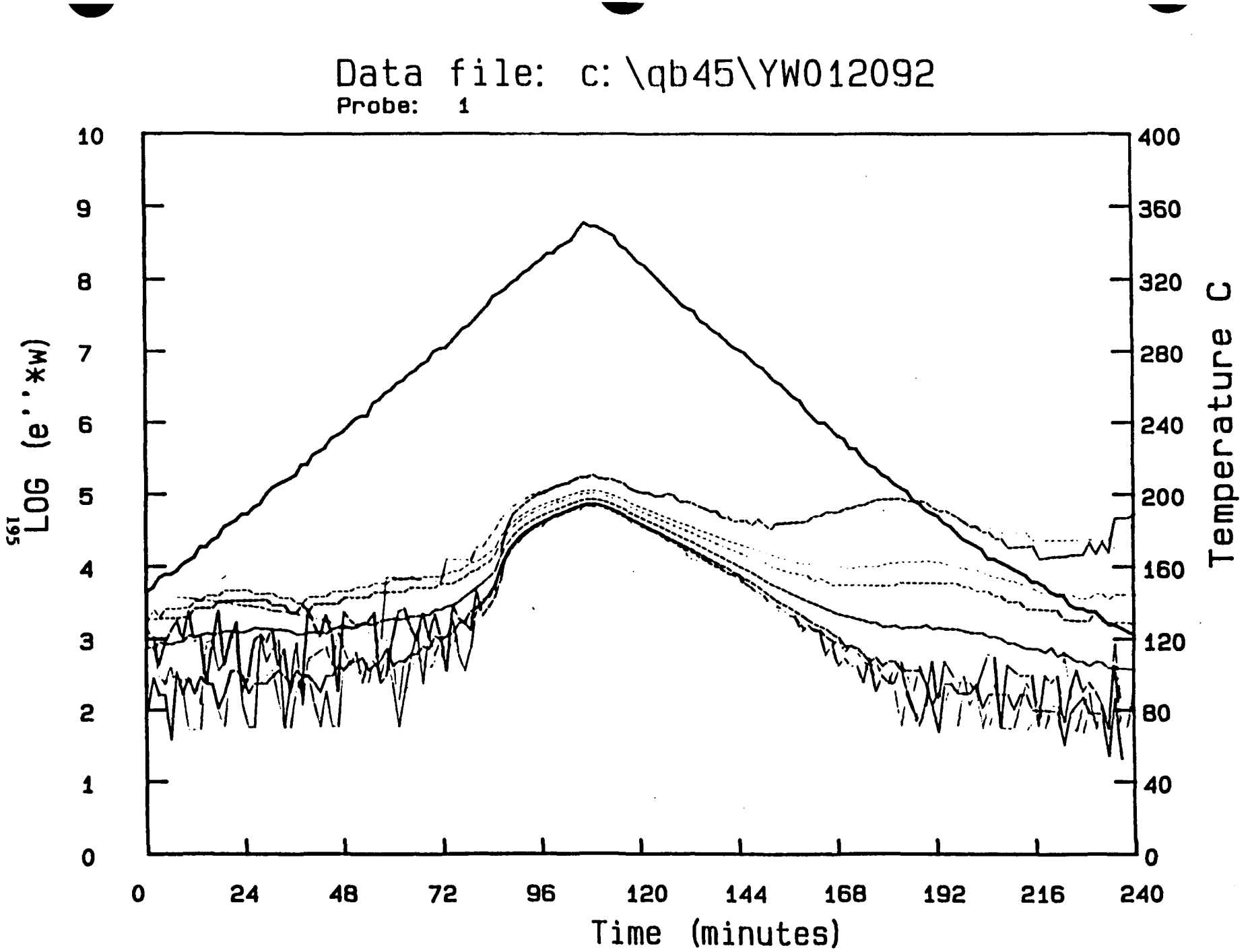
Initial Materials

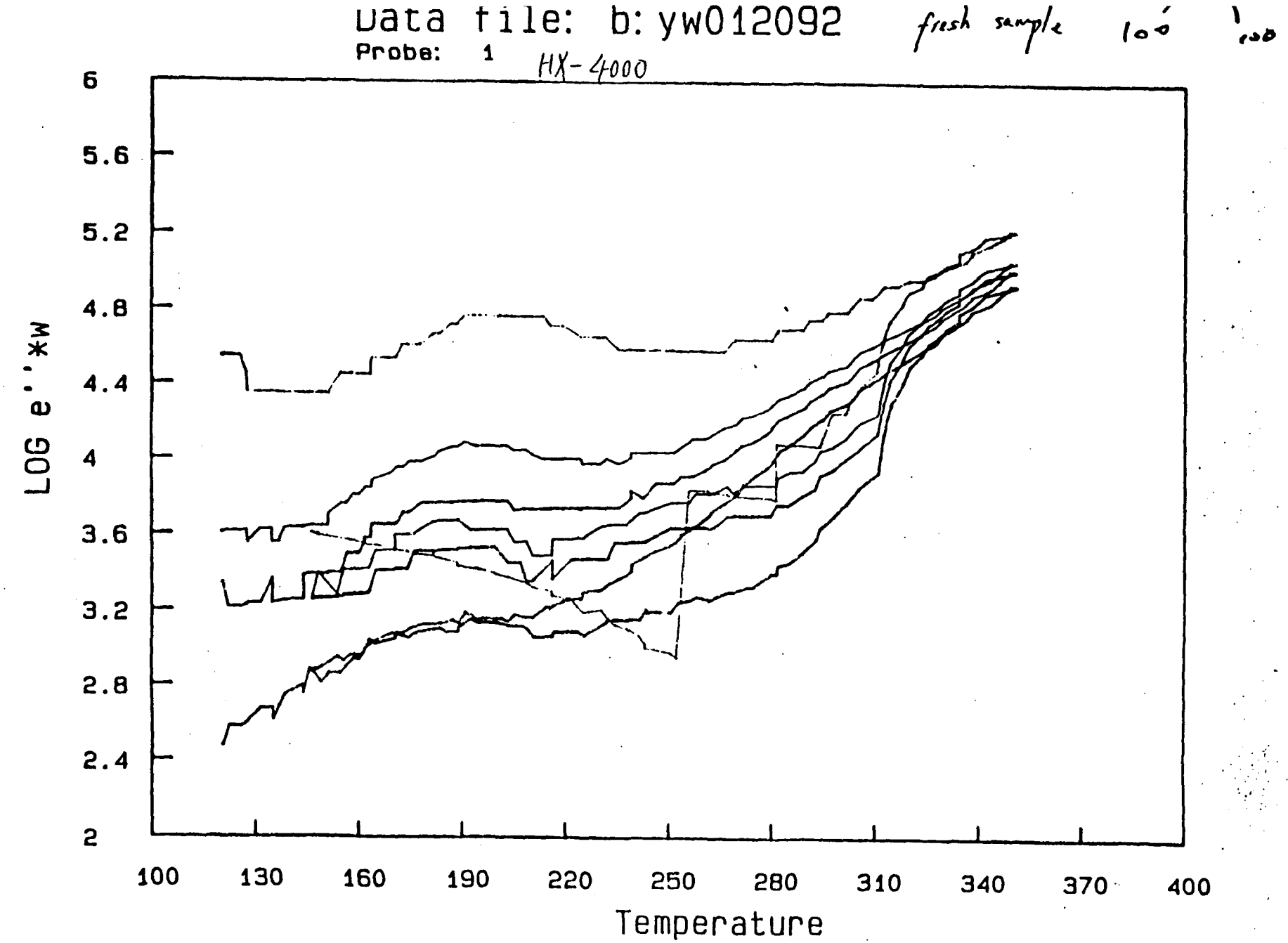
HX–4000

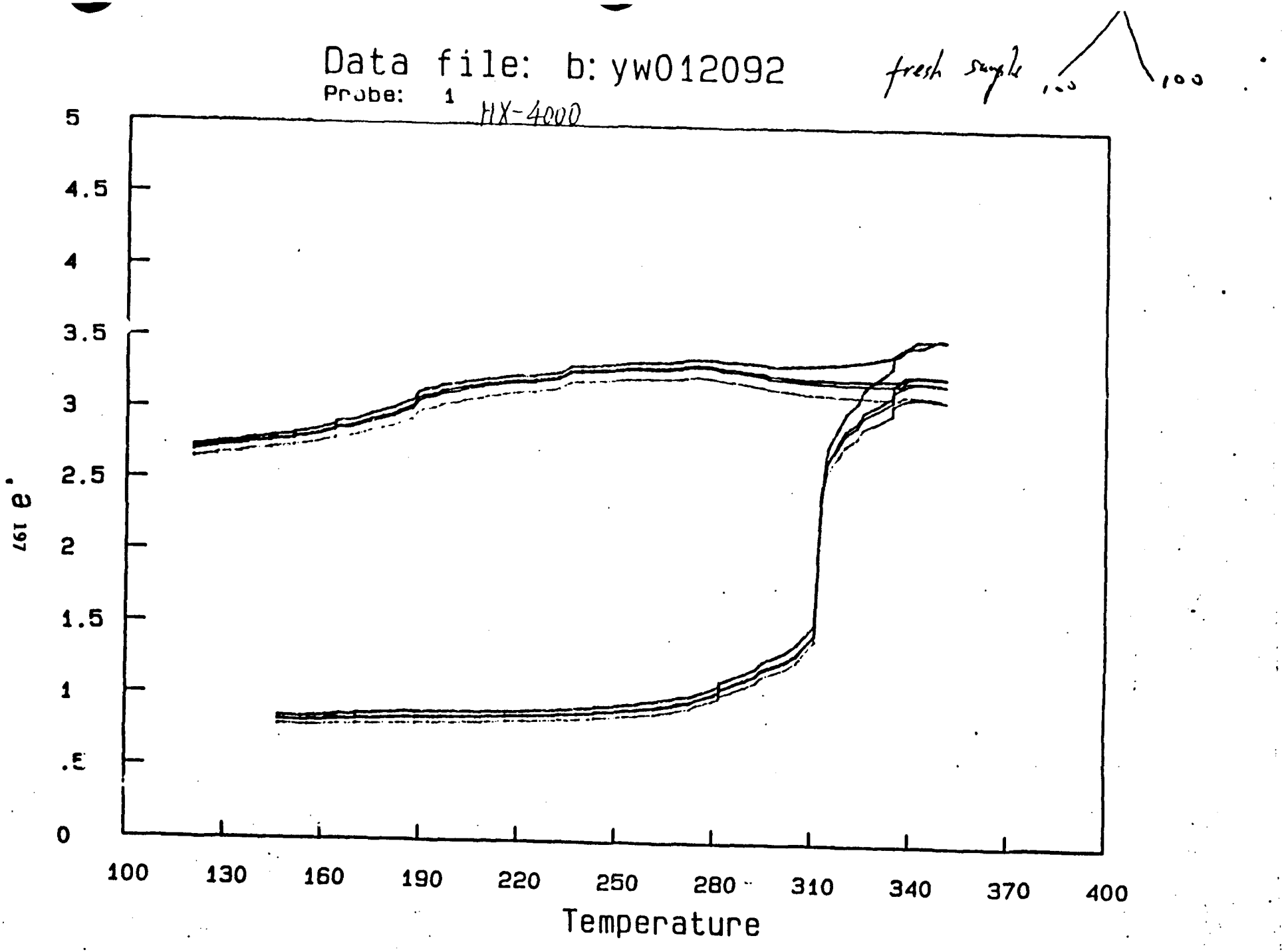
VECTRA A950

VECTRA C950

XYDAR SRT–300


Data file: c:\qb45\YW012092
Probe: 1
LOG (e''*w)
195
Temperature C
Time (minutes)
0
1
2
3
4
5
6
7
8
9
10
0
40
80
120
160
200
240
280
320
360
400
0
24
48
72
96
120
144
168
192
216
240

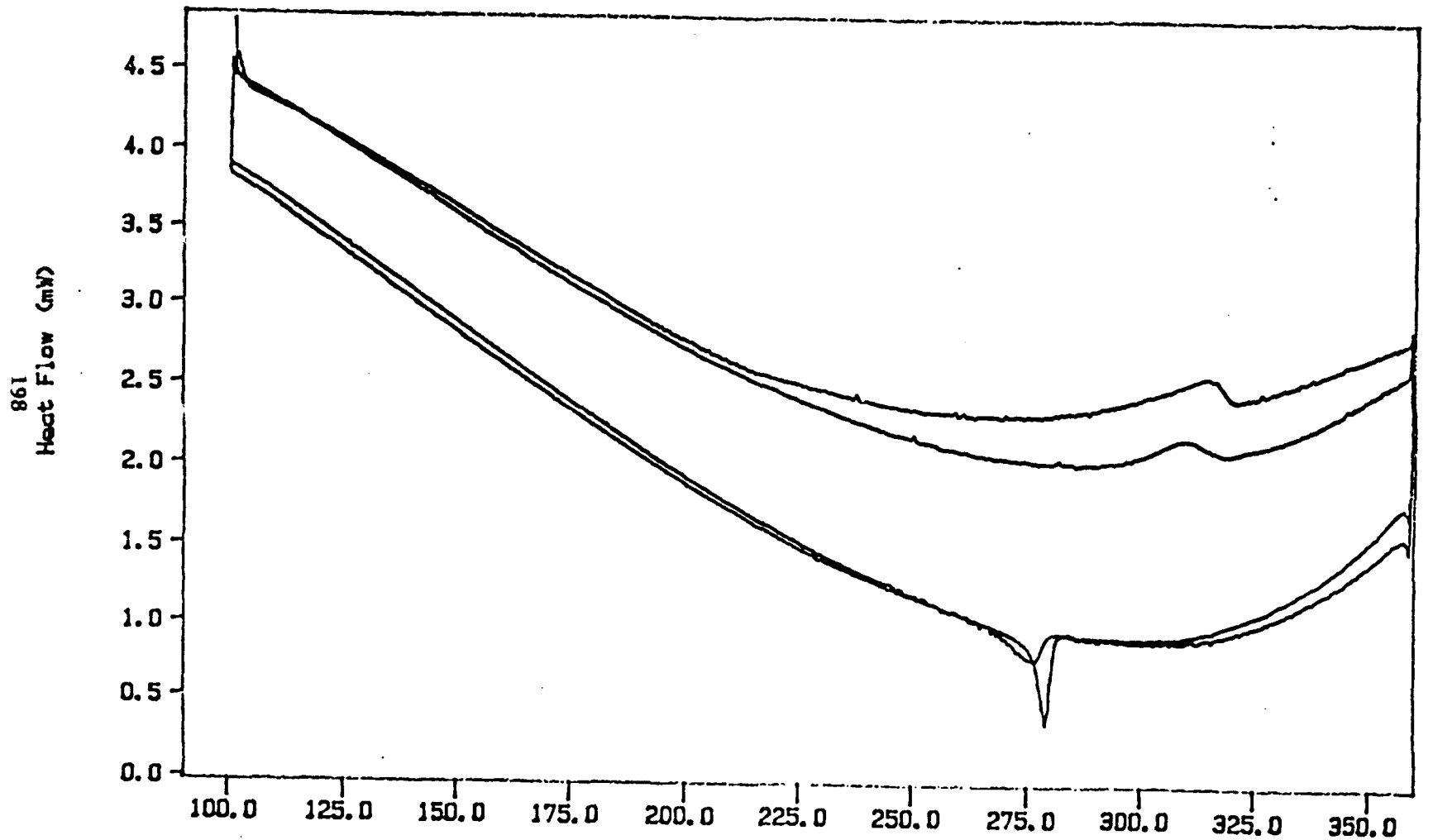

Data file: b:yw012092
Probe: 1
HX-4000
fresh sample 10' 1/100
LOG e''*w
6
5.6
5.2
4.8
4.4
4
3.6
3.2
2.8
2.4
2
100
130
160
190
220
250
280
310
340
370
400
Temperature


Data file: b:yw012092
Probe: 1
HX-4000
fresh sample
100
100
5
4.5
4
3.5
3
2.5
2
1.5
1
.5
0
ε'
100
130
160
190
220
250
280
310
340
370
400
Temperature

f.e.b

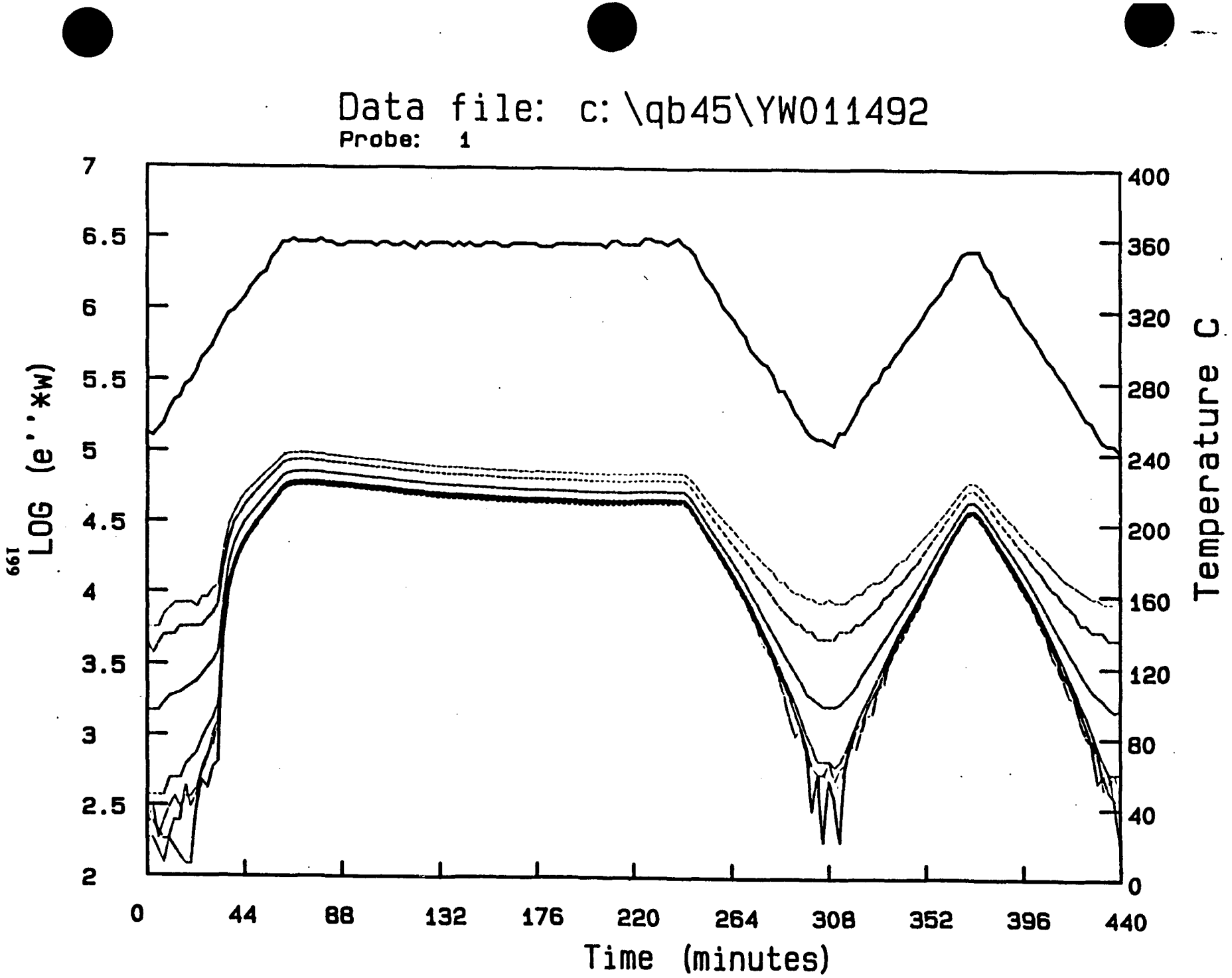
D C Data File: hx410
S mple Weight: 10.000 mg
F 1 Feb 14 07:57:35 1992
hx-4000 freef

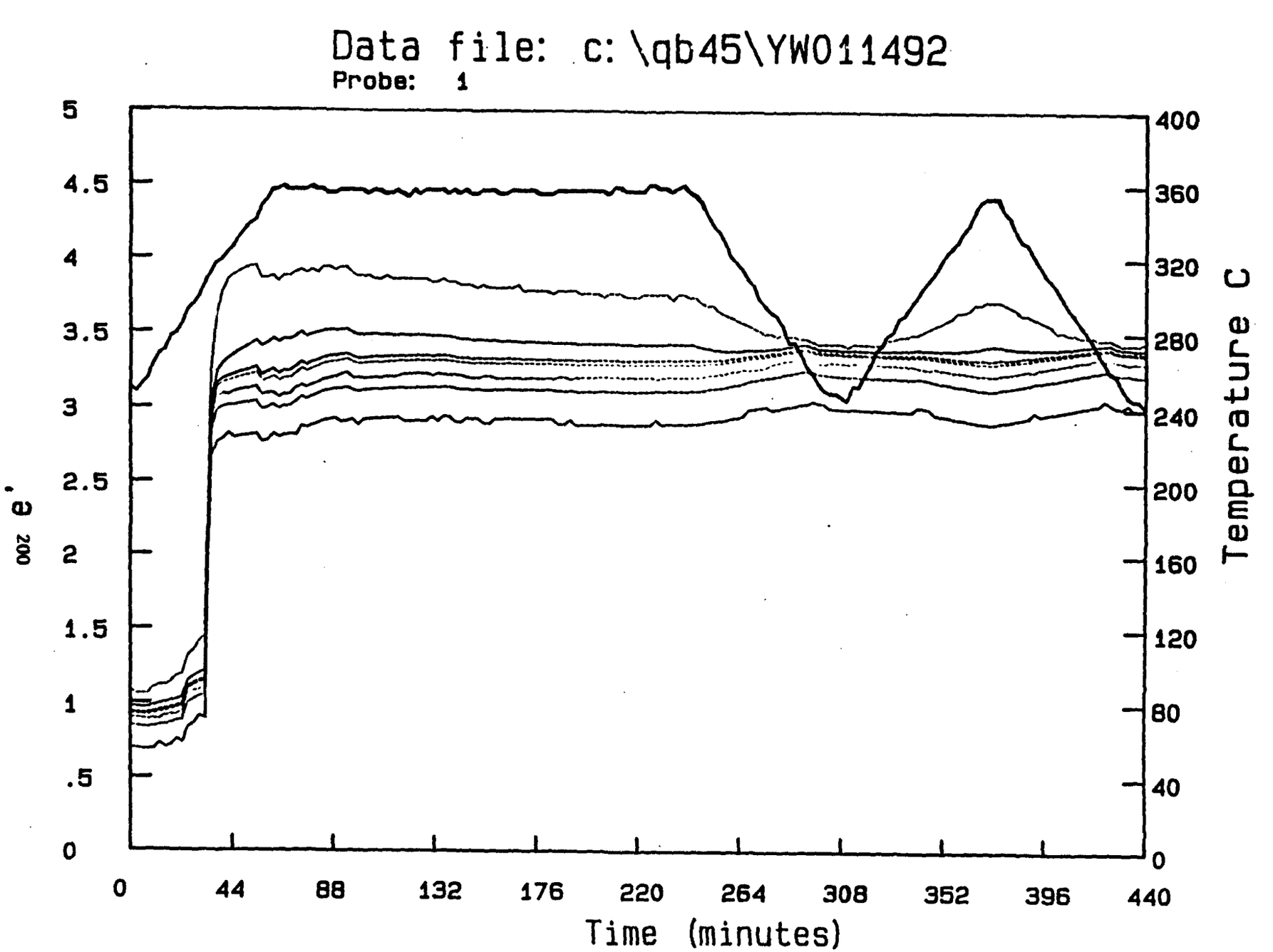
PERKIN-ELMER
7 Series Thermal Analysis System

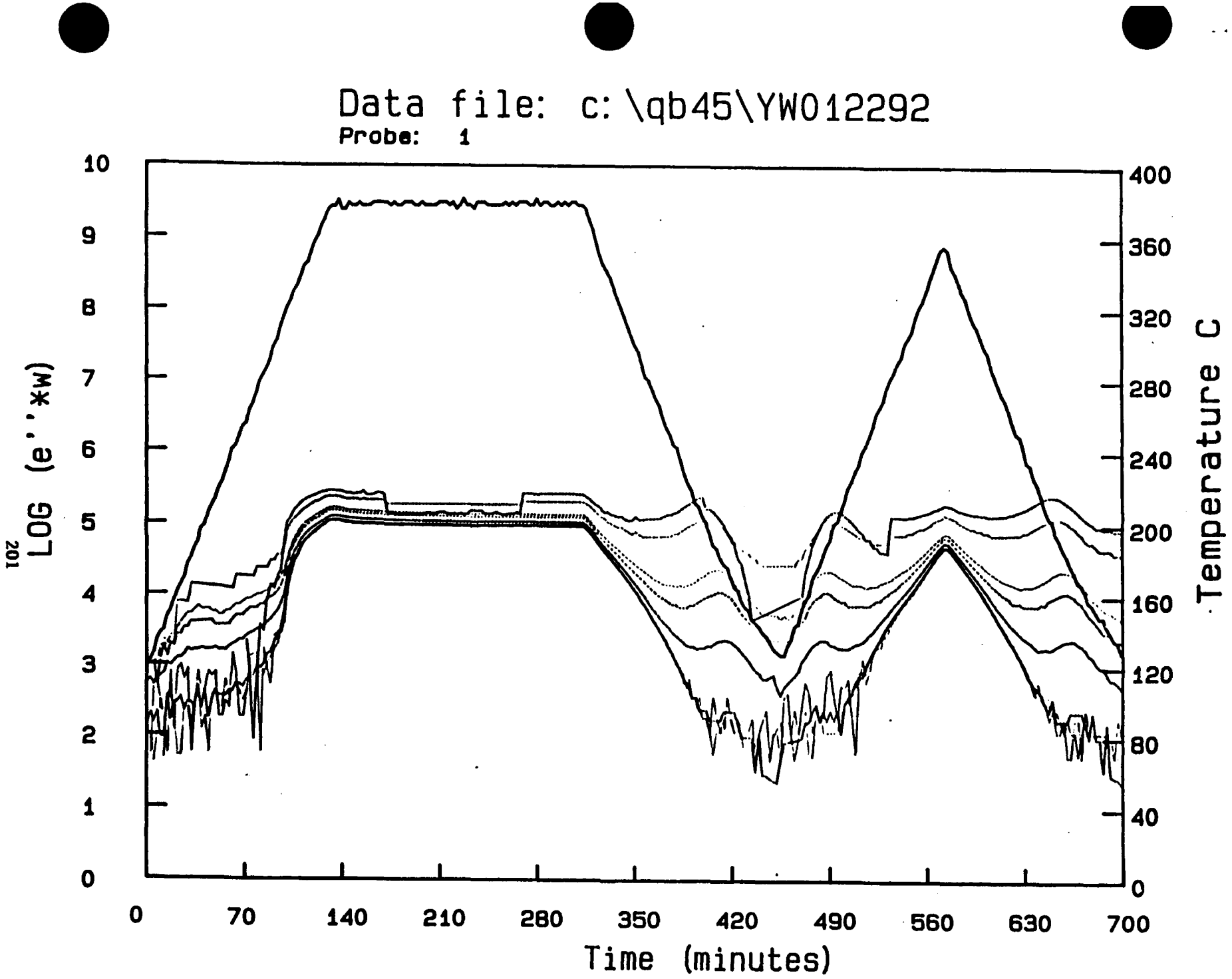


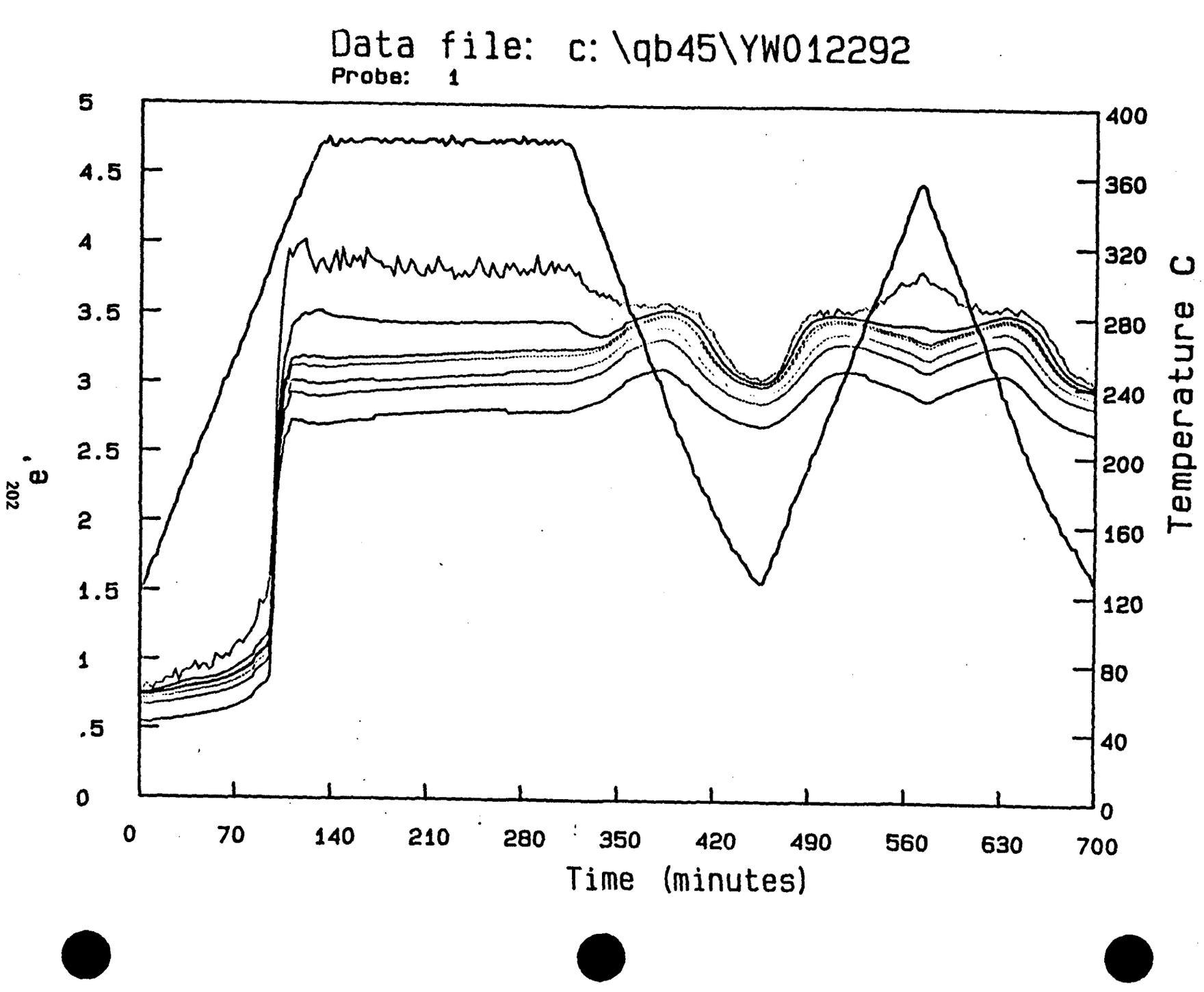
ramp 100c-360c-100c-360c-100c

TEMP 1: 100.0 C TIME 1: 0.0 min RATE 1: 2.0 C/min
TEMP 2: 360.0 C TIME 2: 0.0 min RATE 2: 2.0 C/min
TEMP 3: 100.0 C TIME 3: 0.0 min RATE 3: 2.0 C/min
TEMP 4: 360.0 C TIME 4: 0.0 min RATE 4: 2.0 C/min
TEMP 5: 100.0 C


Data file: c:\qb45\YW011492
Probe: 1
LOG (e''*w)
199
Temperature C
Time (minutes)
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
400
360
320
280
240
200
160
120
80
40
0
0
44
88
132
176
220
264
308
352
396
440


Data file: c:\qb45\YW011492
Probe: 1
5
4.5
4
3.5
3
2.5
2
1.5
1
.5
0
e' 200
400
360
320
280
240
200
160
120
80
40
0
Temperature C
0
44
88
132
176
220
264
308
352
396
440
Time (minutes)

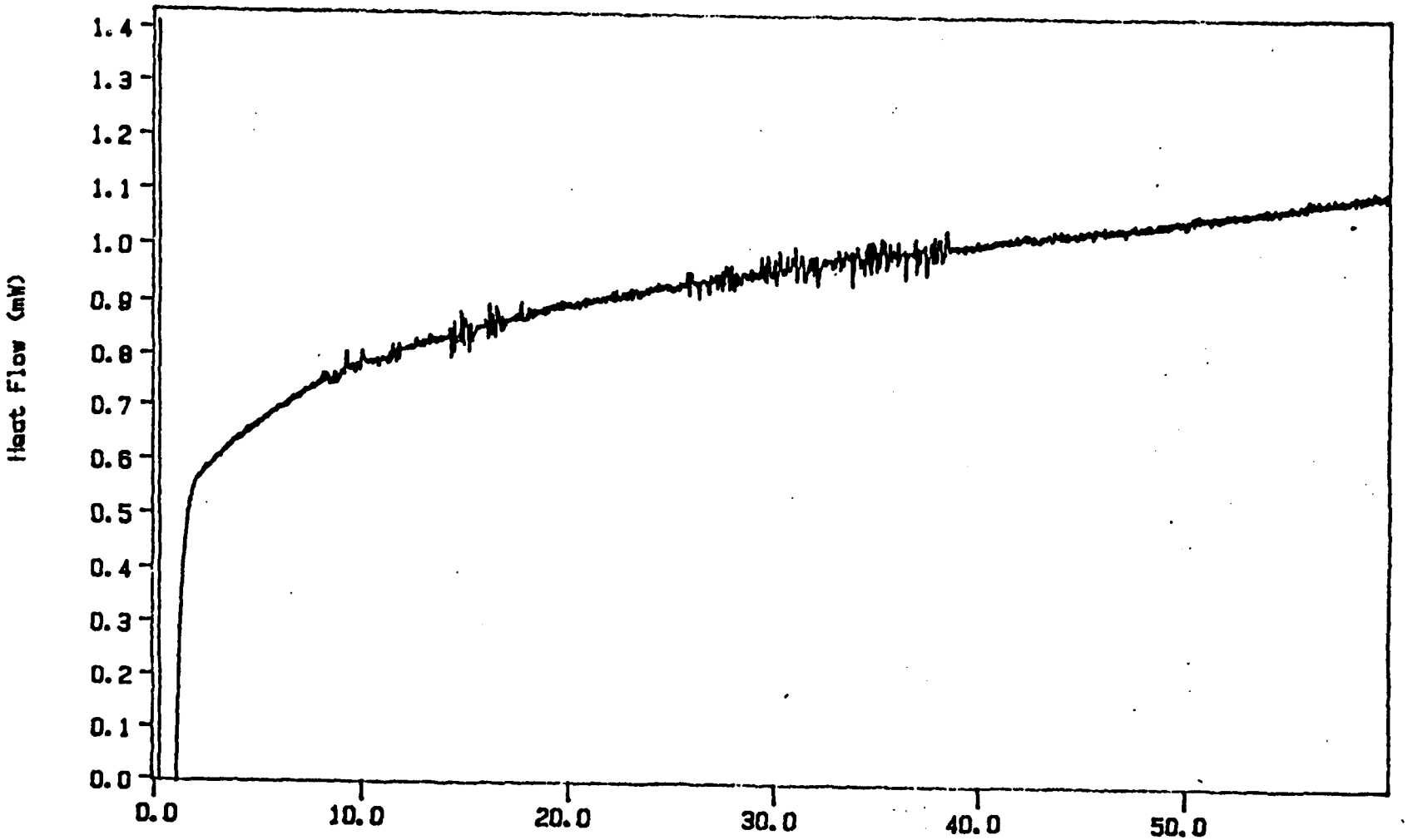

Data file: c:\qb45\YW012292
Probe: 1
LOG (e''*w)
201
Temperature C
Time (minutes)
0
1
2
3
4
5
6
7
8
9
10
40
80
120
160
200
240
280
320
360
400
0
70
140
210
280
350
420
490
560
630
700


Data file: c:\qb45\YW012292
Probe: 1
5
4.5
4
3.5
3
2.5
2
1.5
1
.5
0
202 e'
400
360
320
280
240
200
160
120
80
40
0
Temperature C
0
70
140
210
280
350
420
490
560
630
700
Time (minutes)

Iso 320°C 60 min

DSC Data File: hx411
Sample Weight: 8.100 mg
Fri Feb 14 15:28:35 1992
HX-4000 fresh

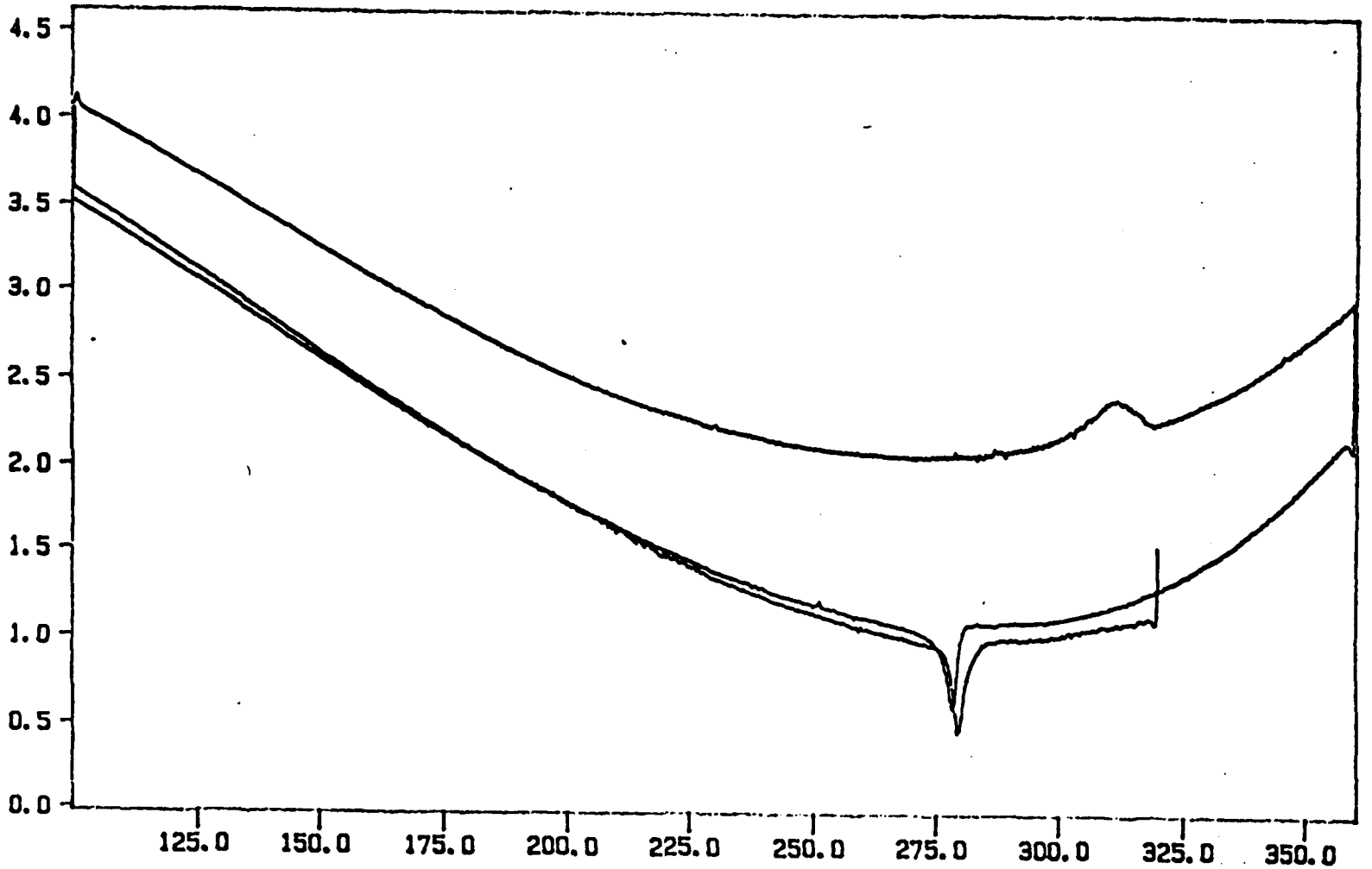
PERKIN-ELMER
7 Series Thermal Analysis System



iso 320c for 60min
TEMP 1: 320.0 C TIME 1: 60.0 min

DSC Data File: hx412
Sample Weight: 8.100 mg
Fri Feb 14 21:42:52 1992
hx-4000 after iso 320o 60min

PERKIN-ELMER
7 Series Thermal Analysis System



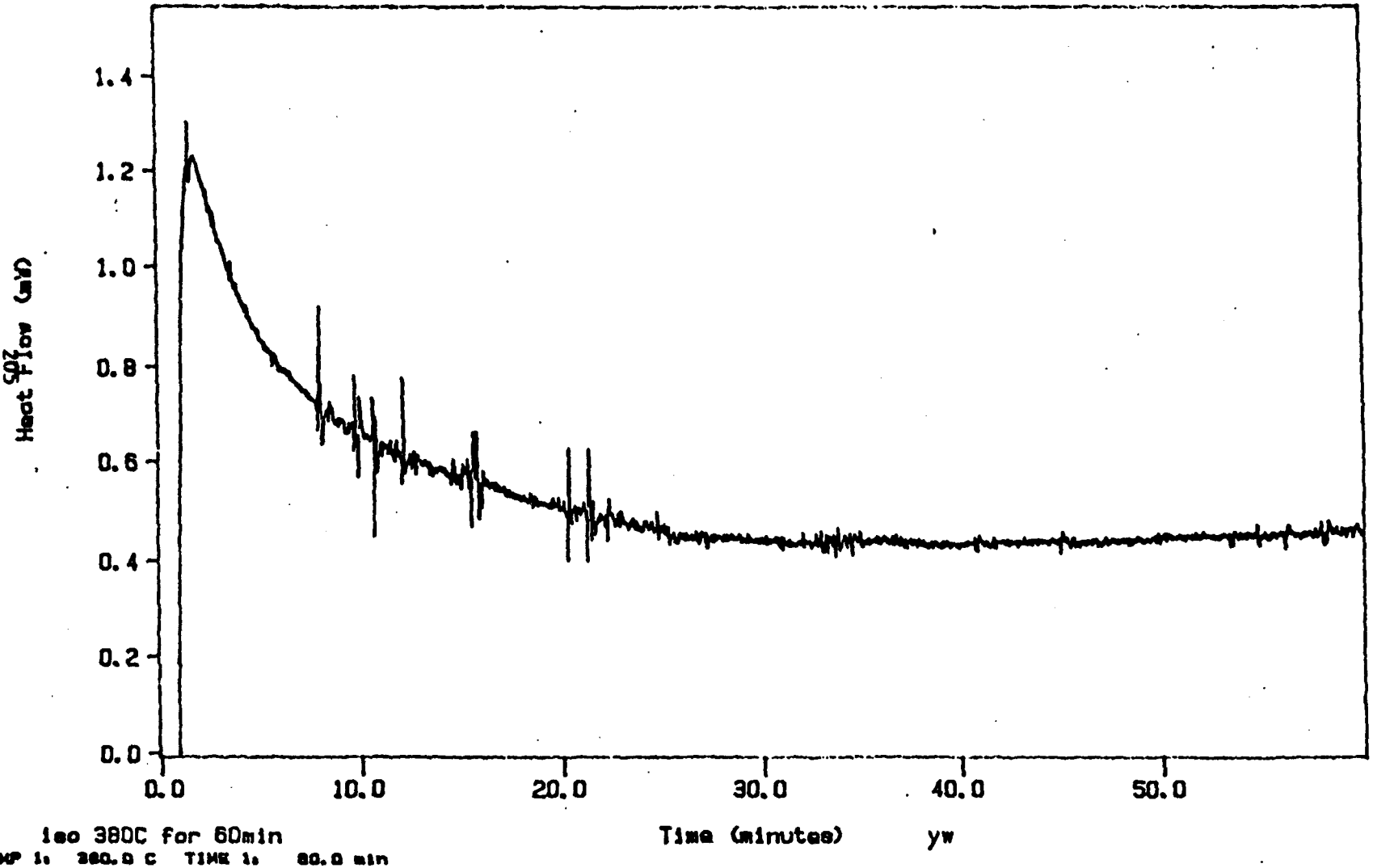
ramp
TEMP 1: 320.0 C TIME 1: 0.0 min RATE 1: 2.0 C/min
TEMP 2: 100.0 C TIME 2: 0.0 min RATE 2: 2.0 C/min
TEMP 3: 380.0 C TIME 3: 0.0 min RATE 3: 2.0 C/min
TEMP 4: 100.0 C

204

ISO 380°C 60 min

DSC Data File: hx413
Sample Weight: 10.000 mg
Sun Feb 16 22:24:28 1992
HX-4000m fresh sample

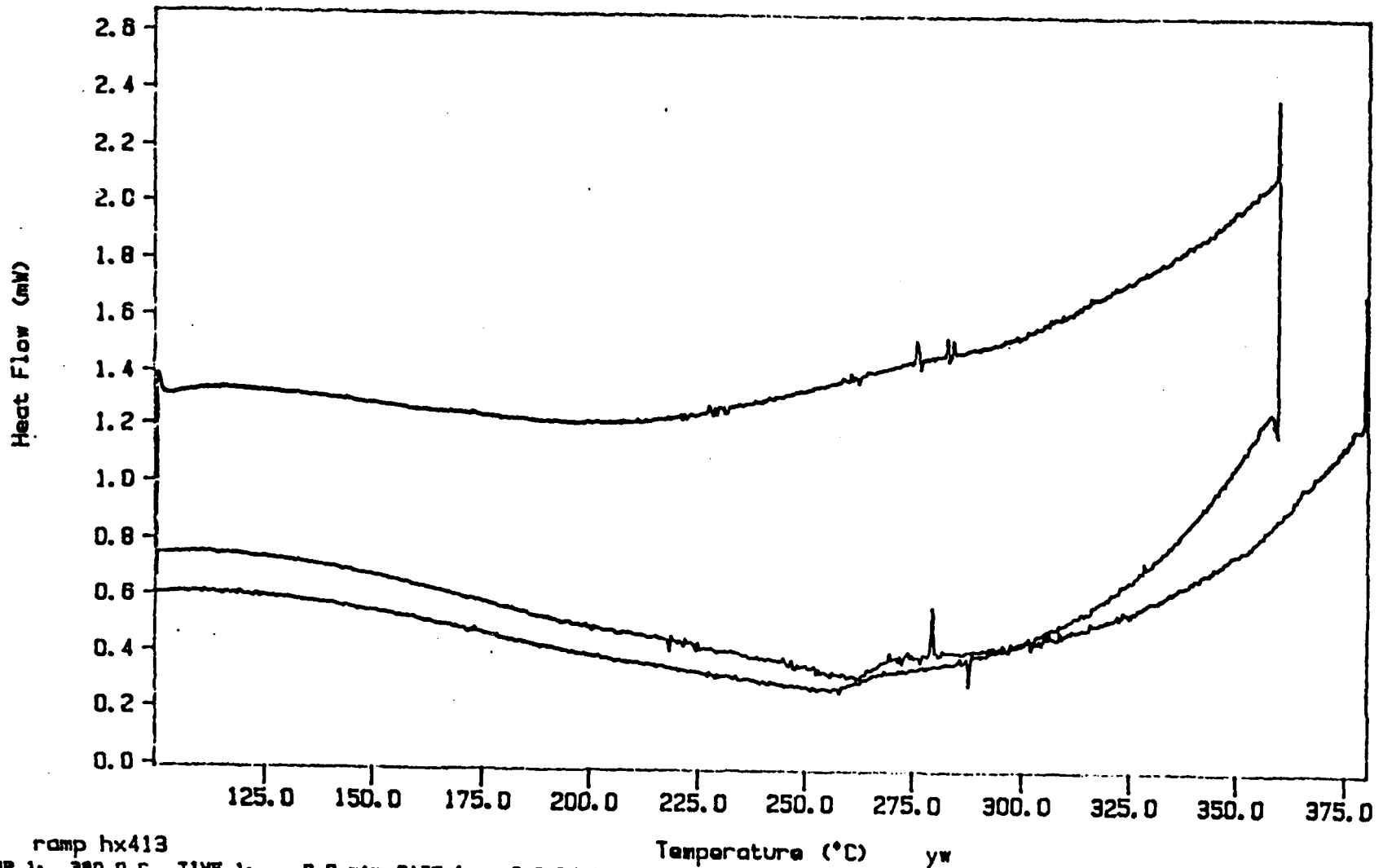
PERKIN-ELMER
7 Series Thermal Analysis System



iso 380C for 60min
TEMP 1: 380.0 C TIME 1: 60.0 min

DSC Data File: hx414
Sample Weight: 10.000 mg
Mon Feb 17 05:08:24 1992
hx4000, after 1ea 380c for 60min

PERKIN-ELMER
7 Series Thermal Analysis System



206

ramp hx413

TEMP 1:	380.0 C	TIME 1:	0.0 min	RATE 1:	2.0 C/min
TEMP 2:	100.0 C	TIME 2:	0.0 min	RATE 2:	2.0 C/min
TEMP 3:	380.0 C	TIME 3:	0.0 min	RATE 3:	2.0 C/min
TEMP 4:	100.0 C				

ADVANCED POLYMER COMPONENTS
RHEOLOGICAL CHARACTERIZATION

TASK 8

DANIEL SCHWARTZ

PHILLIPS LABORATORY
PROPULSION DIRECTORATE
EDWARDS AIR FORCE BASE CA 93523-5000

ABSTRACT

Rheological characterization of polymers is crucial for optimizing material selection and processing conditions, but it can also be used in identifying phase transitions and predicting molecular behavior. Dynamic mechanical measurements conducted over a range of frequencies and temperatures give the materials viscoelastic behavior and dependence on such variables as strain, temperature and frequency. Therefore, insights into the polymer's microstructure and macrostructure may be obtained.

The material property of greatest interest to the Advanced Polymer Components program was the annealing phenomenon exhibited by some LCP resins. These so called annealed resins would show higher strength, chemical resistivity and thermal resistivity in response to a thermal conditioning above the glass transition temperature but below the melt temperature. This would be detectable by observing an increase in the storage modulus or a decrease in the damping factor.

OBJECTIVE

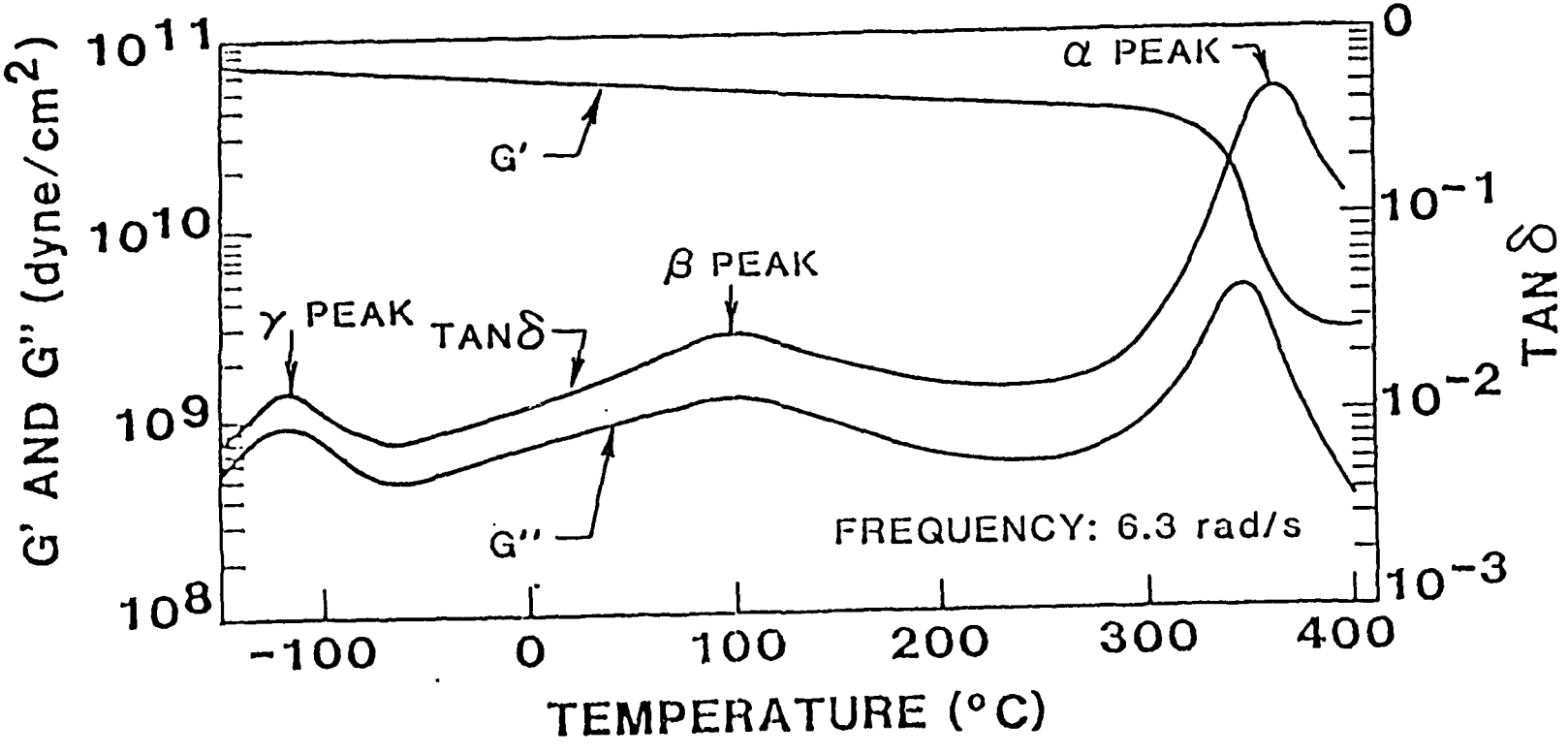
To determine the viscoelastic properties of the LCP resins selected for the APC program. This includes the identification of phase transitions and predictions of molecular behavior. Of particular interest is detection of the annealing phenomenon in those resins where chemical composition allows such behavior.

INTRODUCTION

If dynamic measurements are made at a fixed frequency over a wide temperature range, the Alpha, Beta and Gamma transitions may be identified (figure 1). Transition zones may also determined by conducting a frequency sweep over several decades at a temperature between the glass transition temperature (Tg) and the melt temperature (Tm). The Terminal, Plateau and Transition zones give indications of molecular behavior (figure 2).

Changes in the dynamic moduli are sensitive to materials becoming more stiff or soft, this allows for detection of annealing.

DYNAMIC MECHANICAL PROPERTIES OF A PMR-15 COMPOSITE



R. H. PATER, NASA LEWIS RESEARCH CENTER

Figure 1

DYNAMIC MODULI OF RAW RUBBER VS FREQUENCY

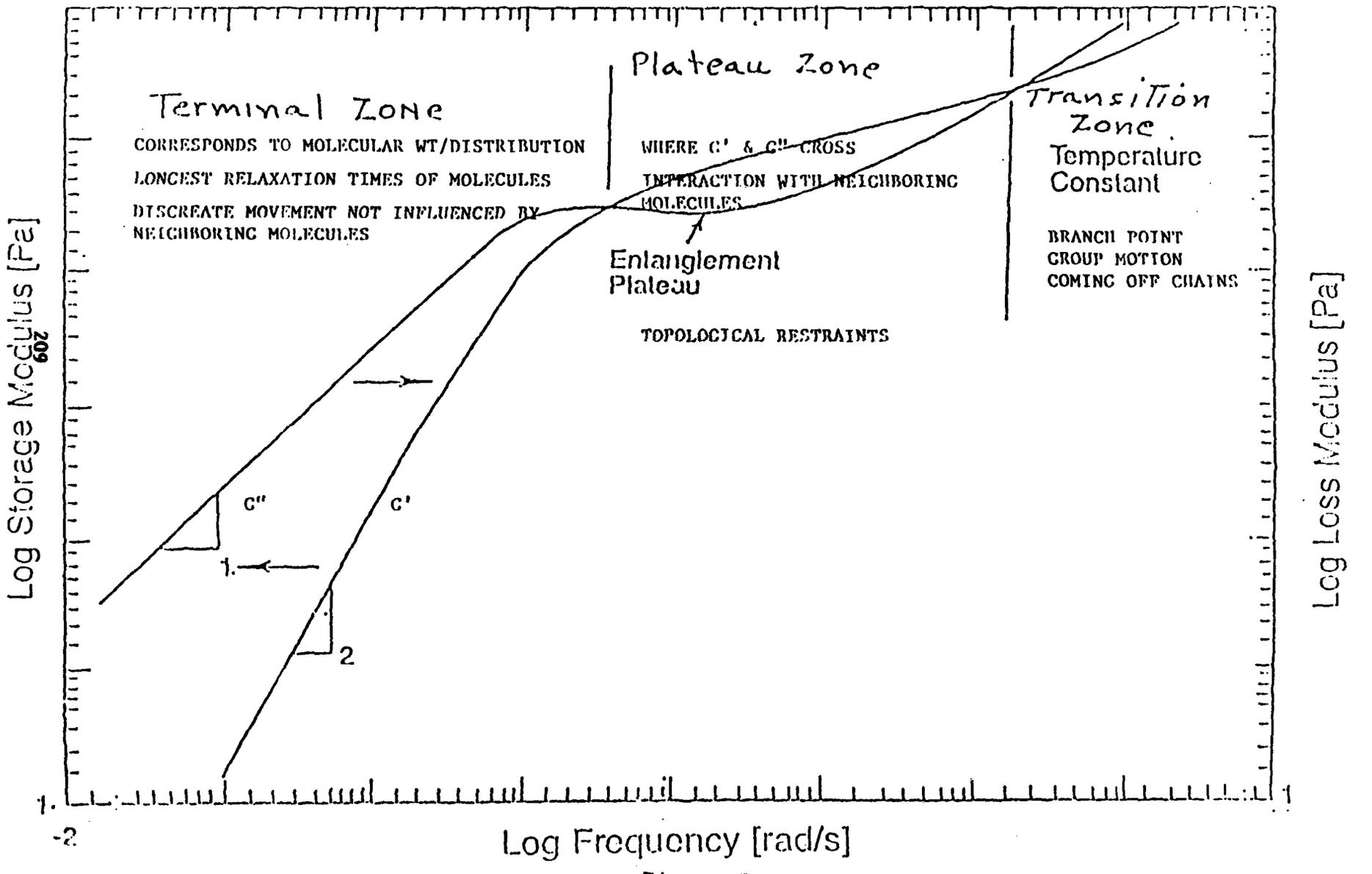


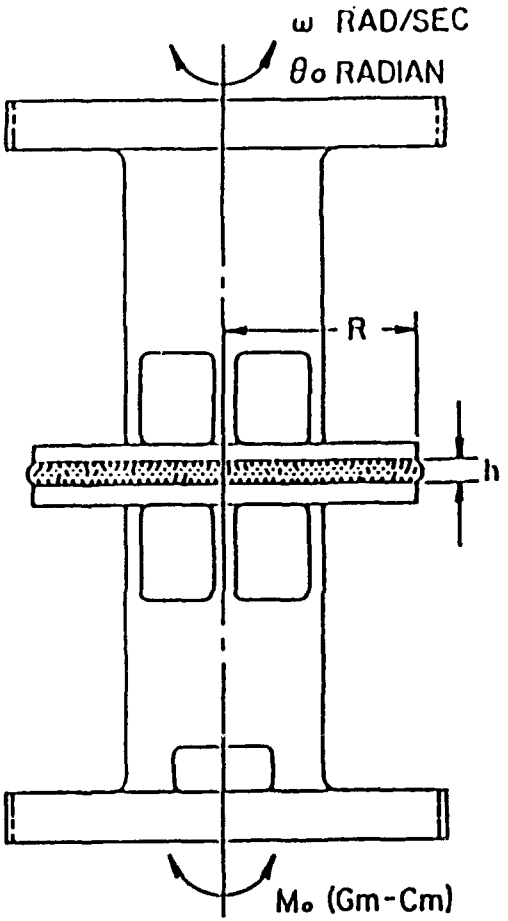
Figure 2

EXPERIMENTAL

The viscoelastic properties of the LCP's were measured on a Rheometrics Mechanical Spectrometer model 605.
Viscoelastic properties are determined by subjecting the sample to a sinusoidal shear history (Dynamic Testing) and measuring its stress response. An entirely elastic material will have a sinusoidal stress response in phase with the inputted strain and a viscous Newtonian material will have a response 90 degrees out of phase. A phase angle lying between these extremes indicates the material is exhibiting a combination of these behaviors. By measuring the stress response of the material and phase angle, complex moduli can be determined (G*). From this the dynamic viscosity (η^*), elastic component (storage modulus, G'), viscous component (loss Modulus, G") and damping factor (Tan Delta, the ratio of energy lost to energy stored) may be calculated (figure 3). G', G", and Tan Delta represent the viscoelastic properties of the material and are functions of Strain, Temperature and Frequency of oscillations (Rate).

For our tests conducted on the liquid crystal polymers, frequency sweeps were run from 0.01 to 100 rad/s (.0016 to 16 Hz) on a Rheometrics Mechanical Spectrometer model 605.
The samples were measured in parallel plate geometry at temperatures above Tm to temperatures approaching Tg. The properties measured were G', G", and Tan Delta. These properties relate to a polymers ability to store or dissipate the energy of the deformations (strain) applied to them and are influenced by the molecular structure of the polymer and the test conditions.

The first frequency sweep was carried out on a sample of HX-4000. At the lower frequencies the viscous component dominates with G" values being higher than G'. The material is in the terminal zone which gives indications about the relaxation times of the polymer molecules, This correspondes to the materials molecular weight and molecular weight distribution. The point where G' crosses over G" begins the plateau zone where nearby molecules begin interacting with one another. The amount of entanglements and crosslinks are obtained in this region. Because of the inverse relationship of frequency to temperature, as the test temperature is raised, the cross-over point is shifted to the right. The entanglement region occurs at higher frequencies due to increased mobility of the molecules (figure 4). For HX-4000 we are unable to go to high enough frequencies to see the next cross over region which would be the transition zone where motion is due to branch point and group motion coming off the chains.

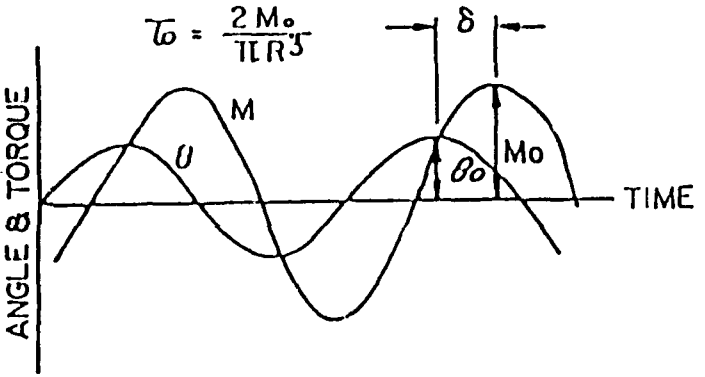


STRAIN AMPLITUDE

$$\gamma_o = \frac{R\theta_o}{h}$$

STRESS AMPLITUDE

$$\tau_o = \frac{2M_o}{\pi R^3}$$



$$G^* = \frac{\tau_o}{\gamma_o}$$

$$\eta^* = \frac{G^*}{\omega} = \frac{\sqrt{G'^2 + G''^2}}{\omega}$$

$$G' = G^* \cos\delta$$

$$G'' = G^* \sin\delta$$

$$\tan\delta = \frac{G''}{G'}$$

Figure 3

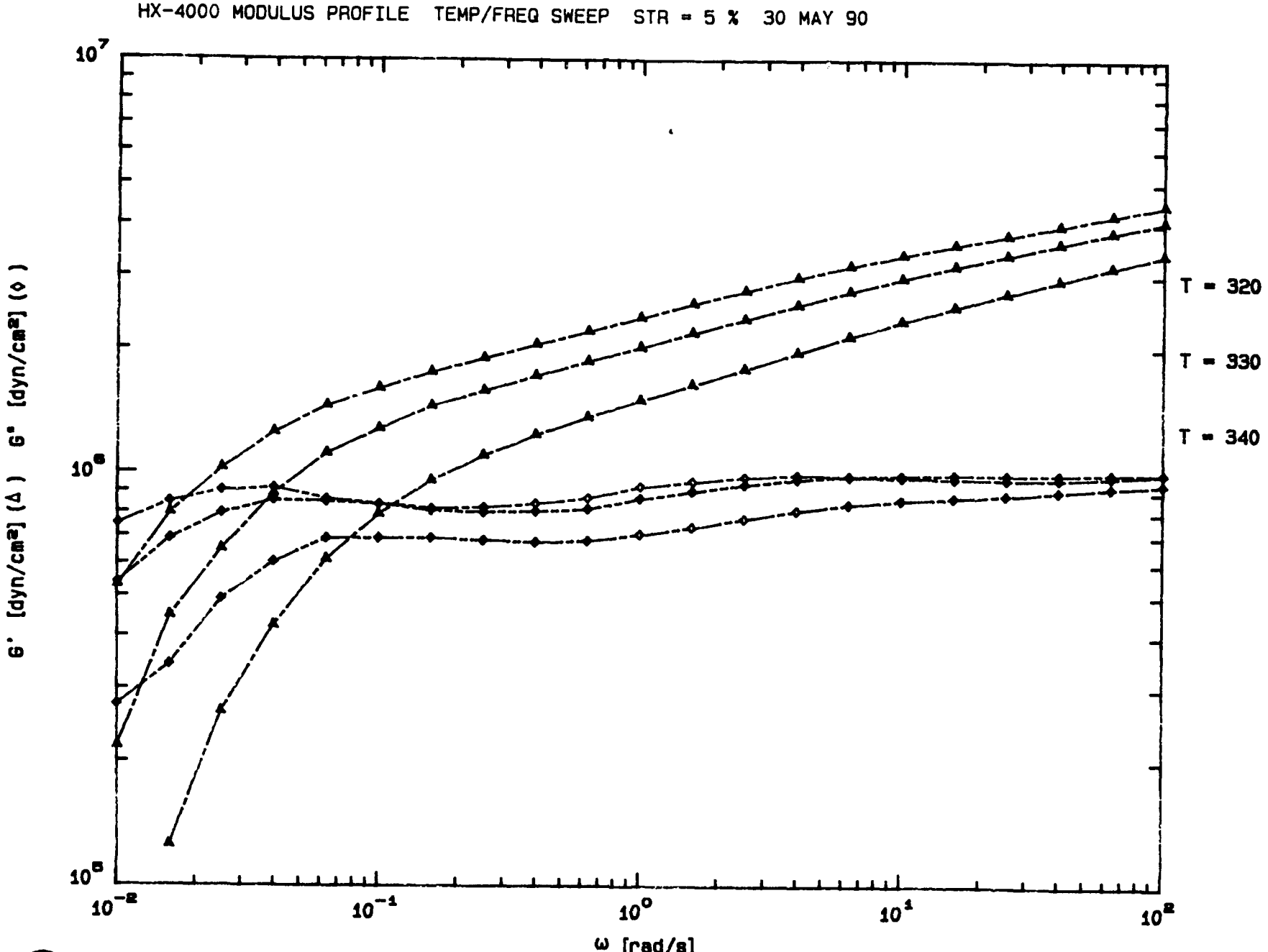

HX-4000 MODULUS PROFILE TEMP/FREQ SWEEP STR = 5 % 30 MAY 90
G' [dyn/cm²] (Δ) G" [dyn/cm²] (◊)
10⁷
10⁶
10⁵
10⁻²
10⁻¹
10⁰
10¹
10²
ω [rad/s]
T = 320
T = 330
T = 340

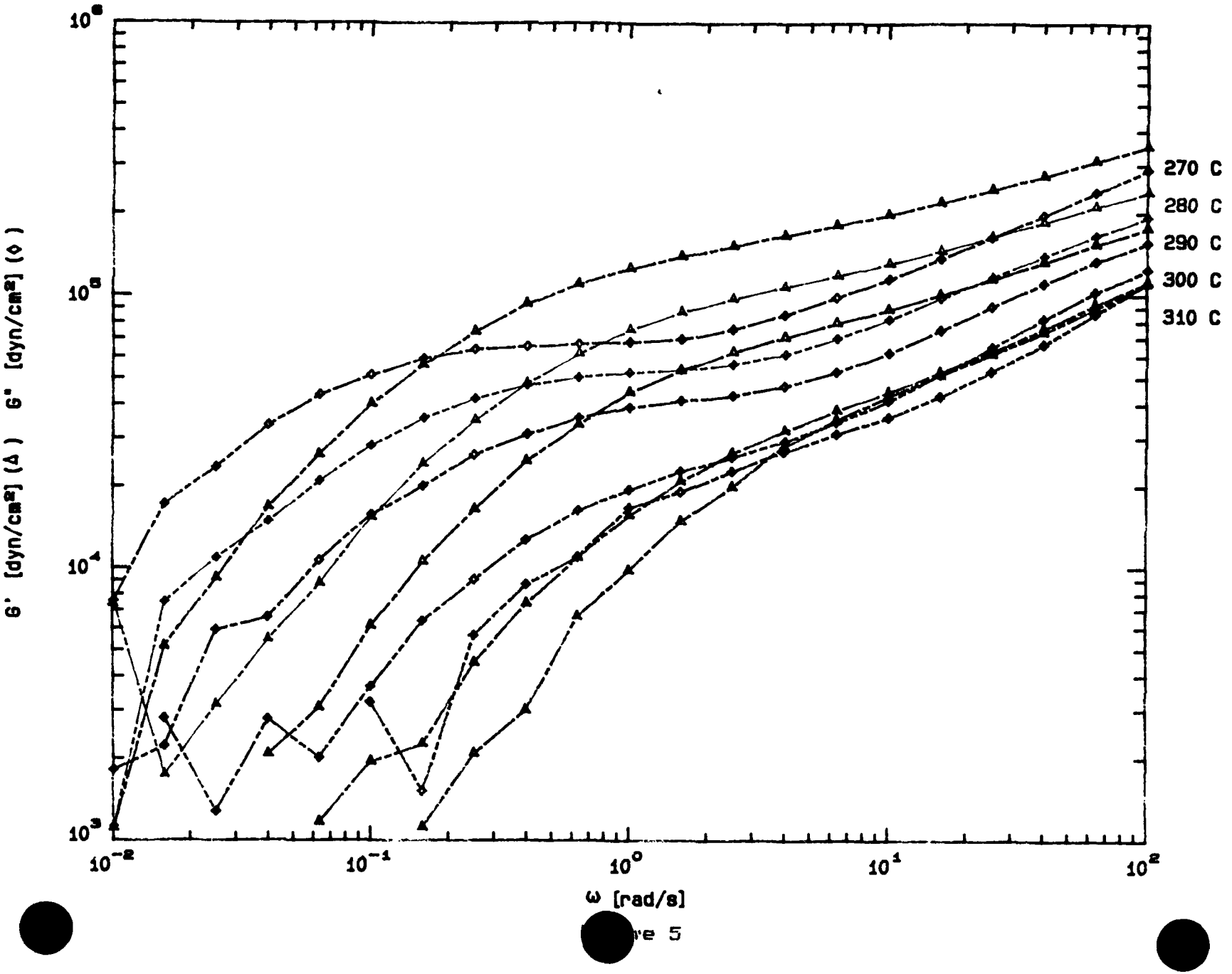
Figure 4

For Vectra A950 we observe the cross-over points occuring at higher frequencies and are able to detect the start of the transition region for the sample tested at 310°C. Vectra appears to have more molecular mobility than HX-4000 and would account for the lower overall modulus values (figure 5).

The next test was to try and detect the annealing phenomenon in a sample of Granlar resin which had been heat treated for three hours at 250°C. If annealing is occuring there should be more structure and rigidity in the annealed sample, therefore, the G' values should be higher. Consequently the increased structure will lower the materials ability to dampen out the energy placed into it through the sinusoidal strain. This would be indicated by lower values of Tan Delta. This behavior can be seen in figures 6 & 7. The sample designated A was heat treated and exhibits higher G' values and lower Tan Delta values than the sample not annealed.

CONCLUSIONS

Dynamic mechanical testing is able to give insights into the microstructure and macrostructure of the liquid crystal polymers selected for this program. The annealing phenomenon was detected in the granlar resin. The testing done thus far is very preliminary, clearly more work needs to be conducted to characterize the rheology of these highly complex polymers.


VECTRA A950 STORAGE/LOSS MODULII TEMP/FREQ SWEEP STR = 5 % 25 MM PP
G' [dyn/cm²] (Δ) G" [dyn/cm²] (◇)
ω [rad/s]
270 C
280 C
290 C
300 C
310 C

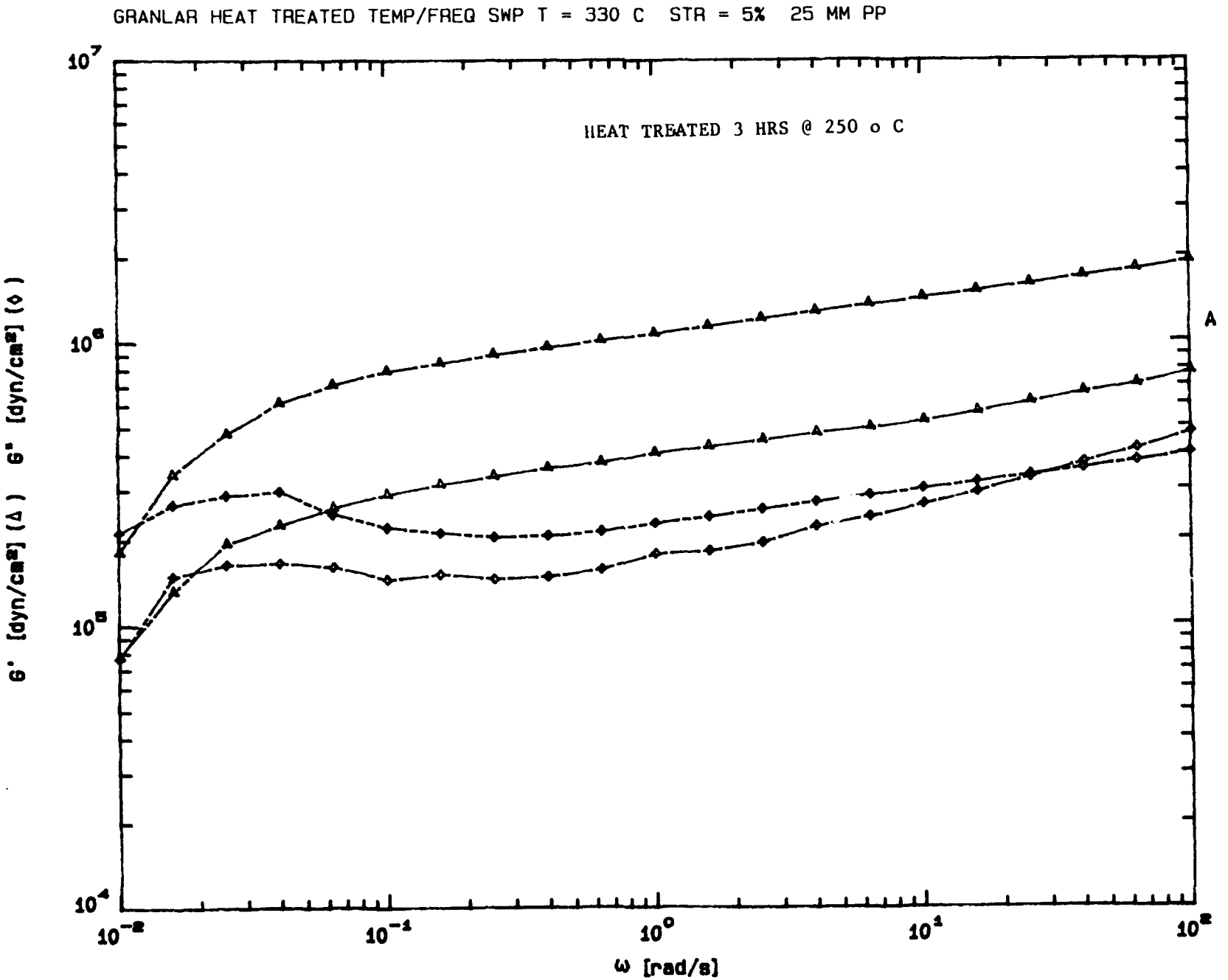
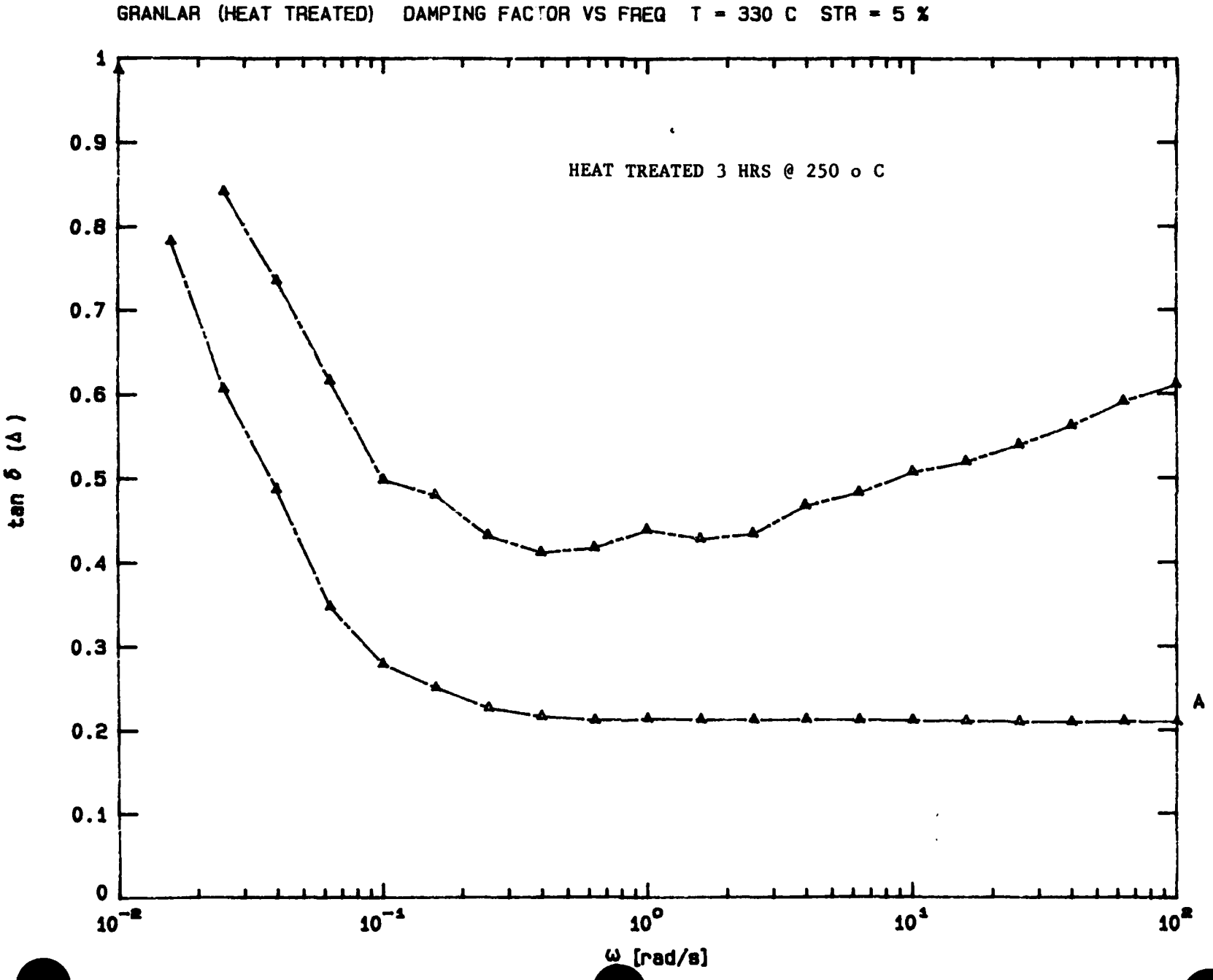

GRANLAR HEAT TREATED TEMP/FREQ SWP T = 330 C STR = 5% 25 MM PP
HEAT TREATED 3 HRS @ 250 o C
A
10^7
10^6
10^5
10^4
10^-2
10^-1
10^0
10^1
10^2
6' [dyn/cm^2] (Δ) 6" [dyn/cm^2] (◊)
ω [rad/s]

Figure 6


GRANLAR (HEAT TREATED) DAMPING FACTOR VS FREQ T = 330 C STR = 5 %
HEAT TREATED 3 HRS @ 250 o C
tan δ (Δ)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
ω [rad/s]
A

ure 7

TASK #9 : MATERIAL PROPERTY DATABASE

Thomas A. Elkins
OL-AC PL/RKAD
Edwards AFB, CA 93523-5000
(805) 275-5303, DSN 525-5303
E-mail : ELKINST@PL-EDWARDS.AF.MIL

ABSTRACT

Presumably the researchers working on discovering the fundamental microscopic and macroscopic properties of these liquid crystal polymers would have a place in which to store their data so that it would be readily available to the other researchers and part designers, and, indeed, there will be one.

The purpose of this task is to develop a database management system (DBMS) capable of storing and manipulating the material properties that will be discovered as the research into liquid crystal polymers continues.

DATABASE DEVELOPMENT

Select conceptual data representation
⇓
Develop logical data representation
⇓
Develop data manipulation language ⇔ Develop data definition language
⇓
Develop syntax checking and parsing algorithms ⊗
⇓
Develop pseudocode for database operations ⊗
⇓
Refine and modularize pseudocode
⇓
Convert pseudocode to real code
⇓
Compile & test code
⇓
Debug ⟹ ⊗
⇓
Develop physical data representation
⇓
Develop advanced user-interface
⇓
Develop plotting capability
⇓
Develop report-generation capability
⇓
Develop data exchange capability
⇓
Write documentation
⇓
Publish

Sub-task 1: SELECT CONCEPTUAL DATA REPRESENTATION

Status : Done

Originally, the database management system (dbms) was supposed to contain only polymeric material properties. Such a system can, and was, developed using a standard record-based system; however, the scope of the project was expanded to handle metals, ceramics, and composites. A conventional record-based system is not feasible because of the inconsistency of the data fields to be represented (a good example would be glass transition temperature which is a valid piece of data for ceramics and polymers, but not metals) and the variability of data (some material properties are highly temperature dependent, others are time dependent...). To represent those dependencies and inconsistencies with a record-based system would waste memory, slow data processing, introduce redundant data, and possibly violate data integrity.

A more feasible approach would be to develop a relational system. Relational database systems are highly flexible, but very complex for both the user and the programmer. A record-based system provides the user with a template, or form, into which the user can enter data, browse, search, or manipulate contents. The relational system allows the user to think of his/her data as being in tables or sets and provides the user with tools with which he/she can manipulate the relations to create new relations with the desired data.

The following is an example of using a record-based system vs. a relational system for an employee database. The data to be stored are the employee I.D. number, full name, home phone, date of birth, in what group he/she works, and the projects on which he/she is currently working.

Record-based system

I.D. Number	Last Name	First Name	Home Phone	D.O.B.	Group	Project
123456789	Doe	John	123-4567	500321	ABC	T5
123456789	Doe	John	123-4567	500321	ABC	P2
123456789	Doe	John	123-4567	500321	ABC	X8
987654321	Johnson	Mike	555-1212	620513	ABZ	P2
987654321	Johnson	Mike	555-1212	620513	ABZ	Q4
393939393	Phillips	Lisa	921-3484	451005	AB	
234970923	Fisbin	George	636-2342	540612	ABZ	

Notice that all of the required information is stored, but there are data redundancies (name, date of birth, phone, I.D., and group do not change because the project changes), and potential problems for data integrity (if John Doe changes his phone number, every record with his old phone number must be changed). Also, this database system is limited as to the information that can be extracted (Who is Mike Johnson's supervisor? Who is the project manager for P2? What are the phone numbers for everyone in ABZ?). Fields can be added to the database to reflect the desired information, but more problems are introduced, i.e. not everyone will be a supervisor or project manager (introducing empty cells), and although everyone has a supervisor, there is not a different supervisor for every employee (introducing more redundancy)

Relational system

Employee-data

I.D. Number	Last Name	First Name	Home Phone	D.O.B.	Group
123456789	Doe	John	123-4567	500321	ABC
987654321	Johnson	Mike	555-1212	620513	ABZ
393939393	Phillips	Lisa	921-3484	451005	AB
234970923	Fisbin	George	636-2343	540612	ABZ

Projects

Project	Employee
T5	123456789
P2	123456789
X8	123456789
P2	987654321
Q4	987654321

Supervisors

Group	Employee
ABZ	234970923
AB	393939393
ABC	123456789

This schema also contains all of the required information, but notice that the redundancy has been minimised. Also the relation Supervisors was created using as little information as is needed to represent that information; similarly, a relation of Project Managers could be created. To extract information, the

user performs operations on relations similar to operations performed on sets. For example, if we wanted to find Mike Johnson's supervisor we could perform operations on the Employee-data and Supervisors relations to extract the required information. Similarly, if we wanted to get a phone listing of everybody in the AB division (including the branches), the user would create a new relation describing the relationships between branches and divisions and then use that relation with the Employee-data relation to retrieve the necessary information.

The relational system allows for tremendous flexibility which makes the job very difficult for the programmer who no longer knows what data will be stored or how the data will be used. The programmer provides the tools to use on relations, and the user is left with the responsibility of using the tools to define and manipulate relations to obtain the desired information.

Sub-task 2: DEVELOP LOGICAL DATA REPRESENTATION

Status : Done

The logical data representation is the way the data will look to the computer and, as will be seen, is much different than the conceptual data representation. The conceptual representation of a relational system is of a series of tables of data (as might appear in a book). The logical data representation consists of the data structures the software will use to store and manipulate the user's data and serves as the basis upon which a physical data representation will be developed.

The following is a list of knowns and unknowns of an implementation of a relational database system.

KNOWN	UNKNOWN
A database has relations	Number of relations in a database
Relations have...	Number of attributes in a relation
a name	Number of tuples in a relation
a creator	Number of domains in a database
a set of attributes	Relationships between relations
a key attribute	Values in cells
a set of tuples	Value types of cells
security restrictions	Which cell of a tuple is used for sorting
users	
Attributes have...	
a name	
a set of cells	
Tuples have...	
a set of cells	
a key cell	
Cells have values	
Values are from a specific domain	
Each cell is associated with an attribute	

Because of the unknowns, a dynamic memory allocation scheme will be used. The maximum number of relations, attributes, tuples, and cells will be determined by the computer's memory and operating system, and backing store if the operating system employs a virtual memory management system (virtual memory operating systems use peripheral storage devices as secondary memory storage, and are t' us not limited to on-board memory).

The programming language that will be used on this project is C, which generates very fast, portable code which will allow the code to be converted (ported) to other machines with very little, if any, modification. The C data structures that will be used on this project are as follows:

```
struct DOMAIN {
        char            name[20];       /* domain name */
        unsigned        type :  4;      /* data type for domain */
        float           format;         /* data format (like printf) */
        int             instances;      /* times domain is used*/
        struct DOMAIN   *next;          /* pointer to next domain */
        struct DOMAIN   *prev;          /* pointer to previous domain */
} ;
```

```
struct FIELD {
        char                    name[20];       /* name of the field */
        struct DOMAIN           *domain;        /* domain of field */
        struct FIELD            *next;          /* pointer to next field */
        struct FIELD            *prev;          /* pointer to previous field */
} ;
typedef struct FIELD            *FIELDPTR;

struct CELL {
        FIELDPTR                field;          /* pointer to field info */
        union {
                int             *i;             /* pointer to an integer value */
                long            *l;             /* pointer to a long integer */
                float           *r;             /* pointer to a real number */
                double          *d;             /* pointer to a double real */
                char            *c;             /* pointer to a string */
                float           *s;             /* pointer to scientific notation */
        } value;
        struct CELL             *next;          /* pointer to next cell */
        struct CELL             *prev;          /* pointer to previous cell */
        struct CELL             *up;            /* pointer to cell above */
        struct CELL             *down;          /* pointer to cell below */
} ;
typedef struct CELL             *CELLPTR;

struct TUPLE {
        CELLPTR                 first_cell;     /* pointer to the first cell */
        CELLPTR                 key_cell;       /* pointer to the key cell */
        CELLPTR                 last_cell;      /* pointer to the last cell */
        struct TUPLE            *next;          /* pointer to next tuple */
        struct TUPLE            *prev;          /* pointer to previous tuple */
} ;
typedef struct TUPLE            *TUPLEPTR;

struct RELATION {
        char                    name[20];       /* name of the relation */
        char                    owner[15];      /* owner's username */
        char                    file[80];       /* file specification of data */
        unsigned                p_read : 1;     /* World can read & use relation */
        unsigned                p_add : 1;      /* World can add tuples */
        unsigned                p_modify : 1;   /* World can modify cell contents */
        unsigned                p_del : 1;      /* World can delete tuples */
        unsigned                ascend : 1;     /* direction for sorting key */
        unsigned                altered : 1;    /* set to 1 if data was altered */
        char                    user[15];       /* name of last user */
        char                    date[6];        /* date relation was last used */
        int                     fields;         /* number of fields */
        int                     tuples;         /* number of tuples */
        struct RELATION         *next;          /* pointer to next relation */
        struct RELATION         *prev;          /* pointer to previous relation */
        FIELDPTR                first_field;    /* pointer to first field */
        FIELDPTR                key_field;      /* pointer to key field */
```

```
    FIELDPTR        last_field;         /* pointer to last field */
    TUPLEPTR        first_tuple;        /* pointer to first tuple */
    TUPLEPTR        current_tuple;      /* pointer to current tuple */
    TUPLEPTR        last_tuple;         /* pointer to last tuple */
} ;
```

NOTE: the protection flags will be used for security purposes. The user's username is first compared to the owner field; if there is a match the protection flags are ignored (the owner can do whatever he/she wants). If the user is not the owner the protection flags affect the following operations: "seeing" the relation (READ), adding tuples (ADD), changing the contents of a tuple (MODIFY), deleting tuples (DEL).

Sub-task 3: DEVELOP DATA DEFINITION/MANIPULATION LANGUAGE

Status : Done

The data definition/manipulation ' guage is the set of commands available to the end user for creating and modifying relations. The language defines how relations, and data within the relations, can be manipulated and modified. The selected language operators and syntax are listed below in the BNF (Backus-Naur Form) notation.

::= defined-as, | = or, [ ] = 0 or 1, {} = 0 or more

DEFINITIONS

< *letter* > ::= A|B|C|D|E|F|...|X|Y|Z|a|b|c|d|...|w|x|y|z

< *digit* > ::= 0|1|2|3|4|5|6|7|8|9

< *symbol* >::=!|@|#|$|%|∧|&|*|(|)|-|−|+|=|'|~|[|{|]|}|;|:|'|"|\|<|>|,|.|/|?

< *integer* >::= [+|−] < *digit* > {< *digit* >}

< *real* >::=< *integer* > .{< *digit* >}[E|e < *integer* >]

< *name* >::=< *letter* > {< *letter* > | < *digit* > |-|−|#|%}

< *domain* >::=< *name* >

< *domaintype* >::= CHARACTER | INTEGER | LONG | REAL | DOUBLE | SCIENTIFIC

< *number* >::=< *integer* > | < *real* >

< *value* >::=< *number* > | < *name* > |{< *letter* > | < *digit* > | < *symbol* >}

< *relation* >::=< *name* >

< *field* >::=< *name* >

< *condition* >::== | ~= | < | <= | > | >= |?| ~?

< *attribute* > ::= NAME | KEY | SORT | PROTECTION

< *fieldlist* >::=< *field* > [, < *fieldlist* >]

< *fieldef* >::=< *name* > : < *domain* > [, < *fieldef* >]

< *predicate* >::=< *field* >< *condition* >< *value* >

Commands

CREATE < *name* > WITH (< *fieldef* >) [USING < *field* > UP| DOWN]

DELETE RELATION < *relation* >

USE < *relation* >

JOIN < *relation* > TO < *relation* > WHERE (< *field* >=< *field* > {, < *field* >=< *field* >})

UNION < *relation* > AND < *relation* >

INTERSECT < *relation* > AND < *relation* > ONTO < *name* >

DIFFERENCE < *relation* > AND < *relation* > ONTO < *name* >

COPY < *relation* > ONTO < *name* > [WHERE < *predicate* > { AND | OR < *predicate* >}]

SAVE

CHANGE RELATION < *attribute* > TO < *value* > {, *attribute* TO *value* }

SHOW [< *relation* >]

LIST

DEFINE < *name* > AS < *domaintype* > < *number* >

UNDEFINE < *domain* >

ADD (< *fieldef* >) [TO < *relation* >]

REMOVE (< *fieldlist* >) [FROM < *relation* >]

CHANGE FIELD (< *field* > TO < *name* > {, < *field* > TO < *name* >}) [IN < *relation* >]

PROJECT (< *fieldlist* >) ONTO < *name* > [WHERE < *predicate* > { AND | OR < *predicate* >}]

COUNT < *field* >
SUM < *field* >
AVERAGE < *field* >
MAX < *field* >
MIN < *field* >
MULTIPLY < *field* > BY < *value* > [WHERE < *predicate* >]
INCREASE < *field* > BY < *value* > [WHERE < *predicate* >]
DECREASE < *field* > BY < *value* > [WHERE < *predicate* >]
DIVIDE < *field* > BY < *value* > [WHERE < *predicate* >]
SET < *field* > TO < *value* > [WHERE < *predicate* >]
FIRST
LAST
NEXT
PREVIOUS
INSERT
EDIT
DISPLAY
DELETE TUPLE [WHERE < *predicate* > { AND | OR < *predicate* >}]
SEARCH FOR < *predicate* > { AND | OR < *predicate* >}
FIND

Please see appendix 1 for a description of each command and how it is used.

Sub-task 4: DEVELOP SYNTAX CHECKING AND PARSING ALGORITHMS

Status : Done

This step involves separating words and symbols from a line entered at the keyboard and comparing them to a syntax template to determine if the user entered the correct command sequence. Naturally, this step requires that the syntax for the language be established. Once parsing and syntax checking is complete, the semantics of the command line must be checked (i.e. the user entered an existing relation/field name)

Sub-task 5: DEVELOP PSEUDOCODE FOR DATABASE OPERATIONS

Status : Completed for current DDL/DML

Using the logical data representation and the database language, describe how the commands will function. For example, the command JOIN might be described as follows:

```
Function JOIN
        create new relation
        add fields from first relation
        add fields from second relation
        make cross-product of tuples from both relations
        insert tuples into new relation
        delete tuples that do not meet requirements
        add relation to database
Endfunction
```

This must be done for all commands.

Sub-task 6: REFINE AND MODULARIZE PSEUDOCODE

Status : Completed for current DDL, DML

The pseudocode routines are further refined, coming closer to actual code. Frequently recurring statements are tagged for possible development as separate modules which could be used by multiple routines (such as the "add fields" lines listed above – there is an add field command, so the same routine might be used). Also, the logic of the routines is checked every time a change is made. Using the example from subtask 5, the "make cross-product" statement definitely needs to be refined because there is no cross-product routine in C, and certainly not one for the data structures used in this code.

Sub-task 7: CONVERT PSEUDOCODE TO REAL CODE

Status : Completed for current DDL/DML

Now comes the hard part, taking the conceptual routines and writing real code that will actually work.

Sub-tasks 8 & 9 : COMPILE & TEST CODE / DEBUG

Status : In progress for current DDL/DML

This is the step where the code is converted to an executable and the routines tested. Compiling will reveal any syntax errors from sub-task 7, linking will reveal any semantic errors, and testing will reveal logical (run-time) errors. Debugging involves returning to sub-task 4 or 5, finding where the logic fails, and correcting it. A test case is developed to test the code and the various DDL/DML routines. Please see appendix 1 for the actual test file and appendix 2 for the output from using the test file. This is the time for any interested users to give their ideas for features/capabilities to be included in the code. (hint, hint!)

Sub-task 10: DEVELOP PHYSICAL DATA REPRESENTATION

Status : not started yet

Once the logic has been proven the logical data representation is finished and it is time to move on to the next level – the physical data representation. The database is useless if the user cannot store data for use later. The physical data representation is the method by which the code transfers data from memory to backing store (hard disks, floppy disks, etc). Some of the methods are sequential access, random access, and indexed, each of which have applicability in database management. Sequential access, as the name indicates, looks at each record in the order it was written to disk – this would not be good for searching, but since the logical data representation calls for keeping the data in memory, sequential access is the cheapest way to store the tuples of a relation. Doing this will require a separate file for each relation; however, it also means that the entire database will not occupy memory, only the current relation and a few others (for doing a join or union). The relation headers will be in a separate file (accessed when a user selects a database) and can use any method, but since the headers are small they will probably be stored sequentially and kept in memory.

Sub-task 11: DEVELOP ADVANCED USER-INTERFACE

Status : not started yet

As is, the software will process user requests through the command line interface and syntax parser; however, this means that the user is required to learn the database language. Currently, it is possible to store commands in a file which is then read by the database syntax parser and executed (this is how the database is being tested). To make the software more user-friendly, an interface must be developed that will make the processing and querying functions easier for the user and be able to translate them into the equivalent language commands. Graphics-oriented interfaces are popular, but require a tremendous amount of development and testing time and must be developed for each platform (not all computers use the same graphics). It would not be uncommon for a graphics user interface (GUI) to be larger than the code for which it is used. A majority of users will be using this software on the VAX systems, so the primary focus will be a user-friendly interface suited for VAX environments. Other interfaces may include an X-windows driver for using the code on remote workstations. Of course if the user does not have access to a graphics terminal, the command line interface is always available.

Additionally, extensions to the current database language and modifications to the parser would allow the user to write "scripts," simple programs which the dbms would execute to perform the data entry/manipulation/extraction tasks for the user automatically.

Sub-task 12: DEVELOP PLOTTING CAPABILITY

Status : not started yet

A plotting capability is not normally provided with generic relational database systems; however, considering the primary purpose for developing this system is to compare material capabilities and applicabilities, it would be very helpful to visualize how one material changes with the environment or how several materials compare with one another. Again, the graphics will be different for different platforms, so a plotting module will be another large program. It is unknown at this time whether to add a plot command with the supplied

database language or tie it to the user-interface. Also unknown are the types of plots and user-controllable attributes. **Input from all interested users is highly encouraged.**

Sub-task 13: DEVELOP REPORT-GENERATION CAPABILITY

Status : not started yet

A database is not completely finished if one cannot get data out of it. A researcher may need to show tables of data in his/her report, or a program manager may need to show why he/she came to a particular conclusion; therefore, the capability to pull data from the database and put it into a format that can be incorporated into text documents is important. A standard ASCII output file will, of course, be included, as well as a TEX file. User-supplied formats will be considered.

Sub-task 14: DEVELOP DATA EXCHANGE CAPABILITY

Status : not started yet

Data can come from a variety of sources, so the capability to take data from external sources must be provided. The process is to write data translators which read data from the format of the source and write data out in the format required by the database software. Since the programmer cannot know every possible source, there must be ways for user-supplied programs to get data into the database. Similarly, data may be needed in other codes (finite element codes need material property data) and must be translated. One possibility is to develop a "universal" file format by which data can be exchanged. Definite translators will be included for the I-DEAS family of analysis codes and also for Lotus 1-2-3 data files (.PRN). Interested users are encouraged to provide data formats with which they are familiar.

Sub-task 15: WRITE DOCUMENTATION

Status : not started yet

This task involves writing a detailed user's manual.

Sub-task 16: PUBLISH

Status : not started yet

APPENDIX 1 : Sample Input Deck

The following pages list the input file used to test the parser, syntax checker, semantics checker, and command processors. The input file also gives a brief description of the command being tested and some notes about capabilities. The file creates and manipulates a database of data from the periodic chart.

The code was developed on a VAX system running VMS 5.4, but was also ported to a Tektronix XD88 workstation running Unix V5 with no changes to the code. The input file was generated on the VAX and FTP'd to the Tektronix, also with no changes. File redirection was used on both platforms. For the Unix system, the command was

```
mpdb < test.dat > test.out
```

For the VAX, the commands were

```
$ ASSIGN TEST.DAT SYS$INPUT
$ ASSIGN TEST.OUT SYS$OUTPUT
$ RUN MPDB
$ DEASSIGN SYS$OUTPUT
```

```
# Sample input file to test the commands for the relational database
# management system (RDBMS).
# NOTE: conventions used in this file are as follows...
#   Command syntax descriptions are preceeded by a line of asterisks '*'
#   Items in brackets '[]' are optional items which may be used once per command.
#   Items in braces '{}' are optional items which may be used many times.
#   Items which are in all capital letters are required keywords.
#   Items delimited by a vertical bar '|' separate the list of valid keywords
#       which may be used.
#   Punctuation marks (other than those listed above) are required where shown.
#
#*************************************************************************
#  DEFINE domain_name AS domain_type field_width[.decimal_places]
# Values in a field must belong to a specific domain.
# Domain_type may be one of the following:
#   CHARACTER  - for textual data
#   INTEGER    - for single precision integer data
#   LONG       - for double precision integer data
#   REAL       - for single precision floating-point data
#   DOUBLE     - for double precision floating-point data
#   SCIENTIFIC - for scientific notation format
define atomic_name as character 20
define junk as scientific 13.6
define atomic_symbol as character 3
define temperature as real 7.3
#
#*************************************************************************
#LIST - Brief list of the contents of the database.
list
#
#*************************************************************************
# DELETE DOMAIN domain_name     or      UNDEFINE domain_name
# Delete unused or unwanted domains.
undefine junk
list
#
#*************************************************************************
# CREATE relation_name WITH (field_name : domain_name {,field_name : domain_name}) [USING field_name UP|DOW ]
# Relations are collections of data organized by fields (columns)                                          ^= o
# and tuples (rows).  The user defines how the data in a relation is
# organized when it is created.
create elements with (
    name    :   atomic_name,
    symbol  :   atomic_symbol,
    boil    :   temperature,
    melt    :   temperature
) using symbol up
# ^^^^^ Sorts the data in this relation by symbol in ascending order.
# If the optional USING clause is not used, the default is to sort the
# data by the first field in descending order.
# Note that BOIL and MELT are from the same domain.  Multiple fields
# may be drawn from the same domain, but fields may not have multiple
# domains.
list
#
#*************************************************************************
# SHOW [relation_name]
# Show detailed information about a relation.  If relation_name is not
# specified, the current relation is displayed (if assigned).
show
show elements
#
#*************************************************************************
# USE relation_name
# Make the relation current.
# Some operations are performed only on the current relation.
use elements
#
#*************************************************************************
# INSERT [data]
# The INSERT command will prompt you for input for each field;
# however, if you know the order of the fields, the data can be
# placed on the command line (unless you have character data
# that may contain spaces).
# Note also that the input can be placed in tabular form.
# (useful for incorporating data from external files)
insert Hydrogen     H     20.268      14.025
insert Helium       He     4.215        .95
insert Lithium      Li  1615         453.7
insert Beryllium    Be  2745        1560
insert Boron        B   4275        2300
insert Carbon       C   4470        4100
insert Nitrogen     N     77.35       63.14
insert Oxygen       O     90.18       50.35
insert Fluorine     F     84.95       53.48
insert Neon         Ne    27.096      24.553
```

```
#
# There should be 10 tuples in the ELEMENTS relation.
# There should also be an asterisk '*' next to ELEMENTS, indicating
# it is the current relation.
list
#
#*************************************************************************
# PROJECT ( field [, field] ) ONTO relation_name [WHERE field condition value [AND|OR field condition value ]
# Copies columns of data from the current relation to a new relation.
project (name) onto names
# No qualifier was used, so the NAME field of all tuples was copied.
list
use names
#
#*************************************************************************
# FIRST -- moves the current tuple pointer to the first tuple in the current relation
# NEXT -- moves the current tuple pointer to the next tuple in the current relation
# DISPLAY -- displays the contents of the current tuple.
# Note how multiple commands may be placed on the same line...
first display
next display
#
use elements
project (boil,name) onto boiling_pts
# Two fields of all tuples are copied.
list
show boiling_pts
#
project (name,symbol) onto hot_ones where melt > 100
# Two fields are copied, but only for tuples that meet the
# stated requirement.
# The conditionals that are accepted are as follows:
#   =       Equals                  !=      Does Not Equal
#   <       Less Than               <=      Less Than or Equal
#   >       Greater Than            >=      Greater Than or Equal
#   ?       Contains                !?      Does Not Contain
list
show hot_ones
#
project (symbol,melt,name) onto junk where
        name    !?  e       and
        boil    <=  1615
# Three fields this time, but the requirements are more rigid.
# The qualifier "name !? e" means select entries in the field
# NAME that do not contain the letter 'e' (like "Lithium")
list
show junk
#
#*************************************************************************
# DELETE RELATION relation_name
# Self explanatory.
delete relation names
delete relation boiling_pts
delete relation hot_ones
delete relation junk
#
#*************************************************************************
# COPY relation ONTO new_relation [WHERE field condition value [AND|OR field condition value]]
# Copies specified tuples with all fields.
# (unlike PROJECT which copies certain fields)
copy elements onto cool_ones where boil <= 100
list
use cool_ones
show
first display
next display
next display
#
# create a new relation with different data
#
define atomic_number as integer 3
define atomic_weight as real 10.5
create atomic_data with (
    number      :   atomic_number,
    symbol      :   atomic_symbol,
    weight      :   atomic_weight
)
list
show atomic_data
use atomic_data
show
#
# Insert the new data.
#
insert  1   H    1.0079
insert  2   He   4.0026
insert  3   Li   6.941
```

```
insert  4   Be   9.01218
insert  5   B   10.81
insert  6   C   12.011
insert  7   N   14.0067
insert  8   O   15.9994
insert  9   F   18.998403
insert 10   Ne  20.179
insert 11   Na  22.98977
# Since no sorting directive was given, the default is the first
# field listed in the CREATE parameter list.  Also the default
# sorting direction is in descending order, so the first tuple
# of this new relation should be the one with the highest number.
# (Sodium - #11)
first display
#
#*************************************************************************
# JOIN relation1 TO relation2 WHERE ( field1 condition field2 [, fieldm condition fieldn] )
# Joins two relations so that the data from both is incorporated
# into one relation.  The acceptable combinations are determined
# by the condition(s) specified.
join atomic_data to elements where (symbol = symbol)
#
# The data is grouped together using the fact that they share SYMBOL
# information.  Notice, though, that ATOMIC_DATA contains a record
# that does not match any in ELEMENTS.  That record is skipped.
# ELEMENTS should now have the same number of tuples (10),
# but two more fields (total 6 fields).
#
list
use elements
show
#
# Display some of the tuples to make sure the data is correct.
#
first display
next display
next display
#
#*************************************************************************
# CHANGE FIELD (old_field_name TO new_field_name [, old TO new ] )
# Rename the fields to something more reasonable (fields are renamed
# to avoid the possibility of duplicate names while joining)
change field (
    elements_name        to  name,
    elements_symbol      to  symbol,
    elements_boil        to  boil,
    elements_melt        to  melt,
    atomic_data_number   to  number,
    atomic_data_weight   to  weight
)
#
# We don't need ATOMIC_DATA any more, so delete it.
#
delete relation atomic_data
list
#
# Make a new relation with the same fields, but new data.
#
create table with (
    name    :   atomic_name,
    symbol  :   atomic_symbol,
    boil    :   temperature,
    melt    :   temperature,
    number  :   atomic_number,
    weight  :   atomic_weight
) using melt down
list
use table
show
insert Sodium       Na  1156     371.0  11  22.98977
insert Magnesium    Mg  1363     922    12  24.305
insert Aluminum     Al  2793     933.25 13  26.98154
insert Silicon      Si  3540    1685    14  28.0855
insert Phosphorus   P    550     317.3  15  30.97376
insert Sulfur       S    717.75  388.36 16  32.06
insert Chlorine     Cl   239.1   172.16 17  35.453
insert Argon        Ar    87.3    83.81 18  39.948
#
first display
next display
next display
#
#*************************************************************************
# UNION relation1 AND relation2
# Appends the contents of relation2 onto relation1.  The two
# relations must be compatible (same # of fields and matching domains
# for each field).
```

```
list    # before
union elements and table
# Of course we could have also inserted the data into ELEMENTS
# directly, but this illustrates how relations can be appended.
list    # after
show elements
use elements
first display
next display
next display
next display
#
#*************************************************************************
# ADD ( field1 : domain_name {, fieldn : domain_name} ) [TO relation]
# Adds fields to an existing relation.  In this example,
# we add a new field to the current relation to store the physical
# state of the element at 305 degrees Kelvin.
define state as character 6
list
add (state : state)
# No qualifier since we are adding it to the current relation.
# Note that a field may have the same name as a domain.
show
#
#*************************************************************************
# SET field_name TO value [WHERE field condition value [AND|OR field condition value]]
# Sets all or some of the field values to a given value.
set state to solid
# Most of the elements are solid, so we set all of the STATE values
# to 'solid' for now.
#
first display
#
# Next, we set the STATE value to 'liquid' for all elements whose
# melting point is below the specified temperature.
#
set state to liquid where melt < 305
first display
#
# Do the same thing for gaseous elements.
# (boiling point < temperature)
#
set state to gas where boil < 305
first display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
#
#*************************************************************************
# DELETE TUPLE [WHERE field condition value [AND|OR field condition value]]
# Deletes either the current tuple (if no qualifier added), or
# specified tuples.
delete tuple where state = solid and number < 7
# This should have deleted Lithium, Beryllium, Boron, and Carbon.
first display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
next display
#
#*************************************************************************
# REMOVE (field1 {, fieldn} ) [FROM relation_name]
# or DELETE FIELD (field1 {, fie'dn} ) [FROM relation_name]
```

```
# Deletes a field and all associated values from a relation.
#
# Let's remove the STATE field so that ELEMENTS and TABLE will
# be compatible.
remove (state) from elements
list
show elements
#
# Since STATE has no instances, we could delete it now.
#
# Add new data to TABLE that will not be in ELEMENTS.
use table
insert Potassium     K   1032      336.35 19  39.0983
insert Calcium       Ca  1757    1112     20  40.08
insert Scandium      Sc  3104    1812     21  44.9559
insert Titanium      Ti  3562    1943     22  47.9
#
#*************************************************************************
# INTERSECT relation1 AND relation2 ONTO new_relation
# Now, lets find the intersection of ELEMENTS and TABLE.
# (those elements that occur in both ELEMENTS and TABLE)
intersect elements and table onto intersect
list
use intersect
first display
next display
next display
next display
next display
next display
next display
next display
#
#*************************************************************************
# DIFFERENCE relation1 AND relation2 ONTO new_relation
# Now let's find the difference of the two relations.
# (elements occuring in one but not the other)
difference elements and table onto differences
list
show differences
use differences
first display
next display
next display
next display
next display
next display
next display
next display
next display
next display
#
#*************************************************************************
# SEARCH FOR field condition value [AND|OR field condition value]
# Searches for tuples in the current relation which satisfy the
# given conditions.
search for symbol ? M or number >= 20
display
#
#*************************************************************************
# FIND -- searches for the next tuple using the conditions from the
#         last SEARCH command.
find display
find display
find display
find display
find display
#
#*************************************************************************
# I have included a few statistical operators.  Their function is
# straightforward, and all use the same format.
#    COUNT   field   -   returns the number of items in the field.
#    SUM     field   -   returns the sum of the items in the field.
#    MAX     field   -   returns the maximum value in the field.
#    MIN     field   -   returns the minimum value in the field.
#    AVERAGE field   -   returns the average value in the field.
count melt
sum weight
max boil
max symbol
min name
min weight
average weight
average symbol
#
# I have also included math operators which can take qualifiers
#*************************************************************************
```

```
# INCREASE field BY value [WHERE field condition value [AND|OR field condition value]]
# DECREASE field BY value [WHERE field condition value [AND|OR field condition value]]
# MULTIPLY field BY value [WHERE field condition value [AND|OR field condition value]]
# DIVIDE   field BY value [WHERE field condition value [AND|OR field condition value]]
increase boil    by 1000 where number  > 15
decrease melt    by 1000 where boil    < 300
multiply weight by  100 where name    !? e    # name does not contain an 'e'
divide   number by    2 where symbol >= M    # symbol alphabetically follows 'M'
#                      | number | old   |  boil | old   | name |  old    | symbol |  old   |
#              Element | > 15   | boil  | < 300 | melt  | !? e | weight  | >= M   | number |
#             ---------------------------------------------------------------------+--------|
first display #CALCIUM |  yes   | 1757  |  no   | 1112  | yes  | 40.08   |  no    |   20   |
next display #FLUORINE |   no   | 84.95 |  yes  | 53.48 |  no  | 18.9984 |  no    |    9   |
next display #HYDROGEN |   no   | 20.26 |  yes  | 14.02 |  no  | 1.0079  |  no    |    1   |
next display #HELIUM   |   no   | 4.215 |  yes  | 0.95  |  no  | 4.0026  |  no    |    2   |
next display #POTASSIUM|  yes   | 1032  |  no   | 336.3 | yes  | 39.0983 |  no    |   19   |
next display #NITROGEN |   no   | 77.35 |  yes  | 63.14 |  no  | 14.0067 |  yes   |    7   |
next display #NEON     |   no   | 27.09 |  yes  | 24.55 |  no  | 20.179  |  yes   |   10   |
next display #OXYGEN   |   no   | 90.18 |  yes  | 50.35 |  no  | 15.9994 |  yes   |    8   |
next display #SCANDIUM |  yes   | 3104  |  no   | 1812  | yes  | 44.9559 |  yes   |   21   |
next display #TITANIUM |  yes   | 3562  |  no   | 1943  | yes  | 47.90   |  yes   |   22   |
list
quit  #deletes all domains and relations and exits to the operating system
```

APPENDIX 2 : Output From Sample Input Deck

```
Command : # Sample input file to test the commands for the relational database
Command : # command parser system (RPSYS).
Command : # NOTE: conventions used in this file are as follows...
Command : #   Command syntax descriptions are preceded by a pair of asterisks "*"
Command : #   Items in brackets "[]" are optional items which may be used once per command.
Command : #   Items in braces "{}" are optional items which may be used many times.
Command : #   Items which are in all capital letters are required keywords.
Command : #   Items delimited by a vertical bar "|" separate the list of valid keywords
Command : #       which may be used.
Command : #   Punctuation marks (other than those listed above) are required where shown.
Command : #
Command : *************************************************************************
Command : #  DEFINE domain_name AS domain_type (field_width[,decimal_places])
Command : # Values in a field must belong to a specific domain.
Command : # domain_type may be one of the following:
Command : #   CHARACTER  - for textual data
Command : #   INTEGER    - for single precision integer data
Command : #   LONG       - for double precision integer data
Command : #   REAL       - for single precision floating-point data
Command : #   DOUBLE     - for double precision floating-point data
Command : #   SCIENTIFIC - for scientific notation format
Command : define atomic_name as character 20
Command : define junk as scientific 13.6
Command : define atomic_symbol as character 3
Command : define temperature as real 7.3
Command : #
Command : #************************************************************************
Command : #LIST - brief list of the contents of the database.
Command : list
DOMAIN            atomic_name  :  CHARACTER, format : 20.00, instances : 0
DOMAIN                   junk  : SCIENTIFIC, format : 13.60, instances : 0
DOMAIN          atomic_symbol  :  CHARACTER, format :  3.00, instances : 0
DOMAIN            temperature  :       REAL, format :  7.30, instances : 0
Command : #
Command : #************************************************************************
Command : # DELETE DOMAIN domain_name     or      UNDEFINE domain_name
Command : # Delete unused or unwanted domains.
Command : undefine junk
Command : list
DOMAIN            atomic_name  :  CHARACTER, format : 20.00, instances : 0
DOMAIN          atomic_symbol  :  CHARACTER, format :  3.00, instances : 0
DOMAIN            temperature  :       REAL, format :  7.30, instances : 0
Command : #
Command : #************************************************************************
Command : # CREATE relation_name WITH (field_name : domain_name (,field_name : domain_name)) [USING field_name, U
Command : # Relations are collections of data organized by fields (columns)
Command : # and tuples (rows).  The user defines how the data in a relation is
Command : # organized when it is created.
Command : create elements with (
    name    :   atomic_name,
    symbol  :   atomic_symbol,
    boil    :   temperature,
    melt    :   temperature
) using symbol up
Command : # ^^^^^ Sorts the data in this relation by symbol in ascending order.
Command : # If the optional USING clause is not used, the default is to sort the
Command : # data by the first field in descending order.
Command : # Note that BOIL and MELT are from the same domain.  Multiple fields
Command : # may be drawn from the same domain, but fields may not have multiple
Command : # domains.
```

```
Command : list
DOMAIN            atomic_name  :  CHARACTER, format : 20.00, instances : 1
DOMAIN          atomic_symbol  :  CHARACTER, format :  3.00, instances : 1
DOMAIN           temperature   :       REAL, format :  7.30, instances : 2
RELATION            elements   :   4 fields,    0 tuples
Command : #
Command : #*************************************************************************
Command : # SHOW [relation_name]
Command : # Show detailed information about a relation.  If relation_name is not
Command : # specified, the current relation is displayed (if assigned).
Command : show
ERROR - No relation is current!
Command : show elements

     RELATION INFORMATION
Name        : elements
Owner       : ELKINST
Data file   :
Protection  : R: 0, A: 0, M: 0, D: 0
Altered     : 1
Fields      : 4
              name : atomic_name                    symbol : atomic_symbol
              boil : temperature                      melt : temperature

Key field   : symbol
Ascend sort : 1
Tuples      : 0
Last user   : ELKINST
Last used   : Tue Feb 18 15:13:24 1992

Command : #
Command : #*************************************************************************
Command : # USE relation_name
Command : # Make the relation current.
Command : # Some operations are performed only on the current relation.
Command : use elements
Command : #
Command : #*************************************************************************
Command : # INSERT (data)
Command : # The INSERT command will prompt you for input for each field:
Command : # however, if you know the order of the fields, the data can be
Command : # placed on the command line (unless you have character data
Command : # that may contain spaces).
Command : # Note also that the input can be placed in tabular form.
Command : # (useful for incorporating data from external files)
Command : insert Hydrogen      H     20.268       14.025
Command : insert Helium        He     4.215         .95
Command : insert Lithium       Li  1615          453.7
Command : insert Beryllium     Be  2745         1560
Command : insert Boron         B   4275         2300
Command : insert Carbon        C   4470         4100
Command : insert Nitrogen      N     77.35        63.14
Command : insert Oxygen        O     90.18        54.35
Command : insert Fluorine      F     84.95        53.48
Command : insert Neon          Ne    27.096       24.553
Command : #
Command : # There should be 10 tuples in the ELEMENTS relation.
Command : # There should also be an asterisk '*' next to ELEMENTS, indicating
Command : # it is the current relation.
Command : list
```

```
DOMAIN            atomic_name  :  CHARACTER, format : 20.00, instances : 1
DOMAIN          atomic_symbol  :  CHARACTER, format :  3.00, instances : 1
DOMAIN           temperature   :       REAL, format :  7.30, instances : 2
RELATION            elements*  :   4 fields,   10 tuples
Command : #
Command : #*************************************************************************
Command : # PROJECT ( field (, field) ) ONTO relation_name [WHERE field condition value (AND|OR field condition
Command : # Copies columns of data from the current relation to a new relation.
Command : project (name) onto names
Command : # No qualifier was used, so the NAME field of all tuples was copied.
Command : list
DOMAIN            atomic_name  :  CHARACTER, format : 20.00, instances : 2
DOMAIN          atomic_symbol  :  CHARACTER, format :  3.00, instances : 1
DOMAIN           temperature   :       REAL, format :  7.30, instances : 2
RELATION            elements*  :   4 fields,   10 tuples
RELATION               names   :   1 field ,   10 tuples
Command : use names
Command : #
Command : #*************************************************************************
Command : # FIRST -- moves the current tuple pointer to the first tuple in the current relation
Command : # NEXT -- moves the current tuple pointer to the next tuple in the current relation
Command : # DISPLAY -- displays the contents of the current tuple.
Command : # Note how multiple commands may be placed on the same line...
Command : first display
name : 'Beryllium'
Command : next display
name : 'Boron'
Command : #
Command : use elements
Command : project (boil,name) onto boiling_pts
Command : # Two fields of all tuples are copied.
Command : list
DOMAIN            atomic_name  :  CHARACTER, format : 20.00, instances : 2
DOMAIN          atomic_symbol  :  CHARACTER, format :  3.00, instances : 1
DOMAIN           temperature   :       REAL, format :  7.30, instances : 3
RELATION            elements*  :   4 fields,   10 tuples
RELATION               names   :   1 field ,   10 tuples
RELATION          boiling_pts  :   2 fields,   10 tuples
Command : show boiling_pts

     RELATION INFORMATION
Name         : boiling_pts
Owner        : ELKINST
Data file    :
Protection   : R: 0, A: 0, M: 0, D: 0
Altered      : 1
Fields       : 2
               boil : temperature                    name : atomic_name

Key field    : boil
Ascend sort  : 1
Tuples       : 10
Last user    : ELKINST
Last used    : Tue Feb 18 15:13:24 1992

Command : #
Command : project (name,symbol) onto hot_ones where melt > 100
Command : # Two fields are copied, but only for tuples that meet the
Command : # stated requirement.
Command : # The conditionals that are accepted are as follows:
```

```
Command : #   =       Equals                  !=      Does Not Equal
Command : #   <       Less Than               <=      Less Than or Equal
Command : #   >       Greater Than            >=      Greater Than or Equal
Command : #   ?       Contains                !?      Does Not Contain
Command : list
DOMAIN            atomic_name   :  CHARACTER, format : 20.00, instances : 4
DOMAIN          atomic_symbol   :  CHARACTER, format :  3.00, instances : 2
DOMAIN            temperature   :       REAL, format :  7.30, instances : 3
RELATION             elements*  :   4 fields,   10 tuples
RELATION                names   :   1 field ,   10 tuples
RELATION           boiling_pts  :   2 fields,   10 tuples
RELATION             hot_ones   :   2 fields,    4 tuples
Command : show hot_ones

     RELATION INFORMATION
Name         : hot_ones
Owner        : ELKINST
Data file    :
Protection   : R: 0, A: 0, M: 0, D: 0
Altered      : 1
Fields       : 2
               name : atomic_name                    symbol : atomic_symbol

Key field    : symbol
Ascend sort  : 1
Tuples       : 4
Last user    : ELKINST
Last used    : Tue Feb 1? 15:12:24 1992

Command : #
Command : project (symbol,melt,name) onto junk where
        name    !?  e       and
        boil    <=  1615
Command : # Three fields this time, but the requirements are more rigid.
Command : # The qualifier "name !? e" means select entries in the field
Command : # NAME that do not contain the letter 'e' (like "Lithium")
Command : list
DOMAIN            atomic_name   :  CHARACTER, format : 20.00, instances : 5
DOMAIN          atomic_symbol   :  CHARACTER, format :  3.00, instances : 3
DOMAIN            temperature   :       REAL, format :  7.30, instances : 4
RELATION             elements*  :   4 fields,   10 tuples
RELATION                names   :   1 field ,   10 tuples
RELATION           boiling_pts  :   2 fields,   10 tuples
RELATION             hot_ones   :   2 fields,    4 tuples
RELATION                junk    :   3 fields,    1 tuple
Command : show junk

     RELATION INFORMATION
Name         : junk
Owner        : ELKINST
Data file    :
Protection   : R: 0, A: 0, M: 0, D: 0
Altered      : 1
Fields       : 3
               symbol : atomic_symbol                melt : temperature
                 name : atomic_name
Key field    : symbol
Ascend sort  : 1
Tuples       : 1
Last user    : ELKINST
```

```
Last used   : Tue Feb 18 15:13:24 1992

Command : #
Command : #*************************************************************************
Command : # DELETE RELATION relation_name
Command : # Self explanatory.
Command : delete relation names
Command : delete relation boiling_pts
Command : delete relation hot_ones
Command : delete relation junk
Command : #
Command : #*************************************************************************
Command : # COPY relation ONTO new_relation [WHERE field condition value (AND|OR field condition value)]
Command : # Copies specified tuples with all fields.
Command : # (unlike PROJECT which copies certain fields)
Command : copy elements onto cool_ones where boil <= 100
Command : list
DOMAIN            atomic_name  :  CHARACTER, format : 20.00, instances : 2
DOMAIN          atomic_symbol  :  CHARACTER, format :  3.00, instances : 2
DOMAIN            temperature  :       REAL, format :  7.3D, instances : 4
RELATION             elements* :   4 fields,   10 tuples
RELATION            cool_ones  :   4 fields,    6 tuples
Command : use cool_ones
Command : show

     RELATION INFORMATION
Name         : cool_ones  (current relation)
Owner        : ELKINST
Data file    :
Protection   : R: D, A: D, M: D, D: D
Altered      : 1
Fields       : 4
                 name : atomic_name                    symbol : atomic_symbol
                 boil : temperature                      melt : temperature

Key field    : symbol
Ascend sort  : 1
Tuples       : 6
Last user    : ELKINST
Last used    : Tue Feb 18 15:13:25 1992

Command : first display
name : 'Fluorine'
symbol : 'F'
boil :  84.950
melt :  53.480
Command : next display
name : 'Hydrogen'
symbol : 'H'
boil :  20.268
melt :  14.025
Command : next display
name : 'Helium'
symbol : 'He'
boil :   4.215
melt :   0.950
Command : #
Command : # create a new relation with different data
Command : #
Command : define atomic_number as integer 3
```

```
Command : define atomic_weight as real 10.5
Command : create atomic_data with (
    number      :   atomic_number,
    symbol      :   atomic_symbol,
    weight      :   atomic_weight
)
Command : list
DOMAIN            atomic_name  :  CHARACTER, format : 20.00, instances : 2
DOMAIN          atomic_symbol  :  CHARACTER, format :  3.00, instances : 3
DOMAIN            temperature  :       REAL, format :  7.30, instances : 4
DOMAIN          atomic_number  :    INTEGER, format :  7.00, instances : 1
DOMAIN          atomic_weight  :       REAL, format : 10.50, instances : 1
RELATION             elements  :   4 fields,   10 tuples
RELATION           cool_ones*  :   4 fields,    6 tuples
RELATION          atomic_data  :   3 fields,    0 tuples
Command : show atomic_data

     RELATION INFORMATION
Name         : atomic_data
Owner        : ELKINST
Data file    :
Protection   : R: 0, A: 0, M: 0, D: 0
Altered      : 1
Fields       : 3
               number : atomic_number                  symbol : atomic_symbol
               weight : atomic_weight
Key field    : number
Ascend sort  : 0
Tuples       : 0
Last user    : ELKINST
Last used    : Tue Feb 18 15:13:25 1992

Command : use atomic_data
Command : show

     RELATION INFORMATION
Name         : atomic_data  (current relation)
Owner        : ELKINST
Data file    :
Protection   : R: 0, A: 0, M: 0, D: 0
Altered      : 1
Fields       : 3
               number : atomic_number                  symbol : atomic_symbol
               weight : atomic_weight
Key field    : number
Ascend sort  : 0
Tuples       : 0
Last user    : ELKINST
Last used    : Tue Feb 18 15:13:25 1992

Command : #
Command : # Insert the new data.
Command : #
Command : insert  1   H    1.0079
Command : insert  2   He   4.0026
Command : insert  3   Li   6.941
Command : insert  4   Be   9.01218
Command : insert  5   B    10.81
Command : insert  6   C    12.011
Command : insert  7   N    14.0067
```

```
Command : insert  F   O   15.9994
Command : insert  .   F   18.998403
Command : insert 10   Ne  20.179
Command : insert 11   Na  22.98977
Command : # Since no sorting directive was given, the default is the first
Command : # field listed in the CREATE parameter list.  Also the default
Command : # sorting direction is in descending order, so the first tuple
Command : # of this new relation should be the one with the highest number.
Command : # (Sodium - #11)
Command : first display
number :  11
symbol : 'Na'
weight :  22.98977
Command : #
Command : #*************************************************************************
Command : # JOIN relation1 TO relation2 WHERE ( field1 condition field2 (, fieldm condition fieldn)
Command : # Joins two relations so that the data from both is incorporated
Command : # into one relation.  The acceptable combinations are determined
Command : # by the condition(s) specified.
Command : join atomic_data to elements where (symbol = symbol)
Command : #
Command : # The data is grouped together using the fact that they share SYMBOL
Command : # information.  Notice, though, that ATOMIC_DATA contains a record
Command : # that does not match any in ELEMENTS.  That record is skipped.
Command : # ELEMENTS should now have the same number of tuples (10),
Command : # but two more fields (total 6 fields).
Command : #
Command : list
DOMAIN            atomic_name  :  CHARACTER, format : 20.00, instances : 2
DOMAIN          atomic_symbol  :  CHARACTER, format :  3.00, instances : 3
DOMAIN            temperature  :       REAL, format :  7.30, instances : 4
DOMAIN          atomic_number  :    INTEGER, format :  3.00, instances : 2
DOMAIN          atomic_weight  :       REAL, format : 10.50, instances : 2
RELATION             cool_ones :   4 fields,    6 tuples
RELATION           atomic_data# :   3 fields,   11 tuples
RELATION              elements  :   6 fields,   10 tuples
Command : use elements
Command : show

     RELATION INFORMATION
Name          : elements  (current relation)
Owner         : ELKINST
Data file     :
Protection    : R: 0, A: 0, M: 0, D: 0
Altered       : 1
Fields        : 6
     elements_name : atomic_name           elements_symbol : atomic_symbol
     elements_boil : temperature             elements_melt : temperature
atomic_data_number : atomic_number      atomic_data_weight : atomic_weight

Key field     : elements_symbol
Ascend sort   : 1
Tuples        : 10
Last user     : ELKINST
Last used     : Tue Feb 18 15:13:25 1992

Command : #
Command : # Display some of the tuples to make sure the data is correct.
Command : #
Command : first display
```

```
elements_name : 'Boron'
elements_symbol : 'B'
elements_boil : 4275.000
elements_melt : 2300.000
atomic_data_number :   5
atomic_data_weight :   10.81000
Command : next display
elements_name : 'Beryllium'
elements_symbol : 'Be'
elements_boil : 2745.000
elements_melt : 1560.000
atomic_data_number :   4
atomic_data_weight :   9.01218
Command : next display
elements_name : 'Carbon'
elements_symbol : 'C'
elements_boil : 4470.000
elements_melt : 4100.000
atomic_data_number :   6
atomic_data_weight :   12.01100
Command : e
Command : #*************************************************************************
Command : # CHANGE FIELD (old_field_name TO new_field_name {, old TO new } )
Command : # Rename the fields to something more reasonable (fields are renamed
Command : # to avoid the possibility of duplicate names while joining)
Command : change field (
    elements_name        to  name,
    elements_symbol      to  symbol,
    elements_boil        to  boil,
    elements_melt        to  melt,
    atomic_data_number   to  number,
    atomic_data_weight   to  weight
)
Command : #
Command : # We don't need ATOMIC_DATA any more, so delete it.
Command : #
Command : delete relation atomic_data
Command : list
DOMAIN              atomic_name  :  CHARACTER, format : 20.00, instances : 2
DOMAIN            atomic_symbol  :  CHARACTER, format :  3.00, instances : 2
DOMAIN              temperature  :         REAL, format :  7.30, instances : 4
DOMAIN            atomic_number  :      INTEGER, format :  3.00, instances : 1
DOMAIN            atomic_weight  :         REAL, format : 10.50, instances : 1
RELATION              cool_ones  :   4 fields,    6 tuples
RELATION               elements  :   6 fields,   10 tuples
Command : e
Command : # Make a new relation with the same fields, but new data.
Command : #
Command : create table with (
    name    :   atomic_name,
    symbol  :   atomic_symbol,
    boil    :   temperature,
    melt    :   temperature,
    number  :   atomic_number,
    weight  :   atomic_weight
) using melt down
Command : list
DOMAIN              atomic_name  :  CHARACTER, format : 20.00, instances : 2
DOMAIN            atomic_symbol  :  CHARACTER, format :  3.00, instances : 2
DOMAIN              temperature  :         REAL, format :  7.30, instances : 4
```

```
DOMAIN          atomic_number  :    INTEGER, format :  3.00, instances : 2
DOMAIN          atomic_weight  :       REAL, format : 10.5C, instances : 2
RELATION            cool_ones  :   4 fields,    4 tuples
RELATION             elements* :   5 fields,   10 tuples
RELATION                table  :   5 fields,    0 tuples
Command : use table
Command : show

     RELATION INFORMATION
Name        : table  (current relation)
Owner       : ELKINST
Data file   :
Protection  : R: 0, A: 0, M: 0, D: 0
Altered     : 1
Fields      : 5
                name : atomic_name                    symbol : atomic_symbol
                boil : temperature                      melt : temperature
              number : atomic_number                  weight : atomic_weight

Key field   : melt
Ascend sort : 0
Tuples      : 0
Last user   : ELKINST
Last used   : Tue Feb 18 15:13:25 1992

Command : insert Sodium       Na  1156     371.0  11  22.98977
Command : insert Magnesium    Mg  1363     922    12  24.305
Command : insert Aluminum     Al  2793     933.25 13  26.98154
Command : insert Silicon      Si  3540    1685    14  28.0855
Command : insert Phosphorus   P    550     317.3  15  30.97376
Command : insert Sulfur       S    717.75  388.36 16  32.06
Command : insert Chlorine     Cl   239.1   172.16 17  35.453
Command : insert Argon        Ar    87.3    83.81 18  39.948
Command : #
Command : first display
name : 'Silicon'
symbol : 'Si'
boil : 3540.000
melt : 1685.000
number :  14
weight :   28.08550
Command : next display
name : 'Aluminum'
symbol : 'Al'
boil : 2793.000
melt : 933.250
number :  13
weight :   26.98154
Command : next display
name : 'Magnesium'
symbol : 'Mg'
boil : 1363.000
melt : 922.000
number :  12
weight :   24.30500
Command : #
Command : #################################################################################
Command : # UNION relation1 AND relation2
Command : # Appends the contents of relation2 onto relation1.  The two
Command : # relations must be compatible (same # of fields and matching domains
```

```
Command : # for each field).
Command : list     # before
DOMAIN              atomic_name  :  CHARACTER, format : 20.00, instances : 3
DOMAIN            atomic_symbol  :  CHARACTER, format :  3.00, instances : 3
DOMAIN              temperature  :       REAL, format :  7.30, instances : 6
DOMAIN            atomic_number  :    INTEGER, format :  3.00, instances : 2
DOMAIN            atomic_weight  :       REAL, format : 10.50, instances : 2
RELATION              cool_ones  :   4 fields,    6 tuples
RELATION               elements  :   6 fields,   10 tuples
RELATION                 table#  :   6 fields,    8 tuples
Command : union elements and table
Command : # Of course we could have also inserted the data into ELEMENTS
Command : # directly, but this illustrates how relations can be appended.
Command : list     # after
DOMAIN              atomic_name  :  CHARACTER, format : 20.00, instances : 3
DOMAIN            atomic_symbol  :  CHARACTER, format :  3.00, instances : 3
DOMAIN              temperature  :       REAL, format :  7.30, instances : 4
DOMAIN            atomic_number  :    INTEGER, format :  3.00, instances : 2
DOMAIN            atomic_weight  :       REAL, format : 10.50, instances : 2
RELATION              cool_ones  :   4 fields,    6 tuples
RELATION               elements  :   6 fields,   18 tuples
RELATION                 table#  :   6 fields,    8 tuples
Command : show elements

     RELATION INFORMATION
Name        : elements
Owner       : ELKINST
Data file   :
Protection  : R: 0, A: 0, M: 0, D: 0
Altered     : 1
Fields      : 6
              name : atomic_name                    symbol : atomic_symbol
              boil : temperature                      melt : temperature
            number : atomic_number                  weight : atomic_weight

Key field   : symbol
Ascend sort : 1
Tuples      : 18
Last user   : ELKINST
Last used   : Tue Feb 17 15:13:35 1992

Command : use elements
Command : first display
name : 'Aluminum'
symbol : 'Al'
boil : 2793.000
melt : 933.250
number :  13
weight :  26.98154
Command : next display
name : 'Argon'
symbol : 'Ar'
boil :  87.300
melt :  83.810
number :  18
weight :  39.94800
Command : next display
name : 'Boron'
symbol : 'B'
boil : 4275.000
```

```
melt : 2300.000
number :   5
weight :   10.81000
Command : next display
name : 'Beryllium'
symbol : 'Be'
boil : 2745.000
melt : 1560.000
number :   4
weight :   9.01219
Command : #
Command : #*************************************************************************
Command : # ADD ( field1 : domain_name (, fieldn : domain_name) ) [TO relation]
Command : # Adds fields to an existing relation.  In this example,
Command : # we add a new field to the current relation to store the physical
Command : # state of the element at 305 degrees Kelvin.
Command : define state as character 6
Command : list
DOMAIN            atomic_name  :  CHARACTER, format : 20.00, instances : 3
DOMAIN          atomic_symbol  :  CHARACTER, format :  3.00, instances : 3
DOMAIN            temperature  :       REAL, format :  7.30, instances : 4
DOMAIN          atomic_number  :    INTEGER, format :  3.00, instances : 2
DOMAIN          atomic_weight  :       REAL, format : 10.50, instances : 2
DOMAIN                  state  :  CHARACTER, format :  6.00, instances : 0
RELATION            cool_ones  :   4 fields,    6 tuples
RELATION             elements* :   6 fields,   18 tuples
RELATION                table  :   6 fields,    8 tuples
Command : add (state : state)
Command : # No qualifier since we are adding it to the current relation.
Command : # Note that a field may have the same name as a domain.
Command : show

     RELATION INFORMATION
Name        : elements  (current relation)
Owner       : ELKINST
Data file   :
Protection  : R: 0, A: 0, M: 0, D: 0
Altered     : 1
Fields      : 7
              name : atomic_name                    symbol : atomic_symbol
              boil : temperature                     melt : temperature
            number : atomic_number                 weight : atomic_weight
             state : state
Key field   : symbol
Ascend sort : 1
Tuples      : 18
Last user   : ELKINST
Last used   : Tue Feb 18 15:13:25 1992

Command : #
Command : #*************************************************************************
Command : # SET field_name TO value [WHERE field condition value (AND|OR field condition value)]
Command : # Sets all or some of the field values to a given value.
Command : set state to solid
Command : # Most of the elements are solid, so we set all of the STATE values
Command : # to 'solid' for now.
Command : #
Command : first display
name : 'Aluminum'
symbol : 'Al'
```

```
boil : 2793.000
melt : 933.250
number :  13
weight :  26.98154
state : 'solid'
Command : #
Command : # Next, we set the STATE value to 'liquid' for all elements whose
Command : # melting point is below the specified temperature.
Command : #
Command : set state to liquid where melt < 305
Command : first display
name : 'Aluminum'
symbol : 'Al'
boil : 2793.000
melt : 933.250
number :  13
weight :  26.98154
state : 'solid'
Command : #
Command : # Do the same thing for gaseous elements.
Command : # (boiling point < temperature)
Command : #
Command : set state to gas where boil < 305
Command : first display
name : 'Aluminum'
symbol : 'Al'
boil : 2793.000
melt : 933.250
number :  13
weight :  26.98154
state : 'solid'
Command : next display
name : 'Argon'
symbol : 'Ar'
boil :  87.300
melt :  83.810
number :  18
weight :  39.94800
state : 'gas'
Command : next display
name : 'Boron'
symbol : 'B'
boil : 4275.000
melt : 2300.000
number :  5
weight :  10.81100
state : 'solid'
Command : next display
name : 'Beryllium'
symbol : 'Be'
boil : 2745.000
melt : 1560.000
number :  4
weight :  9.01218
state : 'solid'
Command : next display
name : 'Carbon'
symbol : 'C'
boil : 4470.000
melt : 4100.000
```

```
number :   9
weight :   12.01115
state : 'solid'
Command : next display
name : 'Chlorine'
symbol : 'Cl'
boil : 239.100
melt : 172.160
number :  17
weight :   35.45300
state : 'gas'
Command : next display
name : 'Fluorine'
symbol : 'F'
boil :  84.950
melt :  53.430
number :   9
weight :   18.99840
state : 'gas'
Command : next display
name : 'Hydrogen'
symbol : 'H'
boil :  20.260
melt :  14.025
number :   1
weight :    1.00790
state : 'gas'
Command : next display
name : 'Helium'
symbol : 'He'
boil :   4.215
melt :   0.950
number :   2
weight :    4.00260
state : 'gas'
Command : next display
name : 'Lithium'
symbol : 'Li'
boil : 1615.000
melt : 453.700
number :   3
weight :    6.94100
state : 'solid'
Command : next display
name : 'Magnesium'
symbol : 'Mg'
boil : 1363.000
melt : 922.000
number :  12
weight :   24.30500
state : 'solid'
Command : next display
name : 'Nitrogen'
symbol : 'N'
boil :  77.350
melt :  63.140
number :   7
weight :   14.00670
state : 'gas'
Command : next display
```

```
name : 'Sodium'
symbol : 'Na'
boil : 1156.000
melt : 371.000
number :  11
weight :  22.99977
state : 'solid'
Command : next display
name : 'Neon'
symbol : 'Ne'
boil :  27.096
melt :  24.553
number :  10
weight :  20.17900
state : 'gas'
Command : next display
name : 'Oxygen'
symbol : 'O'
boil :  90.180
melt :  50.350
number :  8
weight :  15.99940
state : 'gas'
Command : next display
name : 'Phosphorus'
symbol : 'P'
boil : 550.000
melt : 317.300
number :  15
weight :  30.97376
state : 'solid'
Command : next display
name : 'Sulfur'
symbol : 'S'
boil : 717.750
melt : 339.760
number :  16
weight :  32.06000
state : 'solid'
Command : next display
name : 'Silicon'
symbol : 'Si'
boil : 3540.000
melt : 1685.000
number :  14
weight :  28.08550
state : 'solid'
Command : #
Command : #*************************************************************************
Command : # DELETE TUPLE [WHERE field condition value (AND|OR field condition value)]
Command : # Deletes either the current tuple (if no qualifier added), or
Command : # specified tuples.
Command : delete tuple where state = solid and number < 7
Command : # This should have deleted Lithium, Beryllium, Boron, and Carbon.
Command : first display
name : 'Aluminum'
symbol : 'Al'
boil : 2793.000
melt : 933.250
number :  13
```

```
weight :   [illegible]
state : 'solid'
Command : next display
name : 'Argon'
symbol : 'Ar'
boil :  87.300
melt :  83.810
number :  18
weight :   39.94800
state : 'gas'
Command : next display
name : 'Chlorine'
symbol : 'Cl'
boil : 239.100
melt : 172.160
number :  17
weight :   35.45300
state : 'gas'
Command : next display
name : 'Fluorine'
symbol : 'F'
boil :  84.950
melt :  53.480
number :   9
weight :   18.99840
state : 'gas'
Command : next display
name : 'Hydrogen'
symbol : 'H'
boil :  20.268
melt :  14.025
number :   1
weight :    1.00790
state : 'gas'
Command : next display
name : 'Helium'
symbol : 'He'
boil :   4.215
melt :   0.950
number :   2
weight :    4.00260
state : 'gas'
Command : next display
name : 'Magnesium'
symbol : 'Mg'
boil : 1363.000
melt : 922.000
number :  12
weight :   24.30500
state : 'solid'
Command : next display
name : 'Nitrogen'
symbol : 'N'
boil :  77.350
melt :  63.140
number :   7
weight :   14.00670
state : 'gas'
Command : next display
name : 'Sodium'
```

```
symbol : 'Na'
boil : 1156.000
melt : 371.000
number :  11
weight :   22.98977
state : 'solid'
Command : next display
name : 'Neon'
symbol : 'Ne'
boil :  27.096
melt :  24.553
number :  10
weight :   20.17900
state : 'gas'
Command : next display
name : 'Oxygen'
symbol : 'O'
boil :  90.180
melt :  50.350
number :  8
weight :   15.99940
state : 'gas'
Command : next display
name : 'Phosphorus'
symbol : 'P'
boil : 550.000
melt : 317.300
number :  15
weight :   30.97376
state : 'solid'
Command : next display
name : 'Sulfur'
symbol : 'S'
boil : 717.750
melt : 388.360
number :  16
weight :   32.06400
state : 'solid'
Command : next display
name : 'Silicon'
symbol : 'Si'
boil : 3540.000
melt : 1685.000
number :  14
weight :   28.08550
state : 'solid'
Command : next display
name : 'Aluminum'
symbol : 'Al'
boil : 2793.000
melt : 933.250
number :  13
weight :   26.98154
state : 'solid'
Command : #
Command : #*****************************************************************************
Command : # REMOVE (field1 (, fieldn) ) FROM relation_name]
Command : # or DELETE FIELD (field1 (, fieldn) ) FROM relation_name]
Command : # Deletes a field and all associated values from a relation.
Command : ^
```

```
Command : # Let's remove the STATE field so that ELEMENTS and TABLE will
Command : # be compatible.
Command : remove (state) from elements
Command : list
DOMAIN              atomic_name  :  CHARACTER, format : 20.00, instances : 3
DOMAIN            atomic_symbol  :  CHARACTER, format :  3.00, instances : 3
DOMAIN              temperature  :         REAL, format :  7.30, instances : 4
DOMAIN            atomic_number  :      INTEGER, format :  3.00, instances : 2
DOMAIN            atomic_weight  :         REAL, format : 10.50, instances : 2
DOMAIN                    state  :  CHARACTER, format :  6.00, instances : 0
RELATION              cool_ones  :   4 fields,    6 tuples
RELATION               elements* :   4 fields,   14 tuples
RELATION                  table  :   6 fields,    8 tuples
Command : show elements

      RELATION INFORMATION
Name         : elements  (current relation)
Owner        : FLKINST
Data file    :
Protection   : R: 0, A: 0, M: 0, D: 0
Altered      : 1
Fields       : 6
               name : atomic_name                    symbol : atomic_symbol
               boil : temperature                      melt : temperature
             number : atomic_number                  weight : atomic_weight

Key field    : symbol
Ascend sort  : 1
Tuples       : 14
Last user    : FLKINST
Last used    : Tue Feb 18 15:13:25 1992

Command : #
Command : # Since STATE has no instances, we could delete it now.
Command : #
Command : # Add new data to TABLE that will not be in ELEMENTS.
Command : use table
Command : insert Potassium     K   1032     336.35 19  39.0993
Command : insert Calcium       Ca  1757    1112    20  40.08
Command : insert Scandium      Sc  3104    1812    21  44.9559
Command : insert Titanium      Ti  3562    1943    22  47.9
Command : #
Command : #*************************************************************************
Command : # INTERSECT relation1 AND relation2 ONTO new_relation
Command : # Now, lets find the intersection of ELEMENTS and TABLE.
Command : # (those elements that occur in both ELEMENTS and TABLE)
Command : intersect elements and table onto intersect
Command : list
DOMAIN              atomic_name  :  CHARACTER, format : 20.00, instances : 4
DOMAIN            atomic_symbol  :  CHARACTER, format :  3.00, instances : 4
DOMAIN              temperature  :         REAL, format :  7.30, instances : 9
DOMAIN            atomic_number  :      INTEGER, format :  3.00, instances : 3
DOMAIN            atomic_weight  :         REAL, format : 10.50, instances : 3
DOMAIN                    state  :  CHARACTER, format :  6.00, instances : 0
RELATION              cool_ones  :   4 fields,    6 tuples
RELATION               elements  :   6 fields,   14 tuples
RELATION                  table* :   6 fields,   12 tuples
RELATION              intersect  :   6 fields,    8 tuples
Command : use intersect
Command : first display
```

```
name : 'Silicon'
symbol : 'Si'
boil : 3540.000
melt : 1685.000
number :  14
weight :   28.04550
Command : next display
name : 'Aluminum'
symbol : 'Al'
boil : 2793.000
melt : 933.250
number :  13
weight :   26.98154
Command : next display
name : 'Magnesium'
symbol : 'Mg'
boil : 1363.000
melt : 922.000
number :  12
weight :   24.30500
Command : next display
name : 'Sulfur'
symbol : 'S'
boil : 717.750
melt : 388.360
number :  16
weight :   32.06000
Command : next display
name : 'Sodium'
symbol : 'Na'
boil : 1156.000
melt : 371.000
number :  11
weight :   22.98977
Command : next display
name : 'Phosphorus'
symbol : 'P'
boil : 550.000
melt : 317.300
number :  15
weight :   30.97376
Command : next display
name : 'Chlorine'
symbol : 'Cl'
boil : 239.100
melt : 172.160
number :  17
weight :   35.45300
Command : next display
name : 'Argon'
symbol : 'Ar'
boil :  87.300
melt :  83.810
number :  18
weight :   39.94800
Command : #
Command : #*****************************************************************************
Command : # DIFFERENCE relation1 AND relation2 ONTO new_relation
Command : # Now let's find the difference of the two relations.
Command : # (elements occuring in one but not the other)
```

```
Command : difference elements and table onto differences
Command : list
DOMAIN              atomic_name  :  CHARACTER, format :  20.00, instances :  5
DOMAIN           atomic_symbol   :  CHARACTER, format :   2.00, instances :  5
DOMAIN             temperature   :         REAL, format :   7.30, instances : 10
DOMAIN            atomic_number  :      INTEGER, format :   3.00, instances :  4
DOMAIN            atomic_weight  :         REAL, format :  10.50, instances :  4
DOMAIN                    state  :  CHARACTER, format :   6.00, instances :  3
RELATION              cool_ones  :   4 fields,    6 tuples
RELATION               elements  :   6 fields,   14 tuples
RELATION                  table  :   6 fields,   12 tuples
RELATION              intersect% :   6 fields,    8 tuples
RELATION            differences  :   6 fields,   10 tuples
Command : show differences

     RELATION INFORMATION
Name         : differences
Owner        : ELKINST
Data file    :
Protection   : R: 0, A: 0, M: 0, D: 0
Altered      : 1
Fields       : 6
                 name : atomic_name                    symbol : atomic_symbol
                 boil : temperature                      melt : temperature
               number : atomic_number                  weight : atomic_weight

Key field    : symbol
Ascend sort  : 1
Tuples       : 10
Last user    : ELKINST
Last used    : Tue Feb 19 15:13:26 1992

Command : use differences
Command : first display
name : 'Calcium'
symbol : 'Ca'
boil : 1757.000
melt : 1112.000
number :  20
weight :   40.08000
Command : next display
name : 'Fluorine'
symbol : 'F'
boil :  84.950
melt :  53.480
number :   9
weight :   18.99840
Command : next display
name : 'Hydrogen'
symbol : 'H'
boil :  20.268
melt :  14.025
number :   1
weight :    1.00790
Command : next display
name : 'Helium'
symbol : 'He'
boil :   4.215
melt :   0.950
number :   2
```

```
weight :    4.03260
Command : next display
name : 'Potassium'
symbol : 'K'
boil : 1032.000
melt : 336.350
number :  19
weight :   39.09830
Command : next display
name : 'Nitrogen'
symbol : 'N'
boil :  77.350
melt :  63.140
number :   7
weight :   14.00670
Command : next display
name : 'Neon'
symbol : 'Ne'
boil :  27.096
melt :  24.553
number :  10
weight :   20.17900
Command : next display
name : 'Oxygen'
symbol : 'O'
boil :  90.180
melt :  50.350
number :   8
weight :   15.99940
Command : next display
name : 'Scandium'
symbol : 'Sc'
boil : 3104.000
melt : 1812.000
number :  21
weight :   44.95590
Command : next display
name : 'Titanium'
symbol : 'Ti'
boil : 3562.000
melt : 1943.000
number :  22
weight :   47.90000
Command : #
Command : #*************************************************************************
Command : # SEARCH FOR field condition value (AND|OR field condition value)
Command : # Searches for tuples in the current relation which satisfy the
Command : # given conditions.
Command : search for symbol = H or number >= 20
Found a match!
Command : display
name : 'Calcium'
symbol : 'Ca'
boil : 1757.000
melt : 1112.000
number :  20
weight :   40.08000
Command : #
Command : #*************************************************************************
Command : # FIND -- searches for the next tuple using the conditions from the
```

```
Command : ?          last SEARCH command.
Command : find display
Found a match!
name : 'Hydrogen'
symbol : 'H'
boil :  20.249
melt :  14.025
number :   1
weight :    1.00794
Command : find display
Found a match!
name : 'Helium'
symbol : 'He'
boil :   4.215
melt :   0.950
number :   2
weight :    4.00260
Command : find display
Found a match!
name : 'Scandium'
symbol : 'Sc'
boil : 3104.000
melt : 1812.000
number :  21
weight :   44.95590
Command : find display
Found a match!
name : 'Titanium'
symbol : 'Ti'
boil : 3562.000
melt : 1943.000
number :  22
weight :   47.90000
Command : find display
No matches found!
ERROR - No current tuple!
Command : #
Command : #*************************************************************************
Command : # I have included a few statistical operators.  Their function is
Command : # straightforward, and all use the same format.
Command : #   COUNT   field   -   returns the number of items in the field.
Command : #   SUM     field   -   returns the sum of the items in the field.
Command : #   MAX     field   -   returns the maximum value in the field.
Command : #   MIN     field   -   returns the minimum value in the field.
Command : #   AVERAGE field   -   returns the average value in the field.
Command : count melt
There are 10 values in the field melt
Command : sum weight
The sum of the values in the weight field is 246.228207
Command : max boil
The maximum value in the boil field is 3562.000000
Command : max symbol
The maximum value in the symbol field is 'Ti'
Command : min name
The minimum value in the name field is 'Calcium'
Command : min weight
The minimum value in the weight field is 1.007900
Command : average weight
The average of the values in the weight field is 24.622821
Command : average symbol
```

```
The symbol field is non-numeric!
Command : #
Command : # I have also included math operators which can take qualifiers
Command : #*****************************************************************
Command : # INCREASE field BY value [WHERE field condition value (AND|OR field condition value)]
Command : # DECREASE field BY value [WHERE field condition value (AND|OR field condition value)]
Command : # MULTIPLY field BY value [WHERE field condition value (AND|OR field condition value)]
Command : # DIVIDE   field BY value [WHERE field condition value (AND|OR field condition value)]
Command : increase boil   by 1000 where number  > 15
Command : decrease melt   by 1000 where boil    < 300
Command : multiply weight by  100 where name   !? e   # name does not contain an 'e'
Command : divide   number by    2 where symbol >= M   # symbol alphabetically follows 'M'
Command : #                    | number | old  |  boil | old  | name |  old   | symbol |  old  |
Command : #             Element | > 15   | boil | < 300 | melt | !? e | weight |  >= M  | number|
Command : #            ---------------------------------------------------------------------------+-------|
Command : first display *CALCIUM |  yes   | 1757 |  no   | 1112 | yes  | 40.08  |   no   |   20  |
name : 'Calcium'
symbol : 'Ca'
boil : 2757.000
melt : 1112.000
number :  20
weight :  40.08000
Command : next display *FLUORINE |   no   | 84.95| yes  | 53.48| no   | 18.9984|   no   |    9  |
name : 'Fluorine'
symbol : 'F'
boil :  84.950
melt : -966.520
number :   9
weight :  18.99840
Command : next display *HYDROGEN |   no   | 20.26| yes  | 14.02| no   | 1.0079 |   no   |    1  |
name : 'Hydrogen'
symbol : 'H'
boil :  20.268
melt : -935.975
number :   1
weight :   1.00790
Command : next display *HELIUM   |   no   | 4.215| yes  | 0.95 | no   | 4.0026 |   no   |    2  |
name : 'Helium'
symbol : 'He'
boil :  4.215
melt : -999.050
number :   2
weight :   4.00260
Command : next display *POTASSIUM|  yes   | 1032 |  no   | 336.3| yes  | 39.0983|   no   |   19  |
name : 'Potassium'
symbol : 'K'
boil : 2032.000
melt : 336.350
number :  19
weight :  39.09830
Command : next display *NITROGEN |   no   | 77.35| yes  | 63.14| no   | 14.0067| yes    |    7  |
name : 'Nitrogen'
symbol : 'N'
boil :  77.350
melt : -936.460
number :   7
weight :  14.00670
Command : next display *NEON     |   no   | 27.0?| yes  | 24.5?| no   | 20.17? | yes    |   10  |
name : 'Neon'
symbol : 'Ne'
```

```
boil :  27.096
melt : -975.447
number :  10
weight :  20.17900
Command : next display *OXYGEN   |   no   | 90.18|  yes  | 50.35|  no  | 15.9994|  yes  |    8  |
name : 'Oxygen'
symbol : 'O'
boil :  90.180
melt : -369.650
number :  8
weight :  15.99940
Command : next display *SCANDIUM |  yes   | 3104 |  no   | 1812 | yes  | 44.9559|  yes  |   21  |
name : 'Scandium'
symbol : 'Sc'
boil : 4104.000
melt : 1812.000
number :  21
weight :  44.95590
Command : next display *TITANIUM |  yes   | 3562 |  no   | 1943 | yes  | 47.90  |  yes  |   22  |
name : 'Titanium'
symbol : 'Ti'
boil : 4562.000
melt : 1943.000
number :  22
weight :  47.90000
Command : list
DOMAIN            atomic_name  :  CHARACTER, format : 20.00, instances : 5
DOMAIN          atomic_symbol  :  CHARACTER, format :  2.00, instances : 5
DOMAIN            temperature  :       REAL, format :  7.10, instances : 10
DOMAIN          atomic_number  :    INTEGER, format :  3.00, instances : 4
DOMAIN          atomic_weight  :       REAL, format : 10.50, instances : 4
DOMAIN                  state  :  CHARACTER, format :  6.00, instances : 9
RELATION            cool_ones  :   4 fields,    6 tuples
RELATION             elements  :   6 fields,   14 tuples
RELATION                table  :   6 fields,   12 tuples
RELATION            intersect  :   6 fields,    8 tuples
RELATION          differences* :   6 fields,   10 tuples
Command : quit  *deletes all domains and relations and exits to the operating syste
```

Macroscopic Material Properties Task

The purpose of this task is to determine the mechanical properties of LCPs to be used for the design and analysis of rocket components. The properties measured are tensile strength and modulus, compressive strength and modulus, and shear strength. This task is using the material's mechanical response to applied load to study several characteristics of LCP's. Effects of processing variables, material anisotropy, the "skin and core" effect, fundamental material behavior, and potentially annealing behavior can all be quantified through the material's mechanical properties. Work on this task up to this point has focused on measuring the tensile moduli and strengths of these materials in an attempt to develop usable processing methods, examine the material anisotropy, quantify the skin and core effect, and develop a material properties database. Future work will continue to examine anisotropy, the skin and core effect, and the material properties database. The effects of physico-chemical annealing on mechanical properties will also be studied.

POC: J. Shelley
OLAC PL/RKCCA
Edwards AFB, CA 93523-5000
Phone: (805) 275-5394
FAX: (805) 275-5144

MECHANICAL PROPERTIES OF LIQUID CRYSTAL POLYMERS

J. Shelley
Phillips Laboratory
OLAC PL/RKCCA
Edwards AFB, CA
Phone: (805) 275-5394
FAX: (805) 275-5527

Challenges...

To Designing with LCPs

- No Established Material Properties Database
- Materials Marketed as Isotropic
- Poor Property Translation

MATERIAL PROPERTIES

Name	Ultimate Tensile Strength (Kpsi)	Tensile Modulus (Mpsi)	Heat Deflection Temperature (°F)
Vectra B230	35.6	5.4	428
Vectra C130	23.5	2.2	464
HX4000	13.0	3.1	504
Xydar G-430	19.8	2.3	592
Granlar	20.0	1.85	609
PPS (Ryton)	12.0	0.63	N/A
BMI	7.7	0.52	N/A
Polypropelene	5.0	0.25	160

Approach

- Determine Suitable Mechanical Properties Test Method
- Test Material Suitability to Propulsion Applications
- Establish Usable Material Properties Database

Test Method Comparison

LCPs

- Neat Resin and Filled Polymers
- Strain Capability 0.5 - 2 %
- Lightly Load

Standard Test Methods:

- ASTM D638
  - Unfilled Polymers
  - Material Strain Capability > 10 %
- ASTM D3039
  - Unidirectional Reinforced Composites
  - Strain Capabilities < 1 %

Test Method Differences

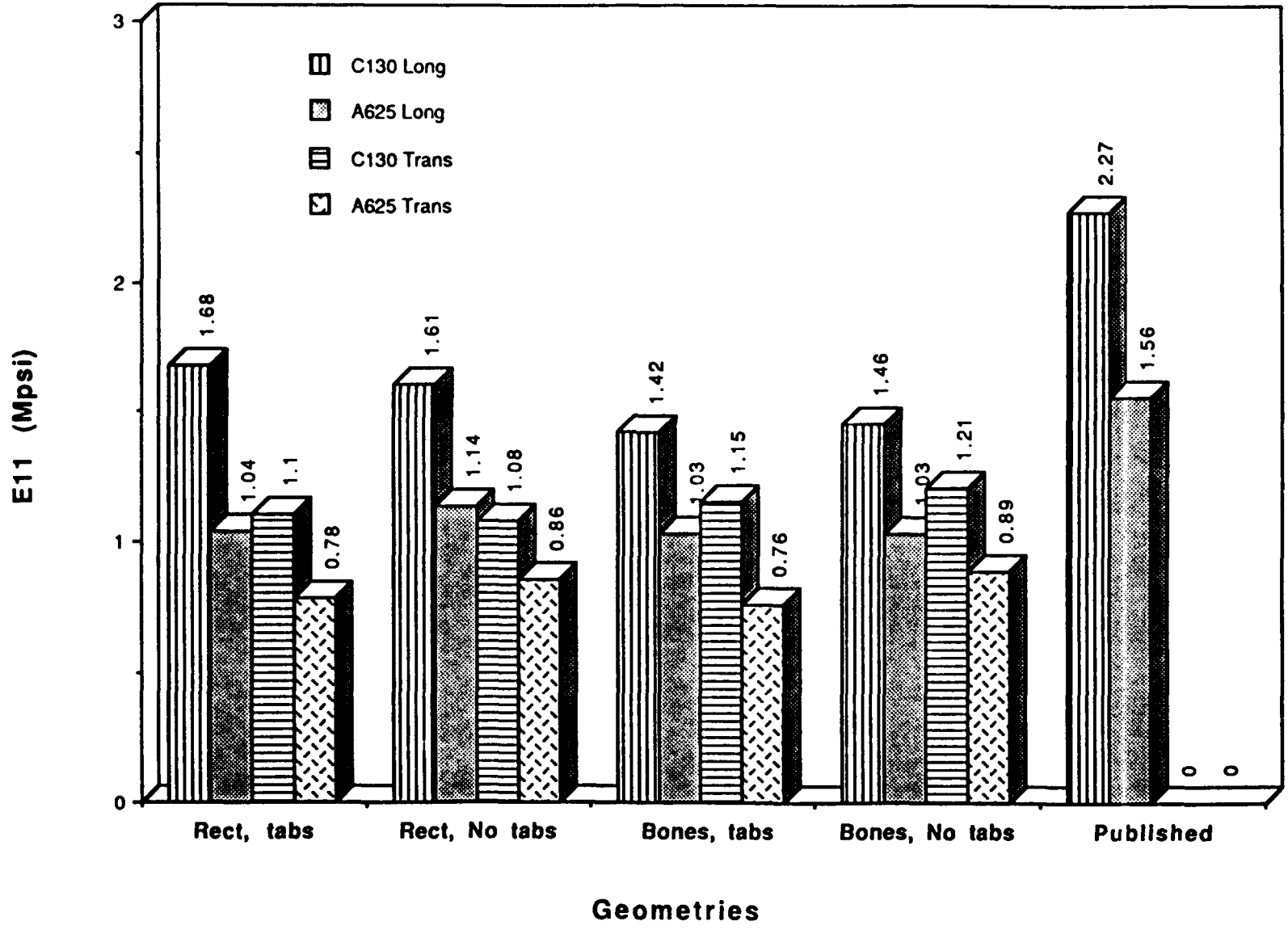
ASTM D638

- "Dog Boned" Specimens
- No Load Tabs
- Smaller Test Specimens

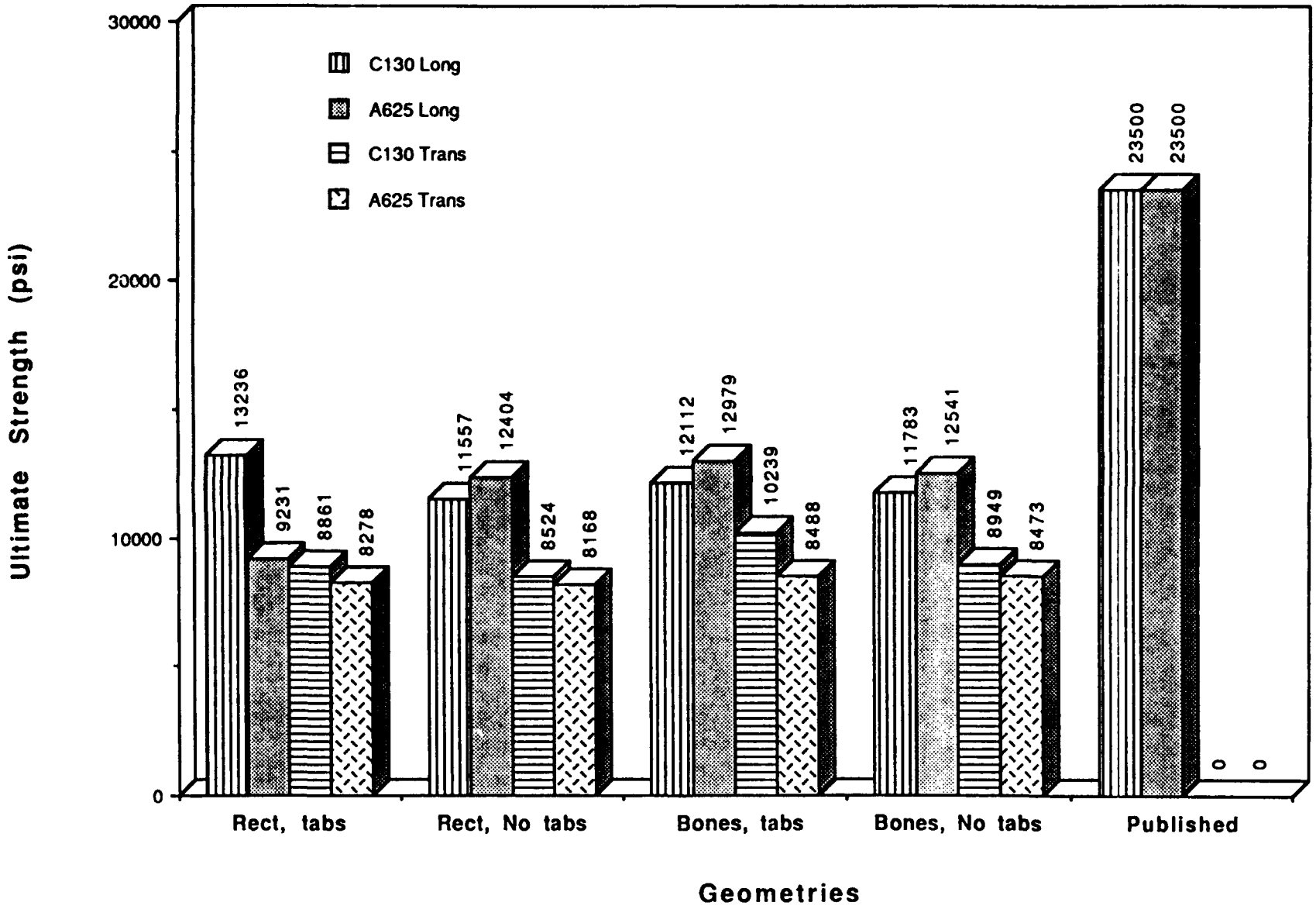
ASTM D3039

- Rectangular Specimens
- Load Tabs
- 12 in Specimens

Longitudinal Modulus Data



Failure Data



Average Tensile Test Data

Material	Longitudinal		Transverse	
	Strength Ksi	Modulus Mpsi	Strength Ksi	Modulus Mpsi
Xydar 500®	23.7	3.9	7.7	1.6
Xydar 300®	14.9	2.9	6.1	0.92
HX-4000®	12.5	1.9	4.9	0.56
Vectra®	11.9	0.77	6.7	0.35
RC 210®	12.1	2.5		

"Skin / Core" Effect

Tensile tests conducted to quantify effect.

- 1/8 in "thin" molded specimens
- 1/4 in "thick" molded specimens
- Core specimens

  (1/4 in thick molded specimenswith 1/16 in thick faces removed)
- Skin specimens

  (1/4 in thick molded specimens milled through leaving 1/16 in thick face)

ASTM D638

- Longintudinal strength and modulus

Skin and Core Effect Data

Specimen	1/8 in "Thin"		1/4 in "Thick"	
Material	Ultimate Strength (Ksi)	Modulus (Mpsi)	Ultimate Strength (Ksi)	Modulus (Mpsi)
Vectra B950	14.32	1.9	17.10	2.49
HX-4000	7.73		7.26	1.64
Xydar SRT-500	13.13	0.84	18.08	1.10
RC210	12.17	0.64	12.83	1.17

Skin and Core Effect Data (cont)

Specimen	Core		Skin	
Material	Ultimate Strength (Ksi)	Modulus (Mpsi)	Ultimate Strength (Ksi)	Modulus (Mpsi)
Vectra B950	14.93	2.54	25.09	2.19
HX-4000	5.54	1.59	11.82	1.69
Xydar SRT-500	15.08	0.97	19.63	1.44
RC210	10.63	2.08	15.49	2.53

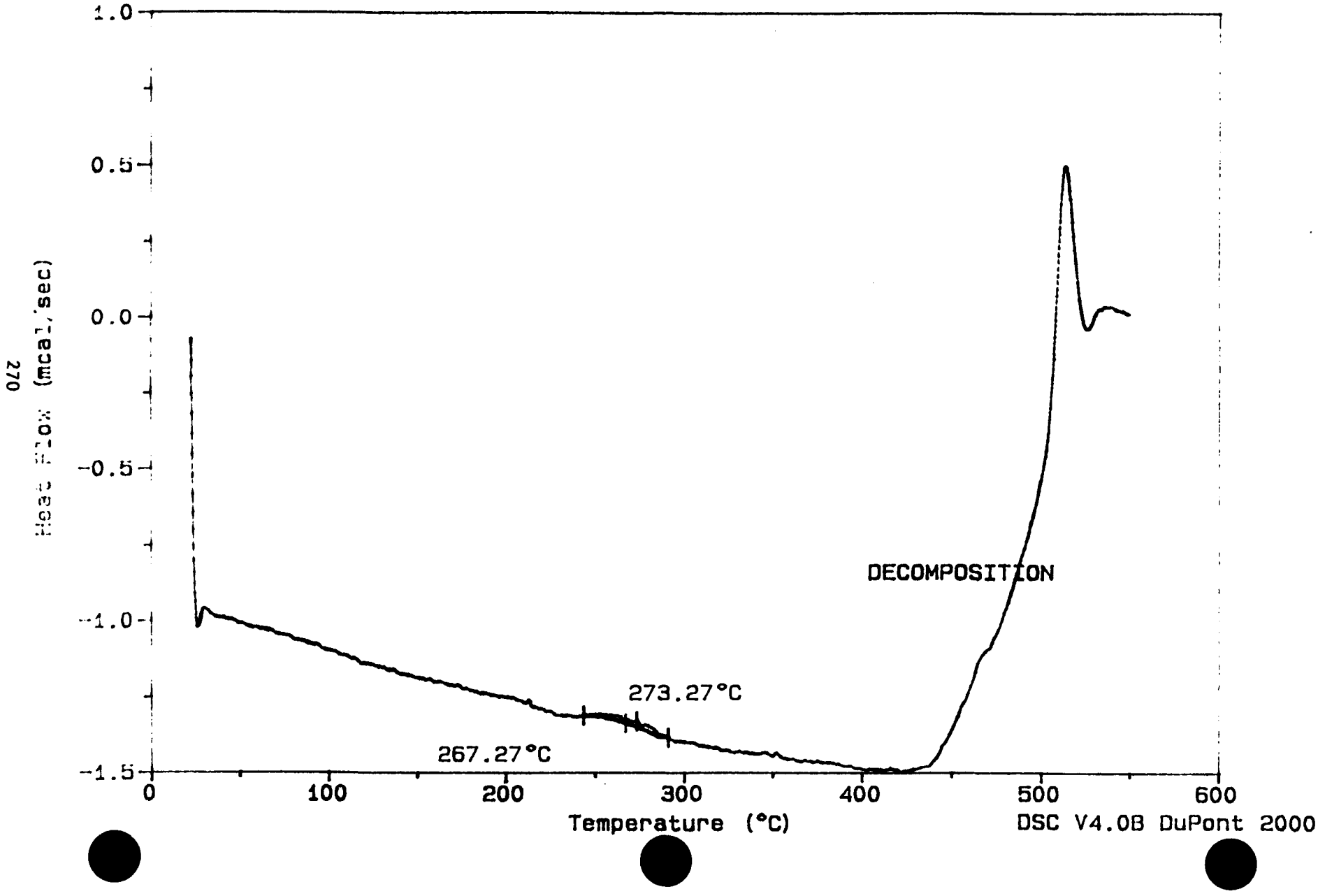
Thermal Analysis in LCP Characterization

Thermal analysis was used to study the effects of annealing on a variety of injection molded HX4000 samples. Results by DSC showed no strong or distinguishing phase transitions occurring in the heat flow curves for any of the HX4000 samples run. Results by the TMA showed that by heating the "annealable" HX4000 for an extended time at a temperature just below its initial melt, an increase in melt temperature then resulted. These same HX4000 samples were then run on the DMA. Tan Delta temperatures and peak shapes were found to be changing to the same extent as the melt temperatures were changing as seen by TMA. As noticed in the DMA results, as the "degree of annealing" increases, the first Tan Delta peak decreases in temperature and becomes more broad while the second Tan Delta peak increases in temperature and becomes sharper. This may be due to some sort of a reaction or break down occurring within the LCP backbone. Another thought is that the two Tan Delta peaks could both be glass transition (Tg) peaks and if true would tend to prove that "ordering" glassy→smectic→nematic phase changes could be occurring during the thermal treatment of the LCP. Future plans are to run the TMA over the same region as the DMA and verifying the Tan Delta peaks as glass transition or not.

Sample: VECTRA A 950
Size: 6.4800 mg
Method: LCP MELT TEMPERATURES
Comment: RATE 10°C/MIN, NITROGEN PURGE 50 ML/MIN, AL PANS

DSC

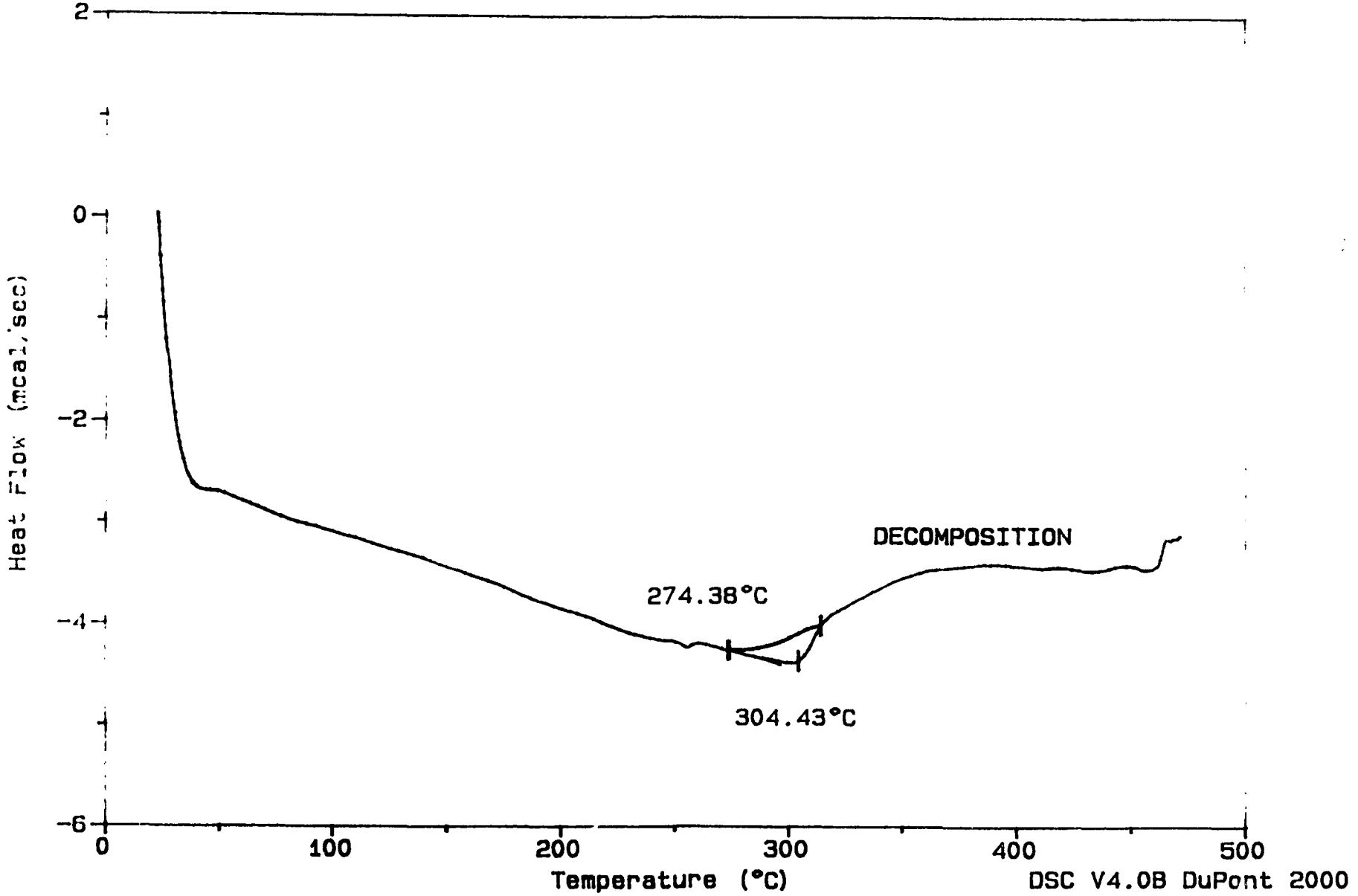
File: A:DSCJOHNR.07
Operator: PAUL JONES
Run Date: 3-Apr-91 15:17



Sample: HX4000
Size: 9.8800 mg
Method: LCP MELT TEMPERATURES
Comment: RATE 30°C/MIN, NITROGEN PURGE 50 ML/MIN, AL PANS

DSC

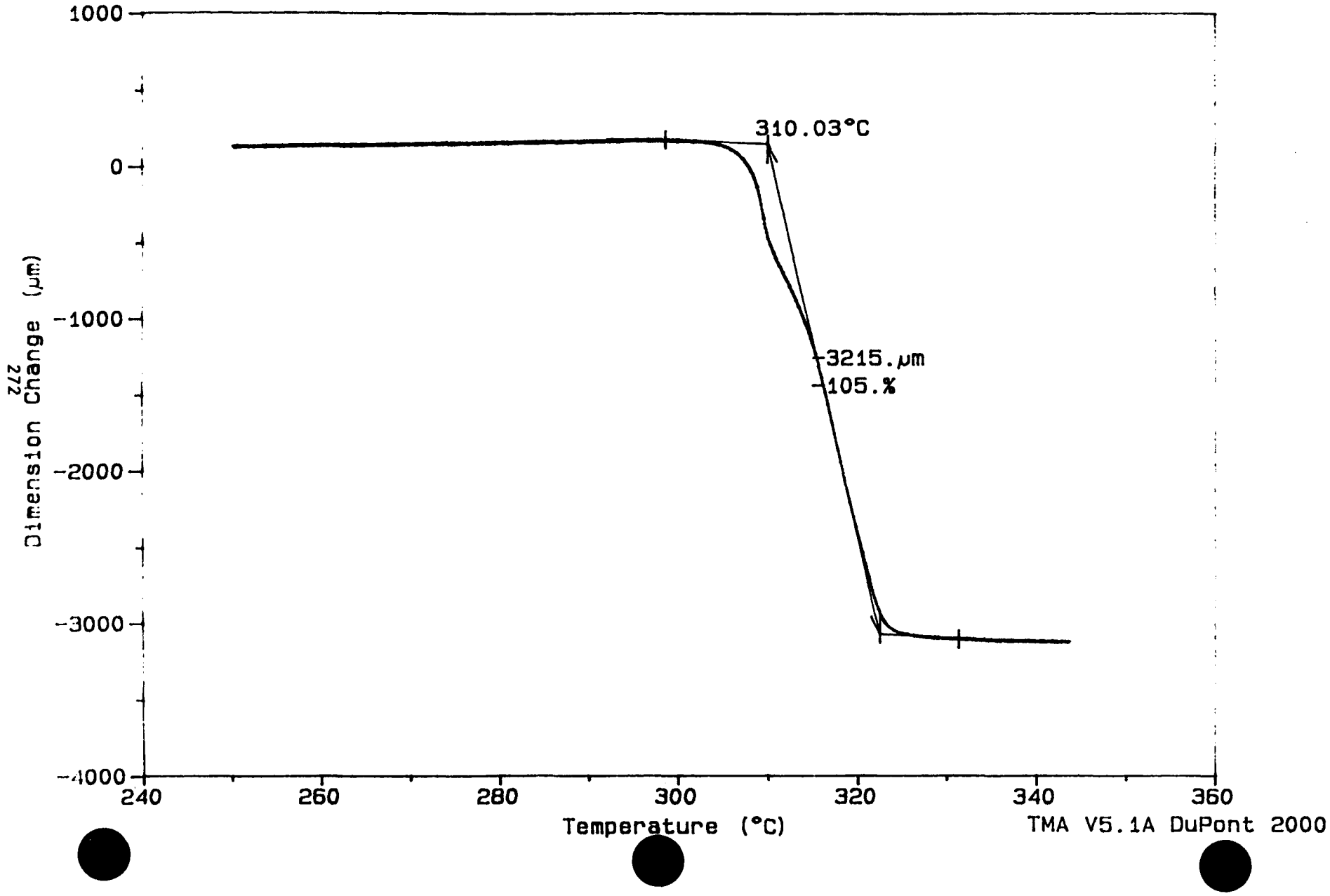
File: A:DSCJOHNR.09
Operator: PAUL JONES
Run Date: 4-Apr-91 07:37



Sample: HX 4000 UNANNEALED
Size: 3.0500 mm
Method: TMA ON LCP
Comment: 3.0°C/MIN. HELIUM PURGE 40 ML/MIN, 10 GRAMS WEIGHT USED

TMA

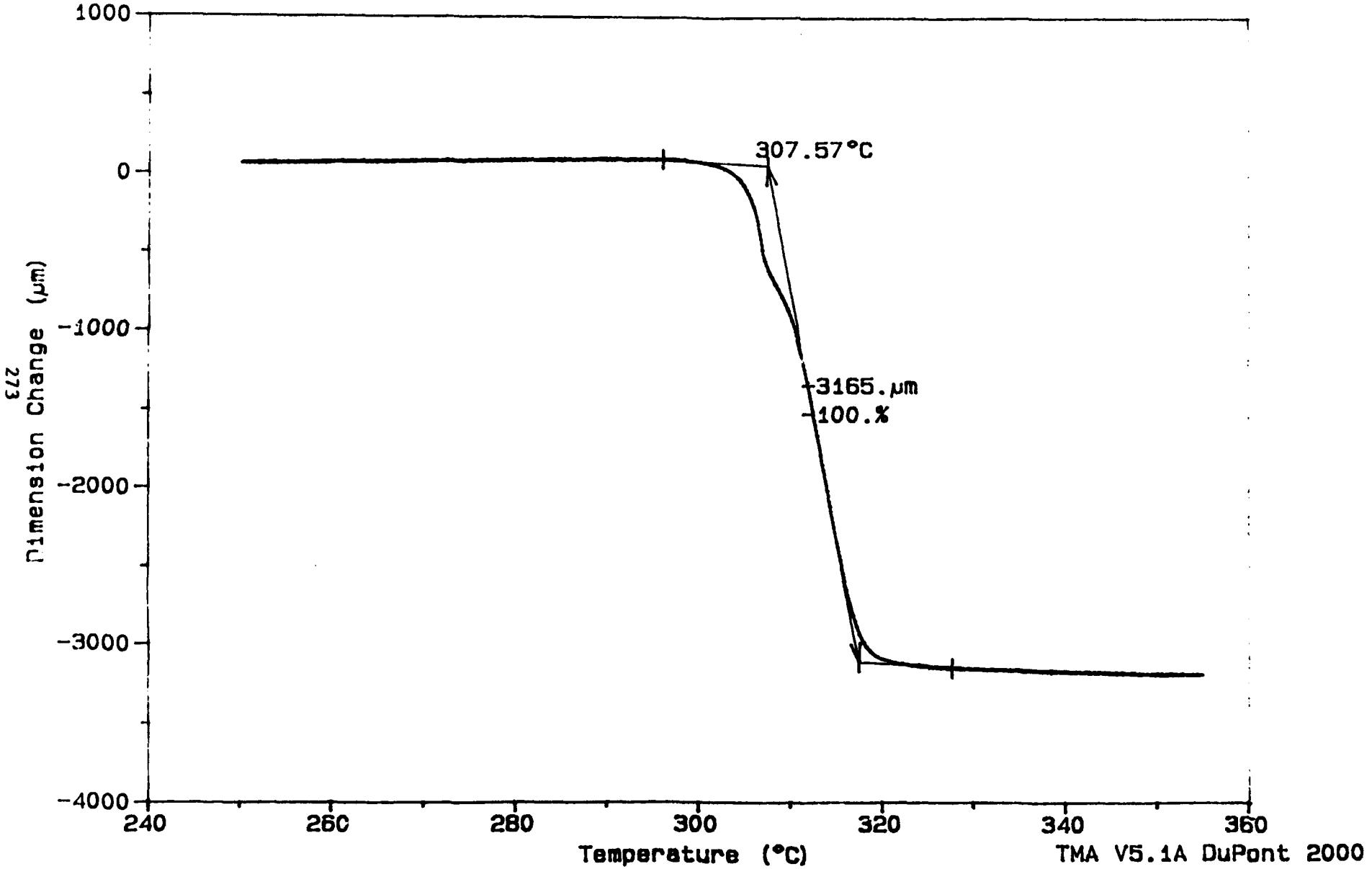
File: A:TMAJOHN.05
Operator: PAUL JONES
Run Date: 8-Aug-91 13:17



Sample: HX 4000 204°C 6.5 HOURS
Size: 3.1590 mm
Method: TMA ON LCP
Comment: 3.0°C/MIN. HELIUM PURGE 40 ML/MIN, 10 GRAMS WEIGHT USED

TMA

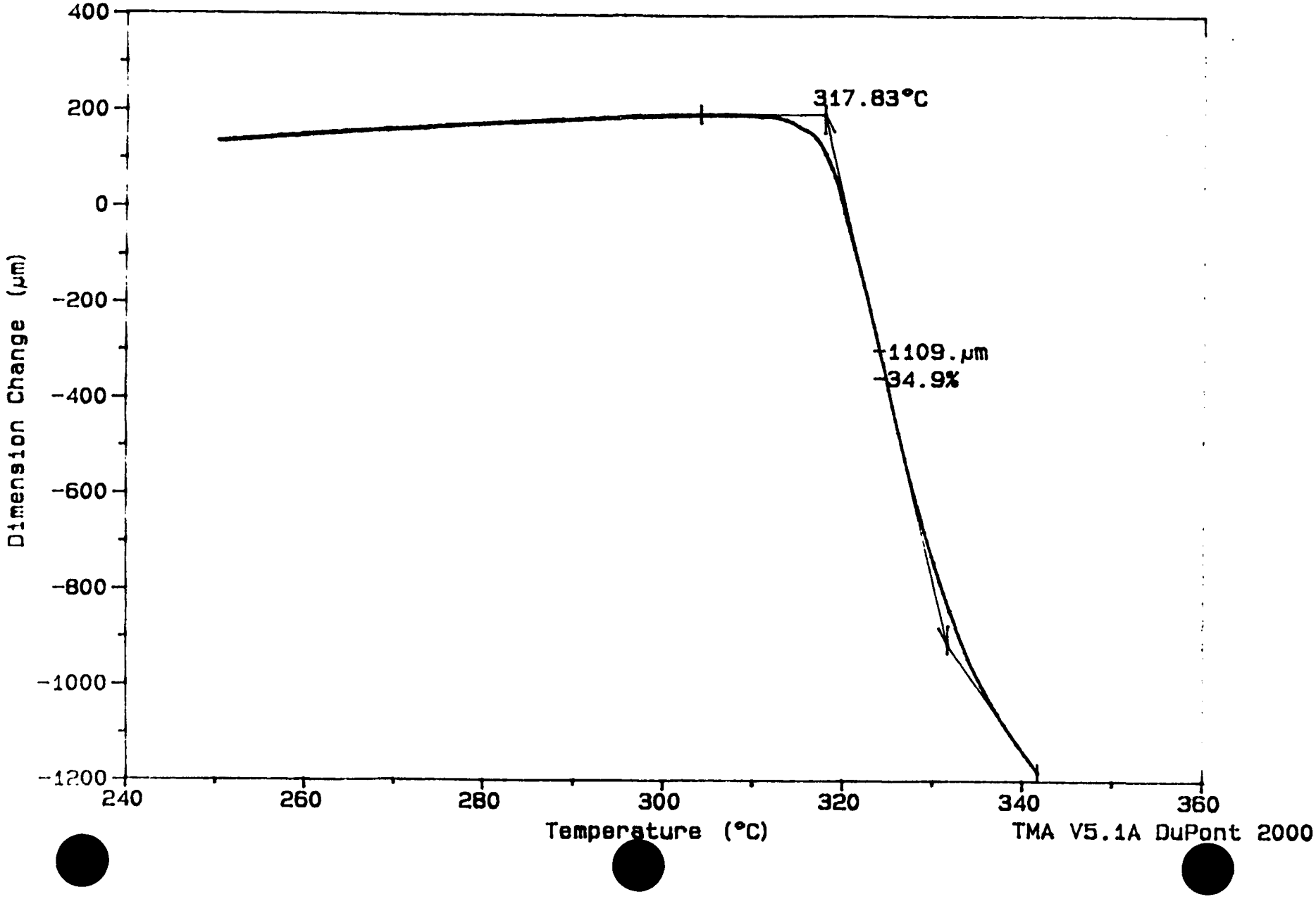
File: A:TMAJOHN.02
Operator: PAUL JONES
Run Date: 8-Aug-91 10:56



Sample: HX 4000 300°C 3.6 HOURS
Size: 3.1770 mm
Method: TMA ON LCP
Comment: 3.0°C/MIN. HELIUM PURGE 40 ML/MIN, 10 GRAMS WEIGHT USED

TMA

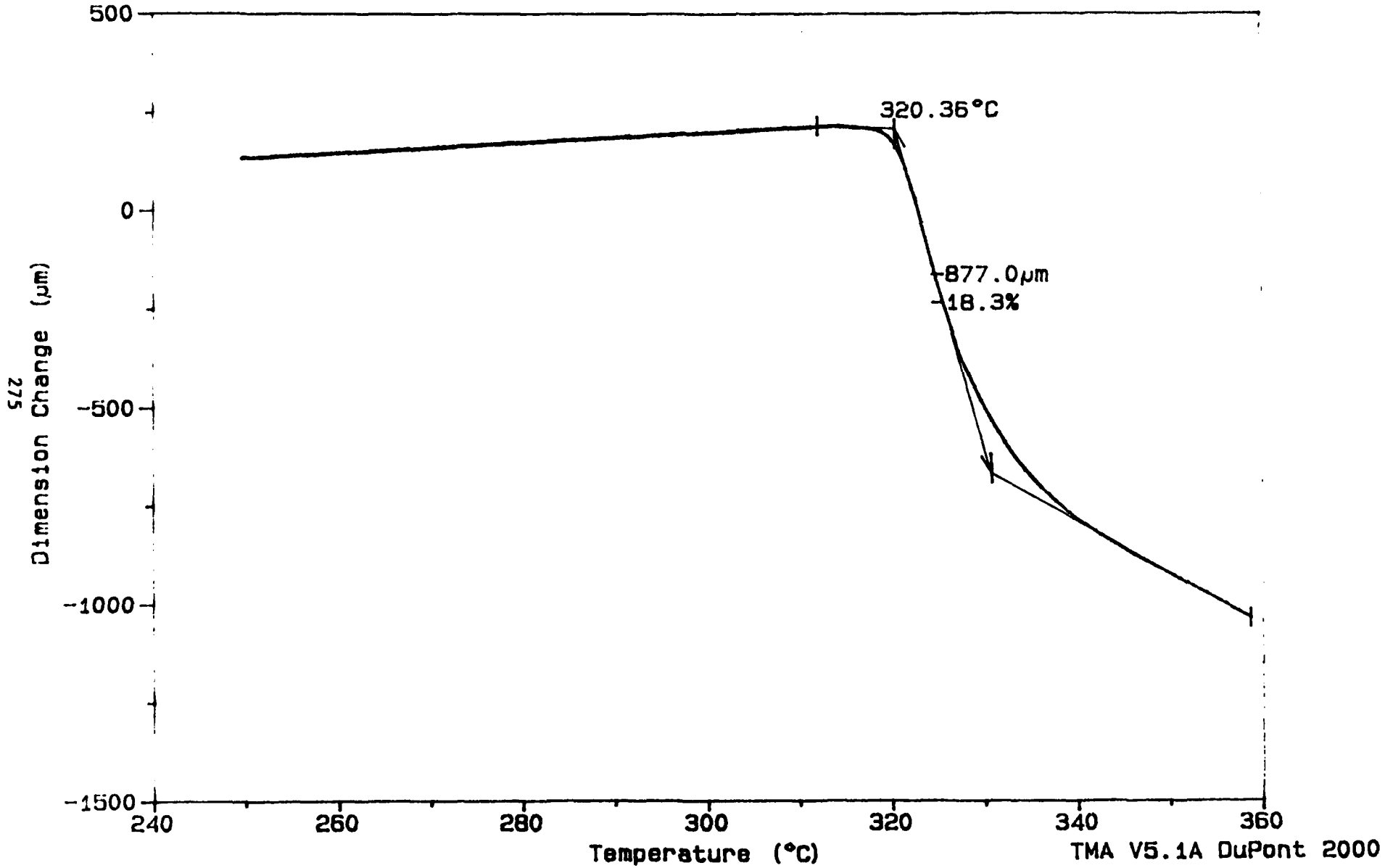
File: A:TMAJOHN.04
Operator: PAUL JONES
Run Date: 8-Aug-91 12:33



Sample: HX 4000 ANNEALED 302°C 24 HOURS
Size: 4.7900 mm
Method: TMA ON LCP
Comment: 3.0°C/MIN. HELIUM PURGE 40 ML/MIN, 10 GRAMS WEIGHT USED

TMA

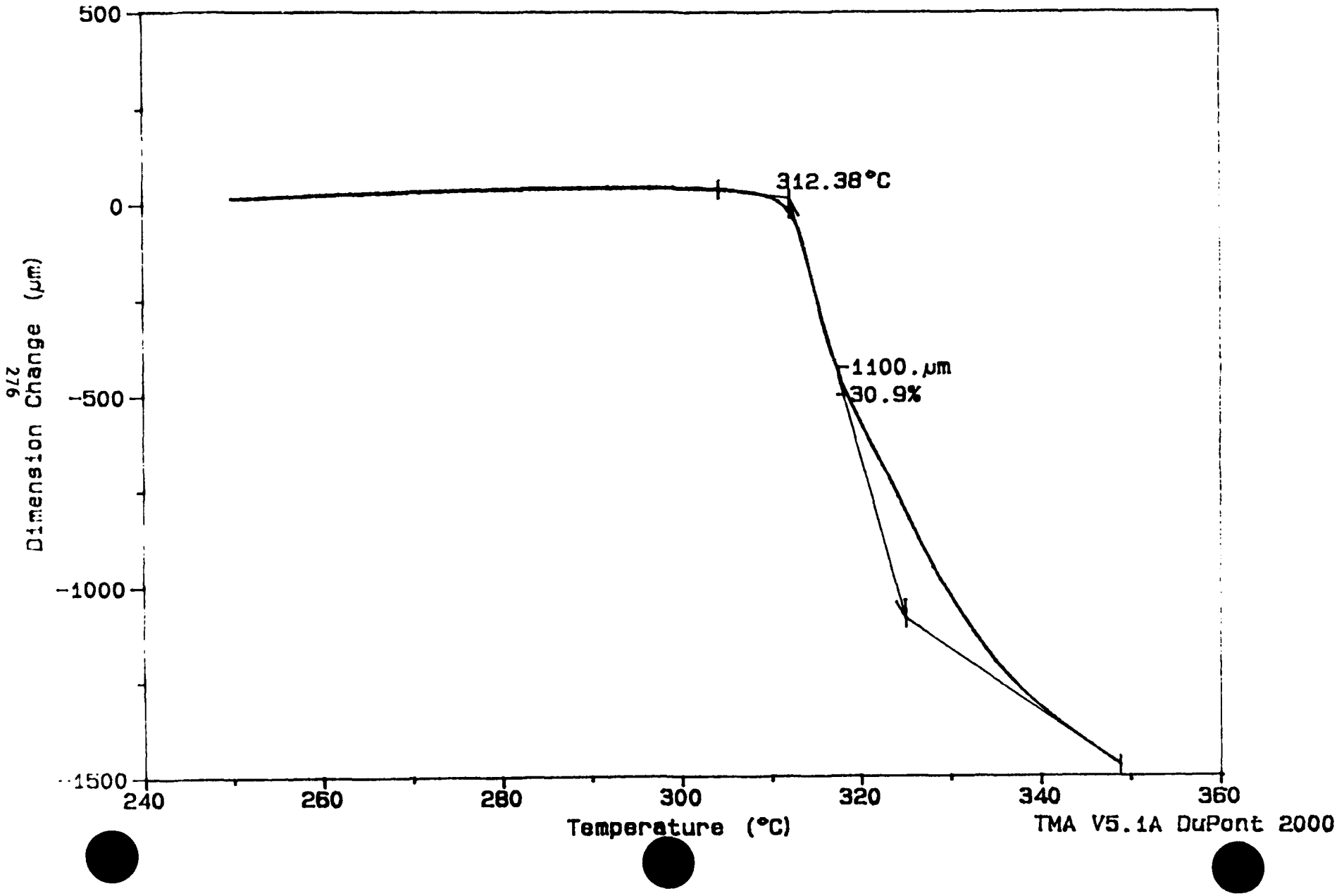
File: A:TMAJOHN.09
Operator: PAUL JONES
Run Date: 16-Aug-91 12:29



Sample: HX 4000 304°C 1.9 HOURS
Size: 3.5620 mm
Method: TMA ON LCP
Comment: 3.0°C/MIN. HELIUM PURGE 40 ML/MIN, 10 GRAMS WEIGHT USED

TMA

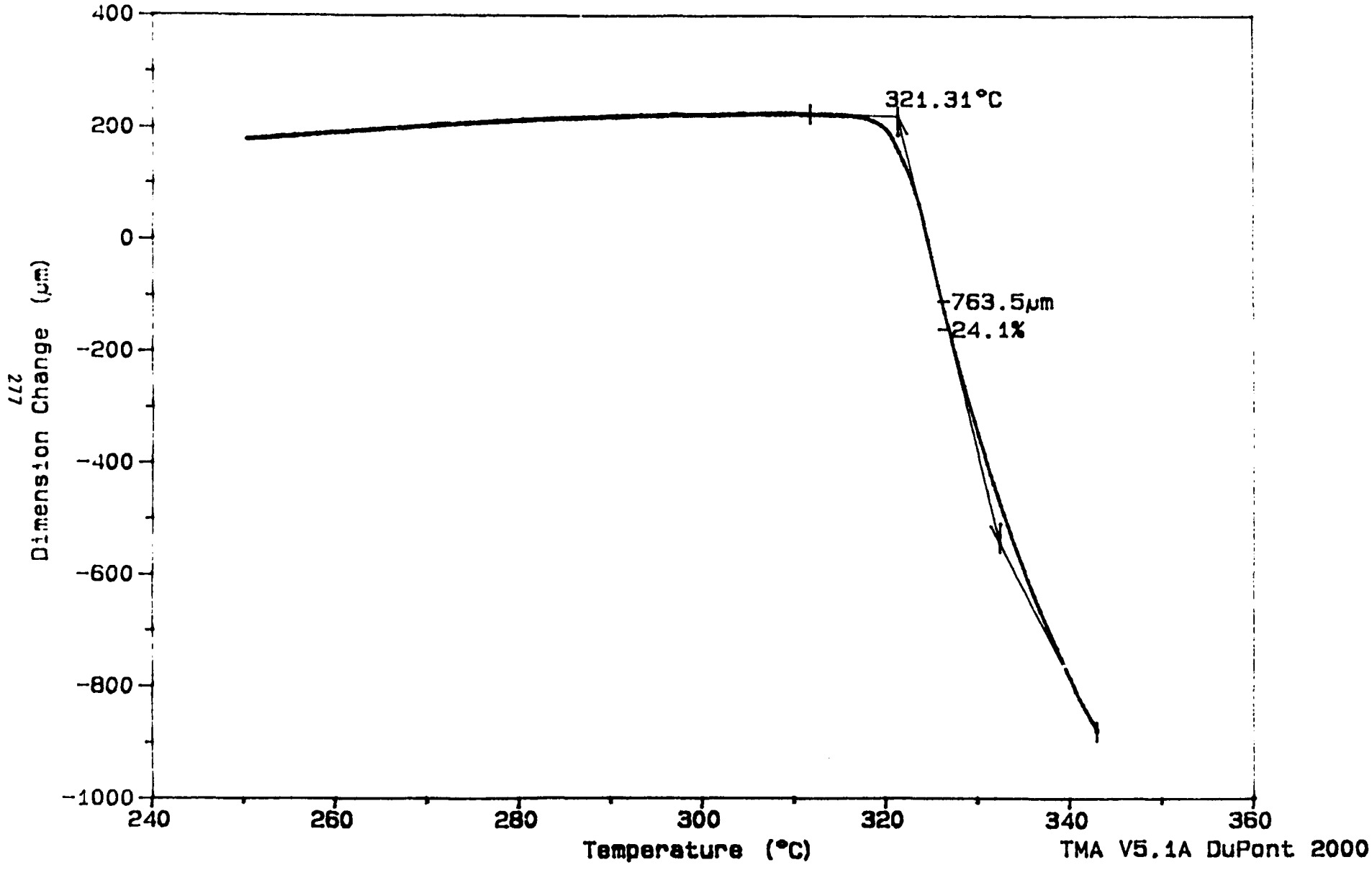
File: A:TMAJOHN.01
Operator: PAUL JONES
Run Date: 8-Aug-91 10:05



Sample: HX 4000 320°C 1.9 HOURS
Size: 3.1690 mm
Method: TMA ON LCP
Comment: 3.0°C/MIN. HELIUM PURGE 40 ML/MIN, 10 GRAMS WEIGHT USED

TMA

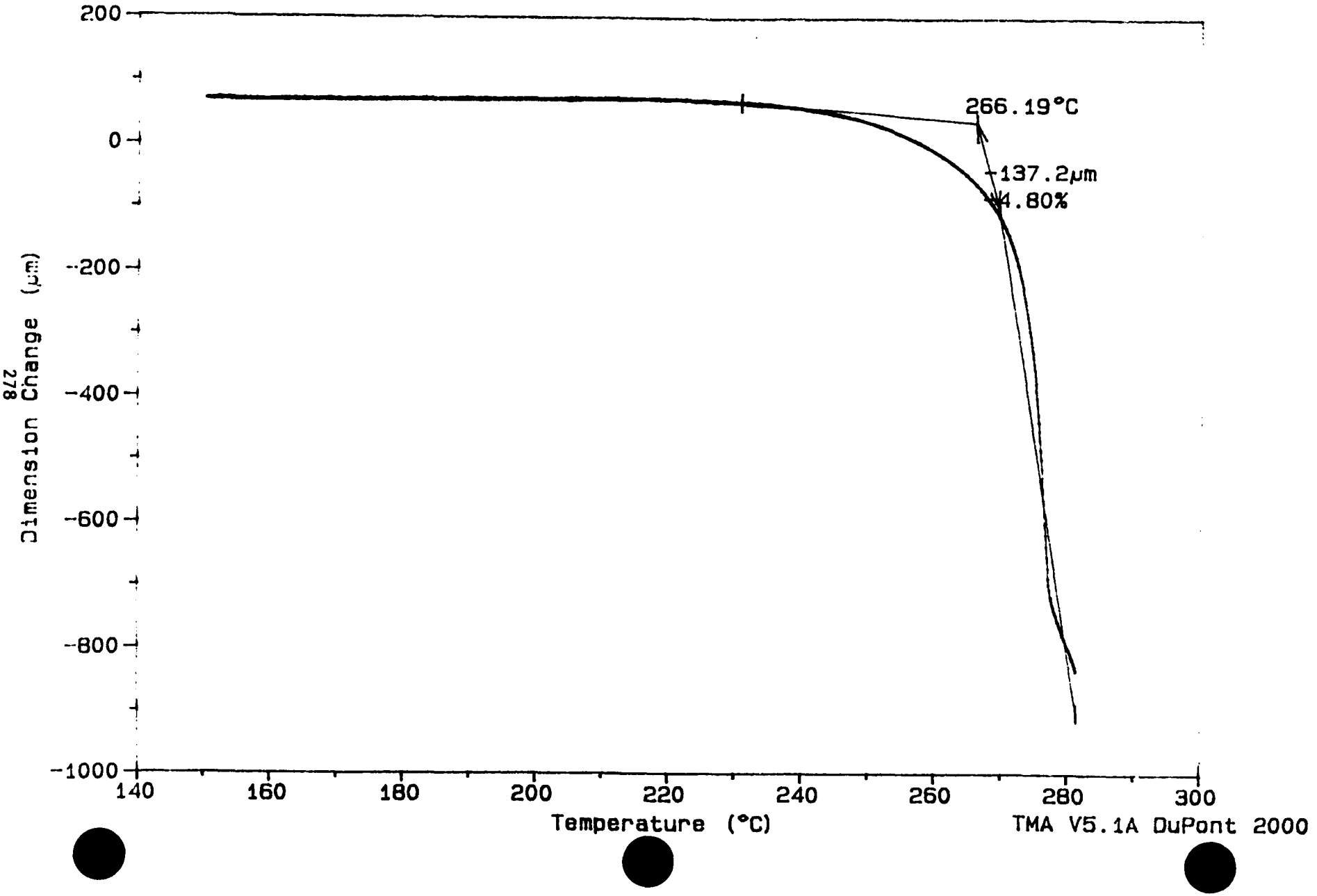
File: A:TMAJOHN.03
Operator: PAUL JONES
Run Date: 8-Aug-91 11:50



Sample: LCP PEHQ/PHQ/TCL SYN 16
Size: 2.8610 mm
Method: TMA ON LCP
Comment: 3.0°C/MIN. HELIUM PURGE 40 ML/MIN, 10 GRAMS WEIGHT USED

TMA

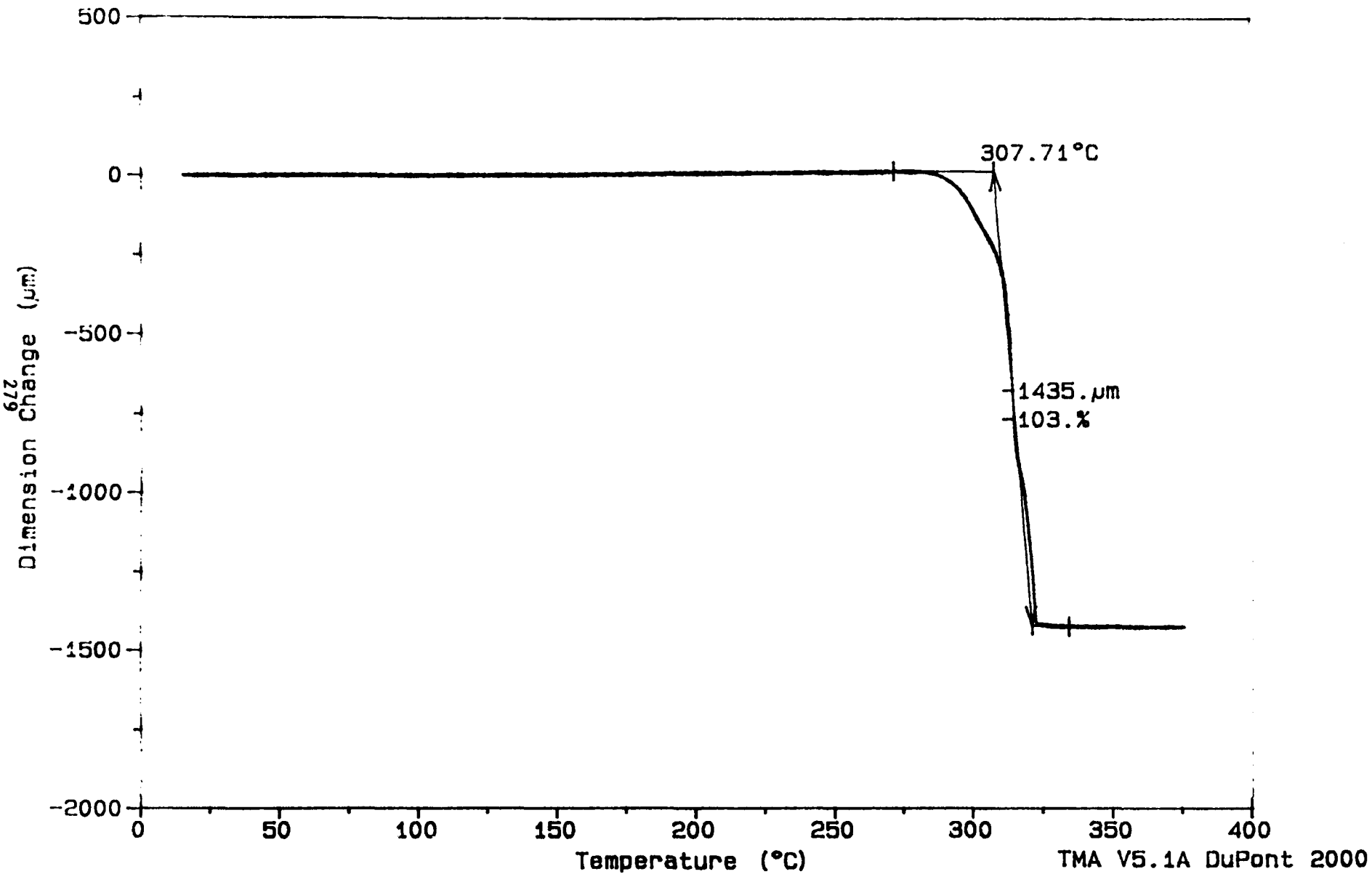
File: A:TMAJOHNR.11
Operator: PAUL JONES
Run Date: 27-Aug-91 14:14



Sample: SYN 16 LCP PEHQ/PHQ/TCL 60 HR AN
Size: 1.3900 mm
Method: TMA ON LCP
Comment: 3°C/MIN, HELIUM PURGE 40 ML/MIN, 10 GRAM WEIGHT USED

TMA

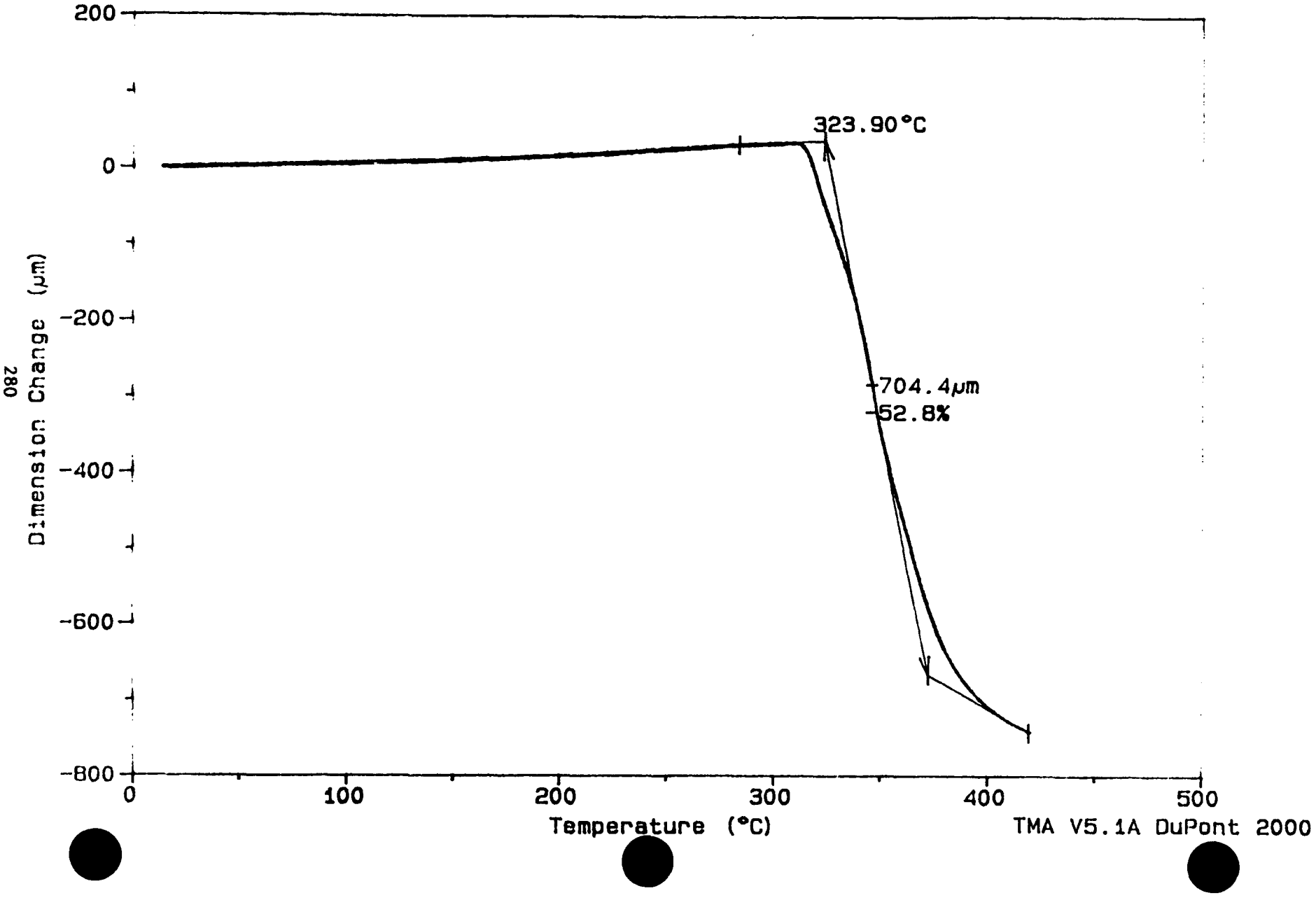
File: C:TMAJOHNR.16
Operator: PAUL JONES
Run Date: 10-Feb-92 09:12



Sample: SYN 16 LCP PEHQ/PHQ/TCL 44 HR AN
Size: 1.3350 mm
Method: TMA ON LCP
Comment: 3°C/MIN, HELIUM PURGE 40 ML/MIN, 10 GRAM WEIGHT USED

TMA

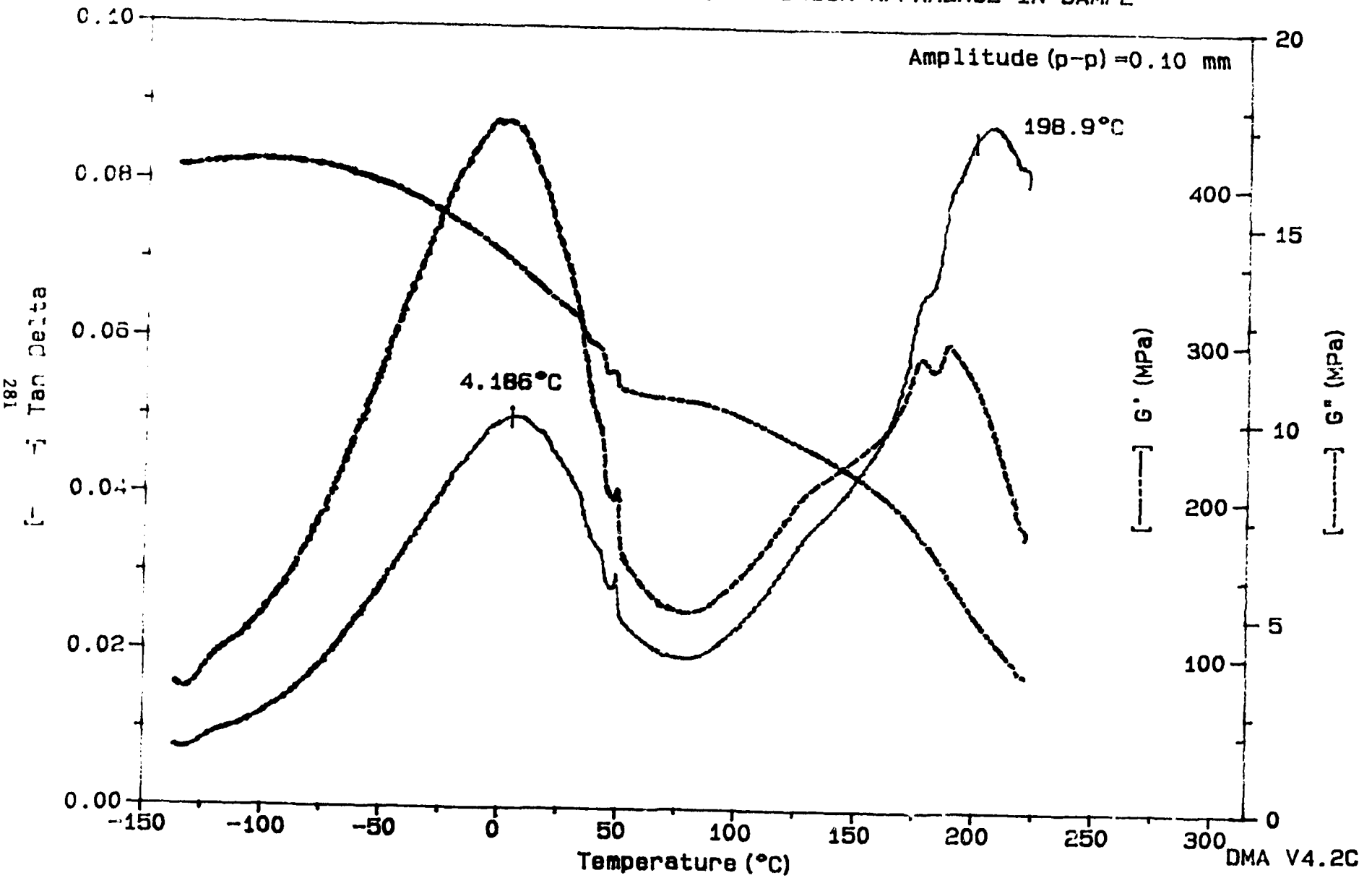
File: C:TMAJOHNR.17
Operator: PAUL JONES
Run Date: 14-Feb-92 07:30



Sample : HX4000 UNANNEALED
Size : 34.3000 x 3.0000 x 12.8000 mm
Method : DMA LCP
Comment: RATE 3.0°C/MIN, NITROGEN ATMOSPHERE, SANDWICH APPARENCE IN SAMPL

DMA

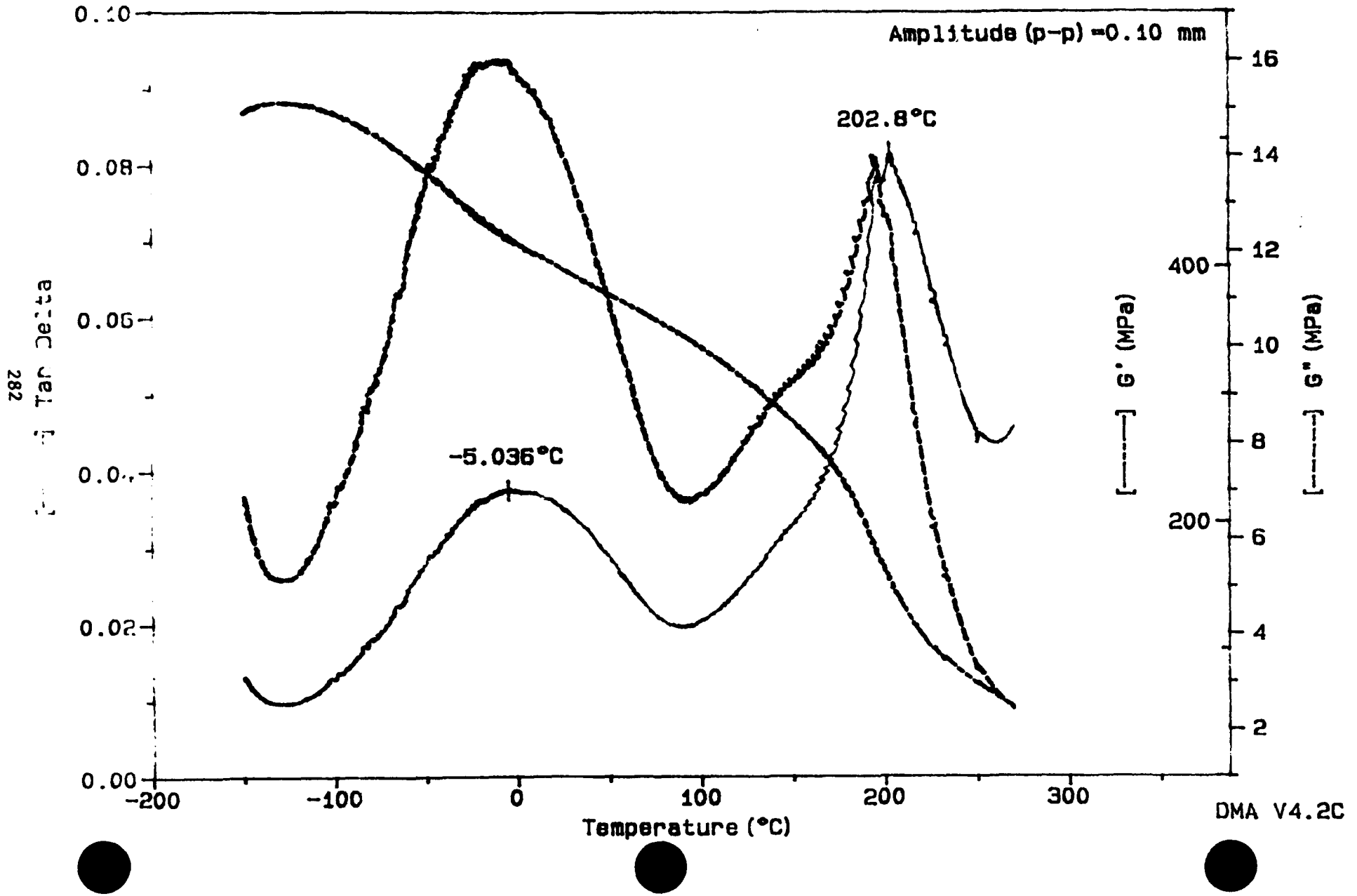
File : A:DMALCP.17
Operator: PAUL JONES
Run Date: 30-Jul-91 12:22



Sample : HX 4000 204°C 6.5 HOURS
Size : 34.3000 x 3.1000 x 12.7000 mm
Method : DMA LCP
Comment: RATE 3.0°C/MIN, NITROGEN ATMOSPHERE, SANDWICH APPEARENCE IN SAMP

DMA

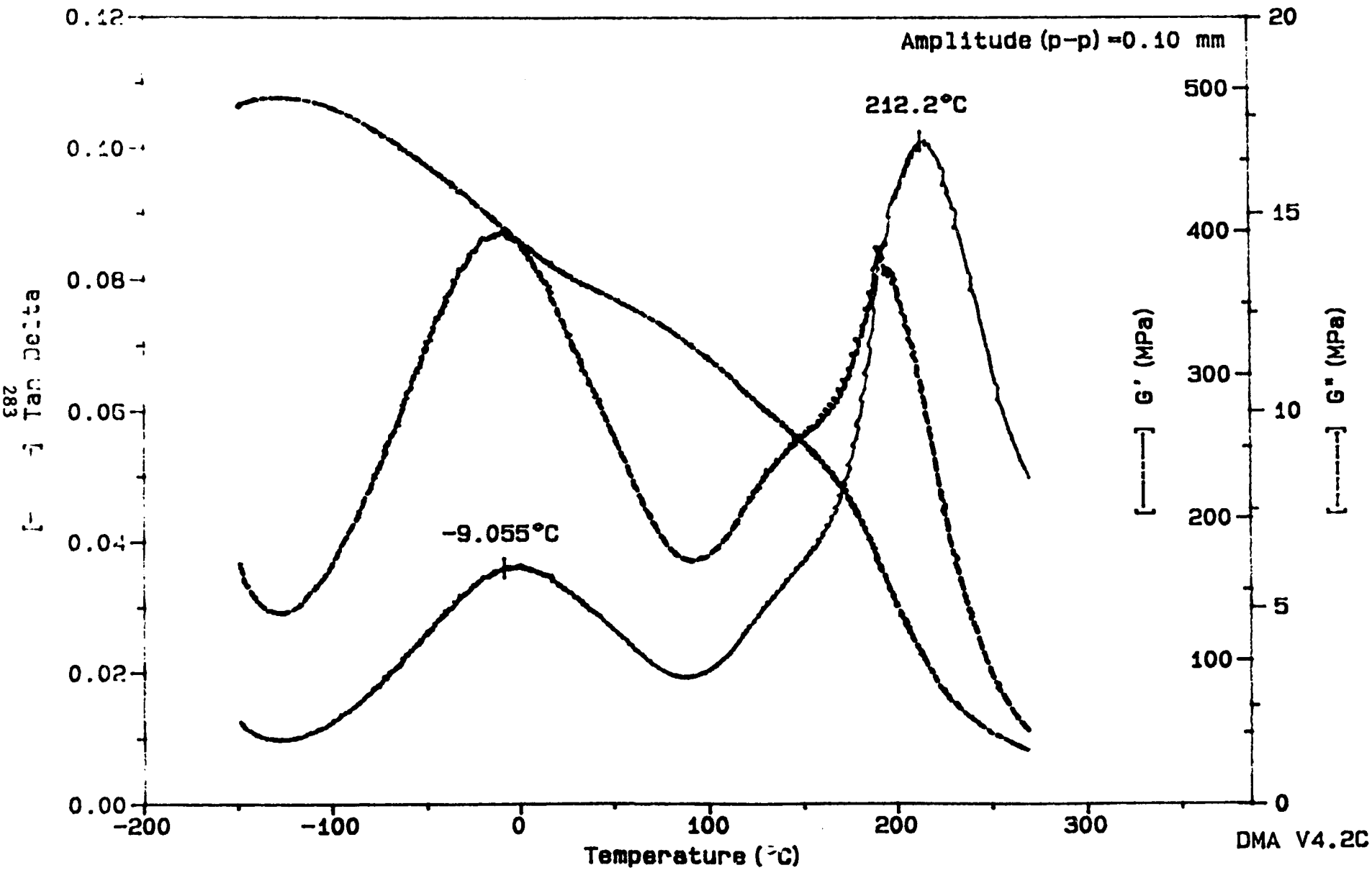
File : A:DMALCP.21
Operator: PAUL JONES
Run Date: 1-Aug-91 12:58



Sample : HX 4000 300°C 3.6 HOURS
Size : 34.3500 x 3.1500 x 12.9500 mm
Method : DMA LCP
Comment: RATE 3.0°C/MIN, NITROGEN ATMOSPHERE, SANDWICH APPEARENCE IN SAMP

DMA

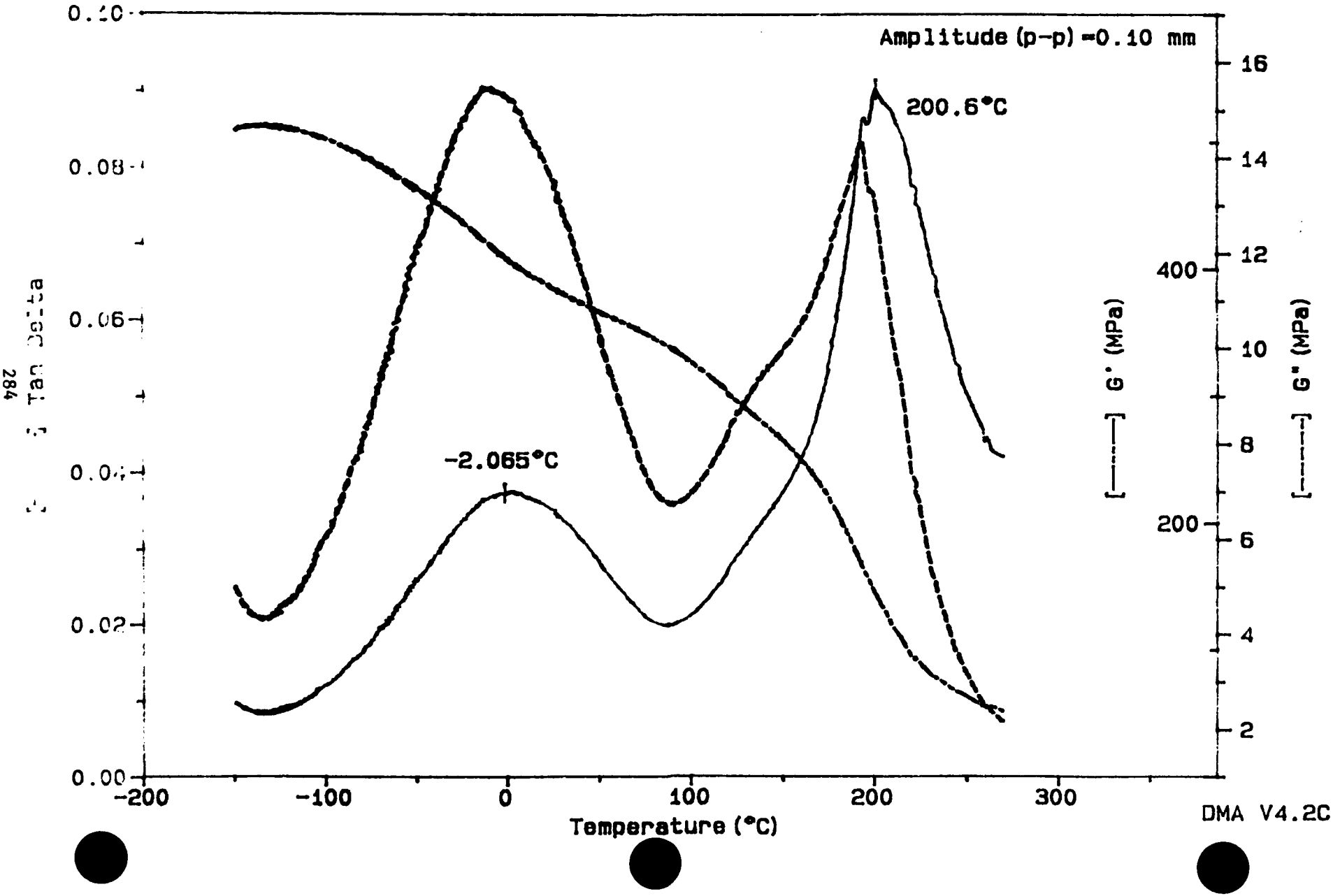
File : A:DMALCP.18
Operator: PAUL JONES
Run Date: 31-Jul-91 13:14



Sample : HX 4000 304°C 1.9 HOURS
Size : 34.2500 x 3.1500 x 12.9500 mm
Method : DMA LCP
Comment: RATE 3.0°C/MIN, NITROGEN ATMOSPHERE, SANDWICH APPEARENCE IN SAMP

DMA

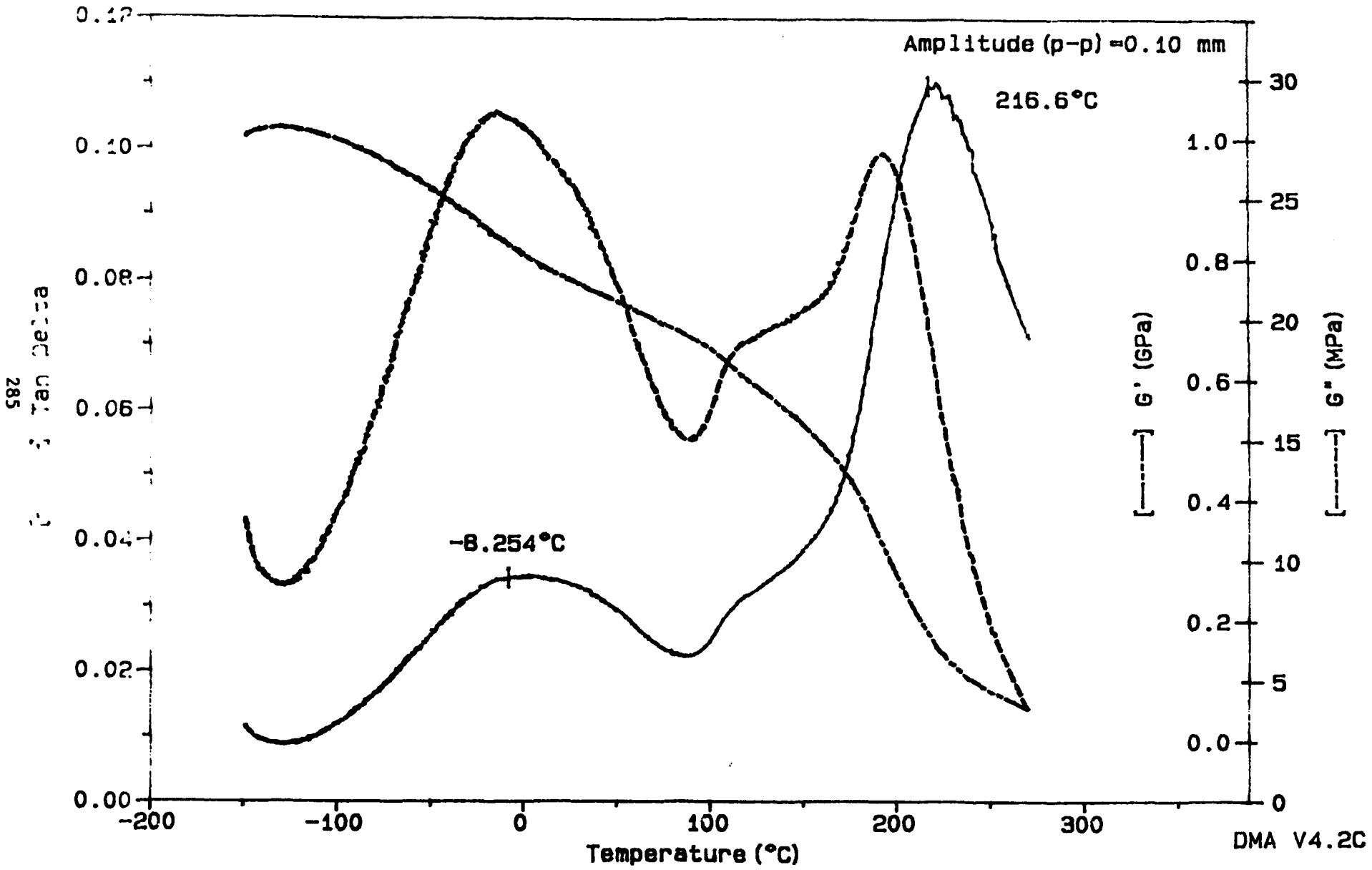
File : A:DMALCP.20
Operator: PAUL JONES
Run Date: 1-Aug-91 08:36



Sample : HX 4000 320°C 1.9 HOURS
Size : 34.3000 x 3.4500 x 7.0000 mm
Method : DMA LCP
Comment: RATE 3.0°C/MIN, NITROGEN ATMOSPHERE, SAMPLE HAD TO BE CUT IN HALF

DMA

File : A:DSCLCP.22
Operator: PAUL JONES
Run Date: 2-Aug-91 08:15



X-RAY/NEUTRON REDUCTION

S. D. Osborn
UDRI, OLAC PL/RKCP

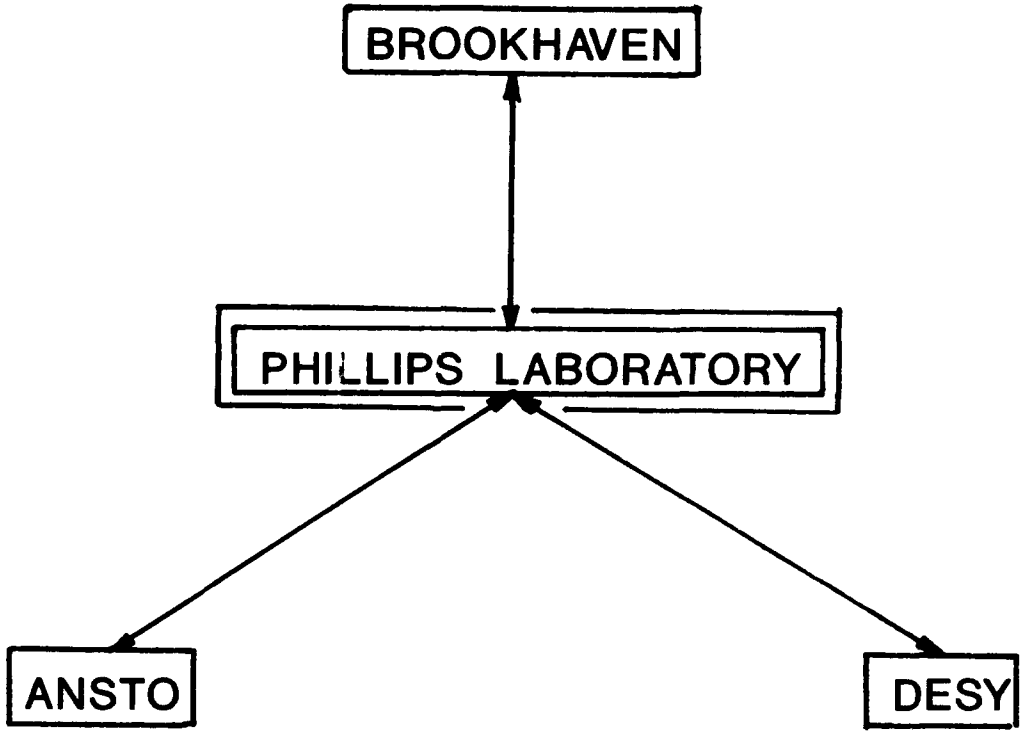
The task objective is to investigate advanced propulsion materials for solid, liquid and next-generation space flight systems. The scope is the support of the Advanced Polymer Components and NEMESIS initiatives. The technical requirements of this task involve the development of algorithms to reduce synchrotron spectroscopy data.

This paper will report on the investigation of the state of the existing analysis tools and techniques. It will include a discussion of the hardware and software used by members of the research team. Platforms will be discussed incorporating these resources to improve the data analysis. This paper also presents an overview of our international collaboration, specifically regarding synchrotron and neutron research. Finally, steps involved in EXAFS data reduction are reviewed in order to give an appreciation of this highly complex and iterative process.

X-RAY AND NEUTRON DATA REDUCTION

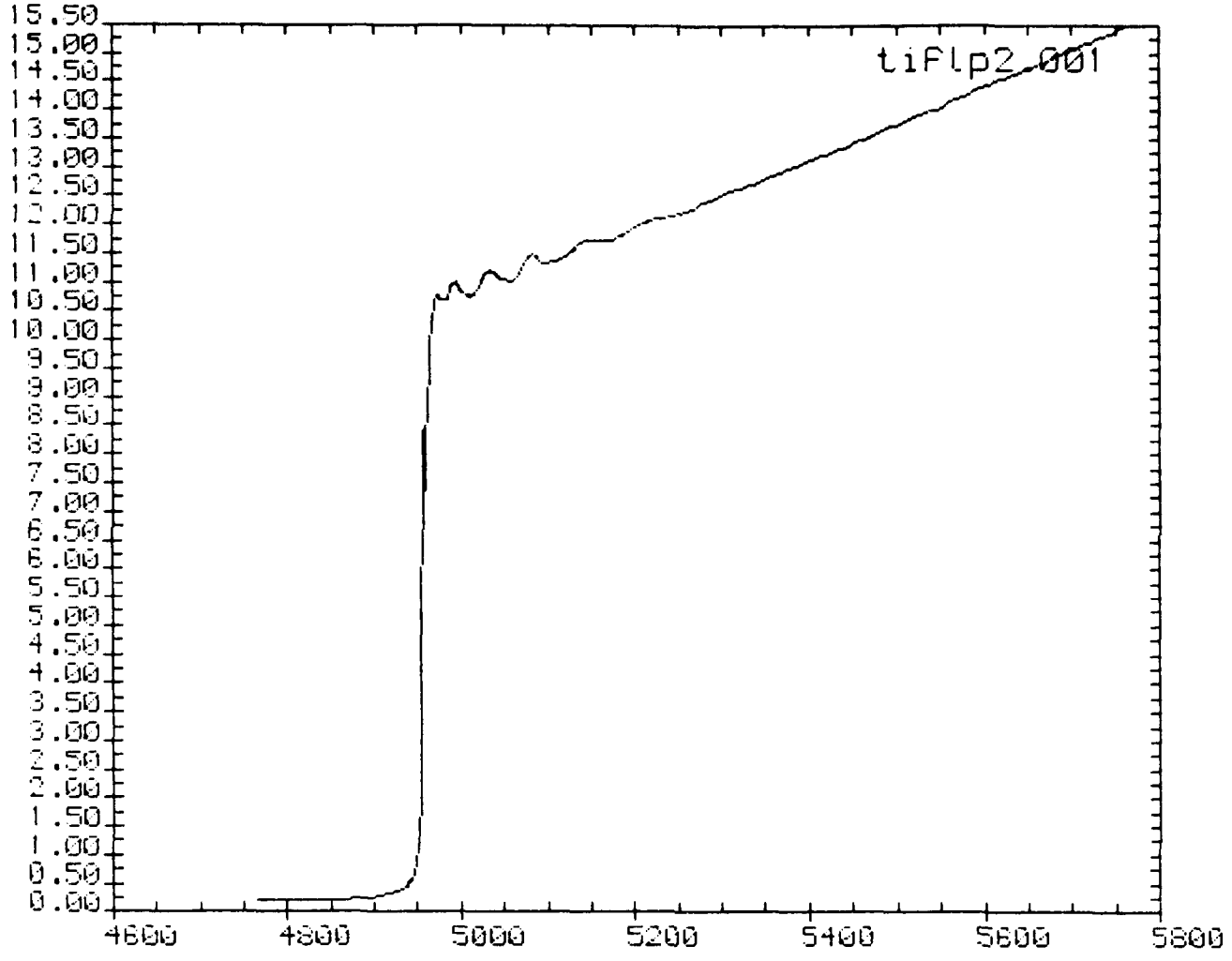
TASK #1

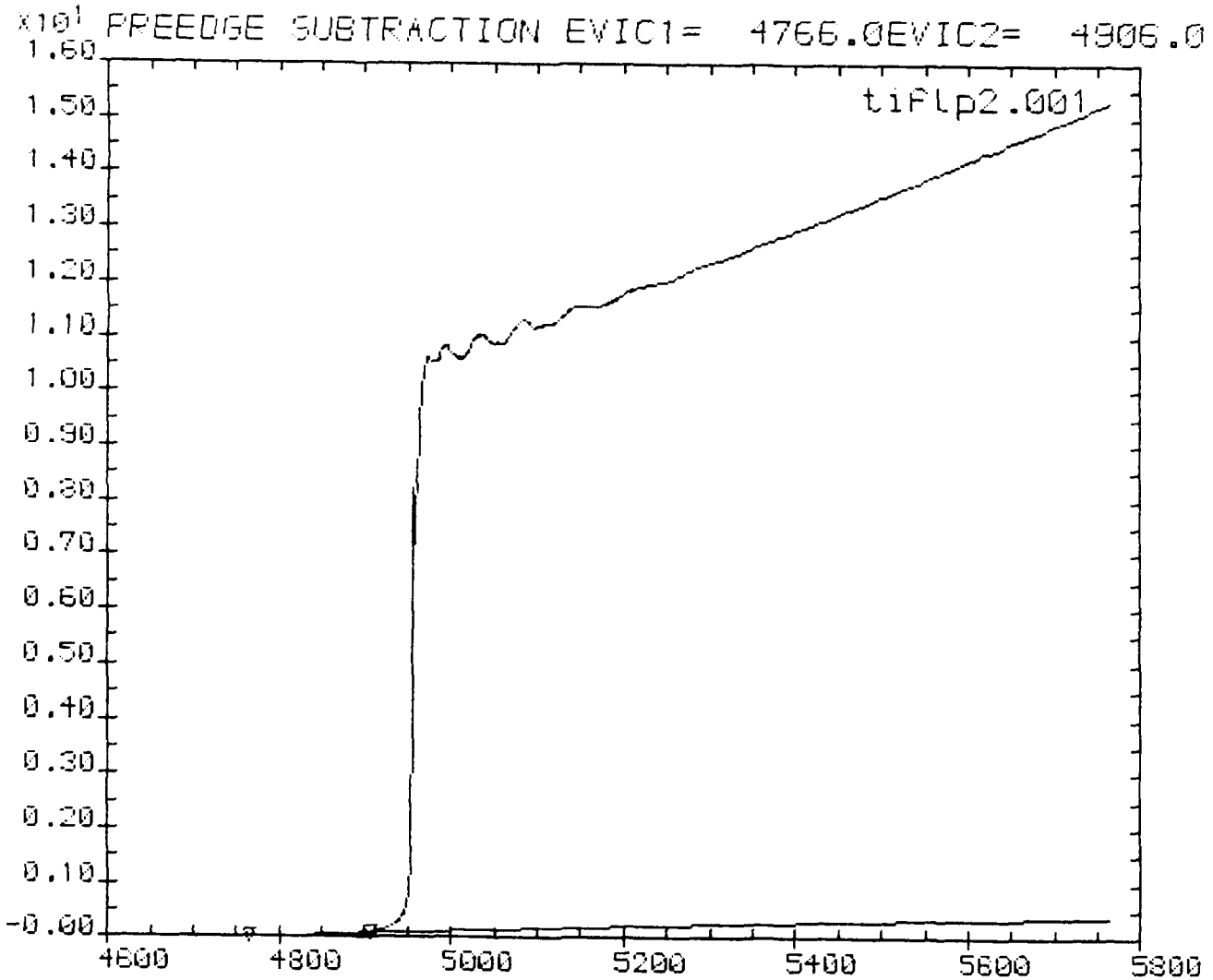
Stephen D. Osborn
Phillips Laboratory
Edwards Air Force Base, CA

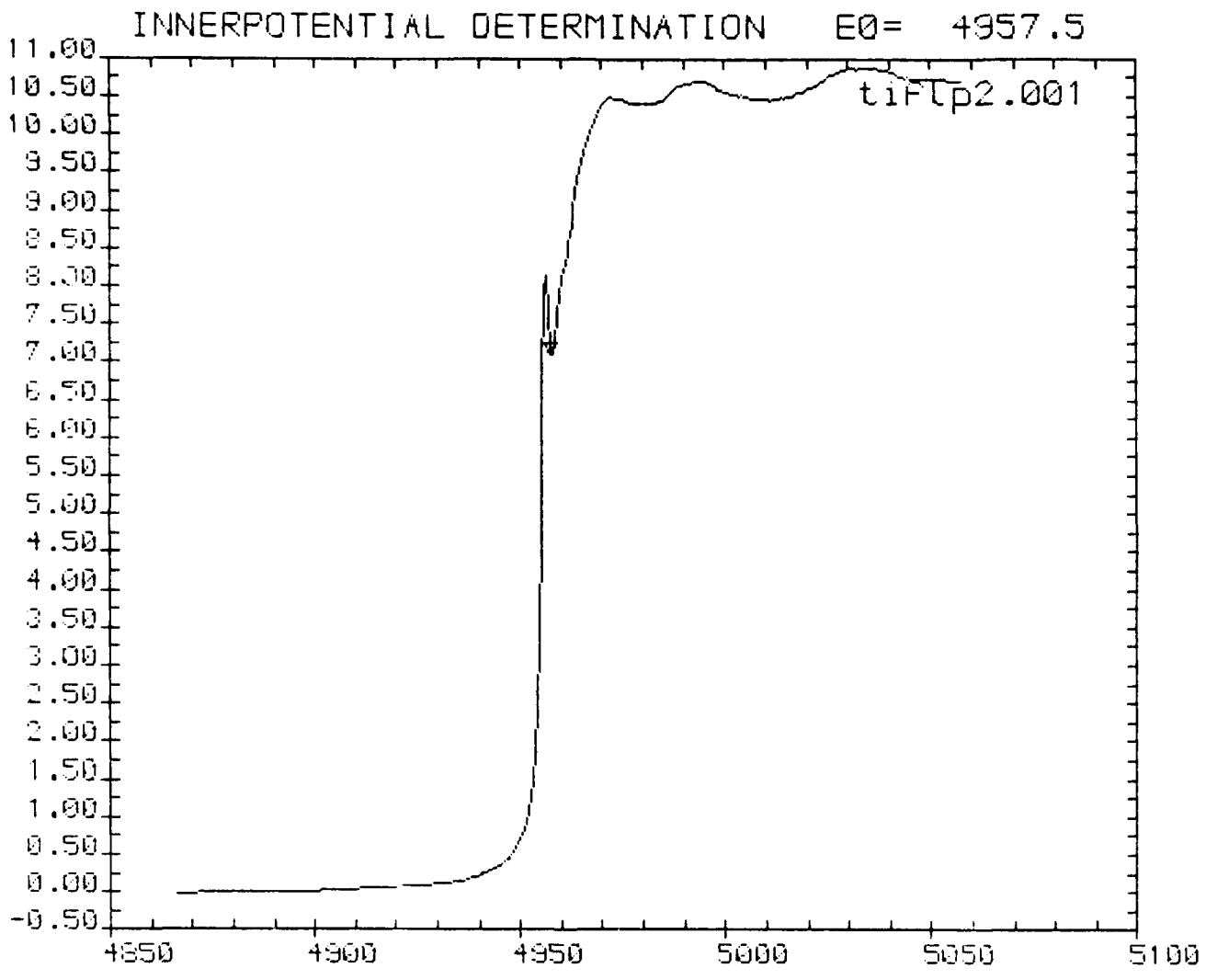

BROOKHAVEN
PHILLIPS LABORATORY
ANSTO
DESY

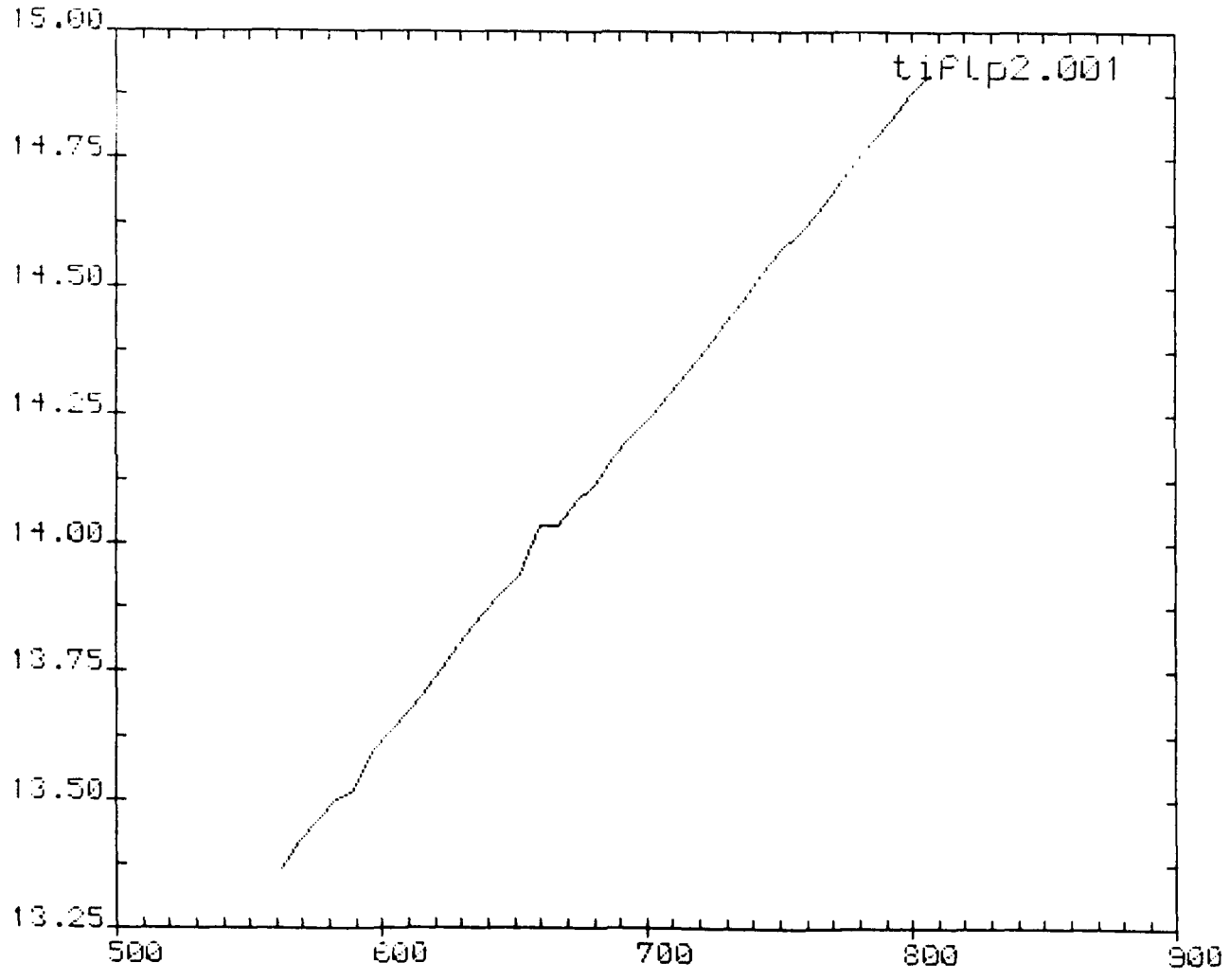
EXAFS DATA REDUCTION STEPS

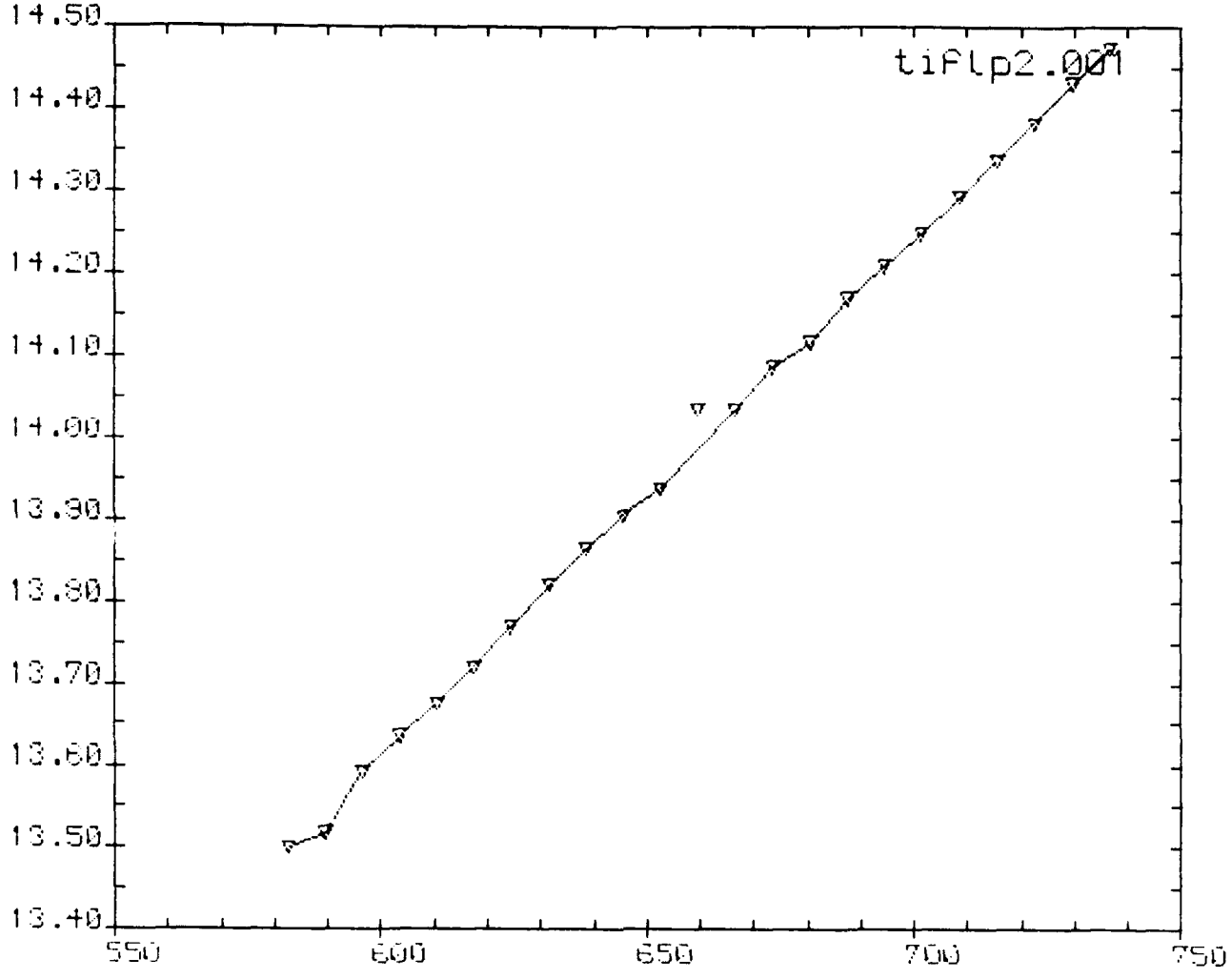
1. SELECT DATA TYPE (FLUORESCENCE,TRANSMISSION,e-YIELD).
2. SUBTRACT PRE-EDGE.
3. INNER POTENTIAL DETERMINATION.
4. DATA SMOOTHING, DEGLITCHING, DEJUMPING.
5. NORMALIZATION.
6. SUBTRACT BACKGROUND.
7. FOURIER TRANSFORM.
8. PHASE AND AMPLITUDE CORRECTION.
9. SHELL ISOLATION.
10. FOURIER BACKTRANSFORM.
11. CHI FITTING AND CALCULATION.

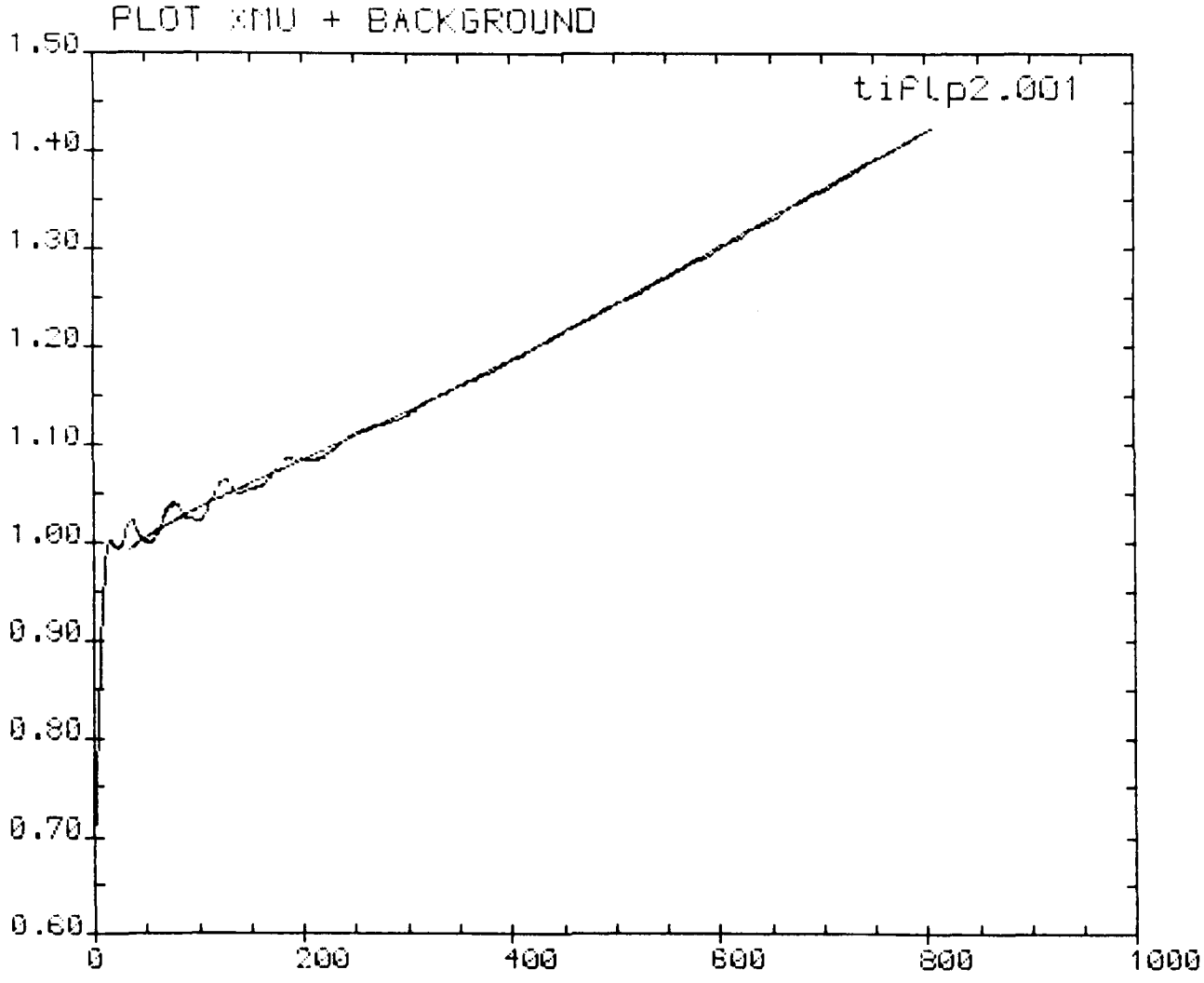

tiFlp2_001
15.50
15.00
14.50
14.00
13.50
13.00
12.50
12.00
11.50
11.00
10.50
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
4600
4800
5000
5200
5400
5600
5800


x10¹ PREEDGE SUBTRACTION EVIC1= 4766.0EVIC2= 4906.0
tiFlp2.001
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
-0.00
4600
4800
5000
5200
5400
5600
5800

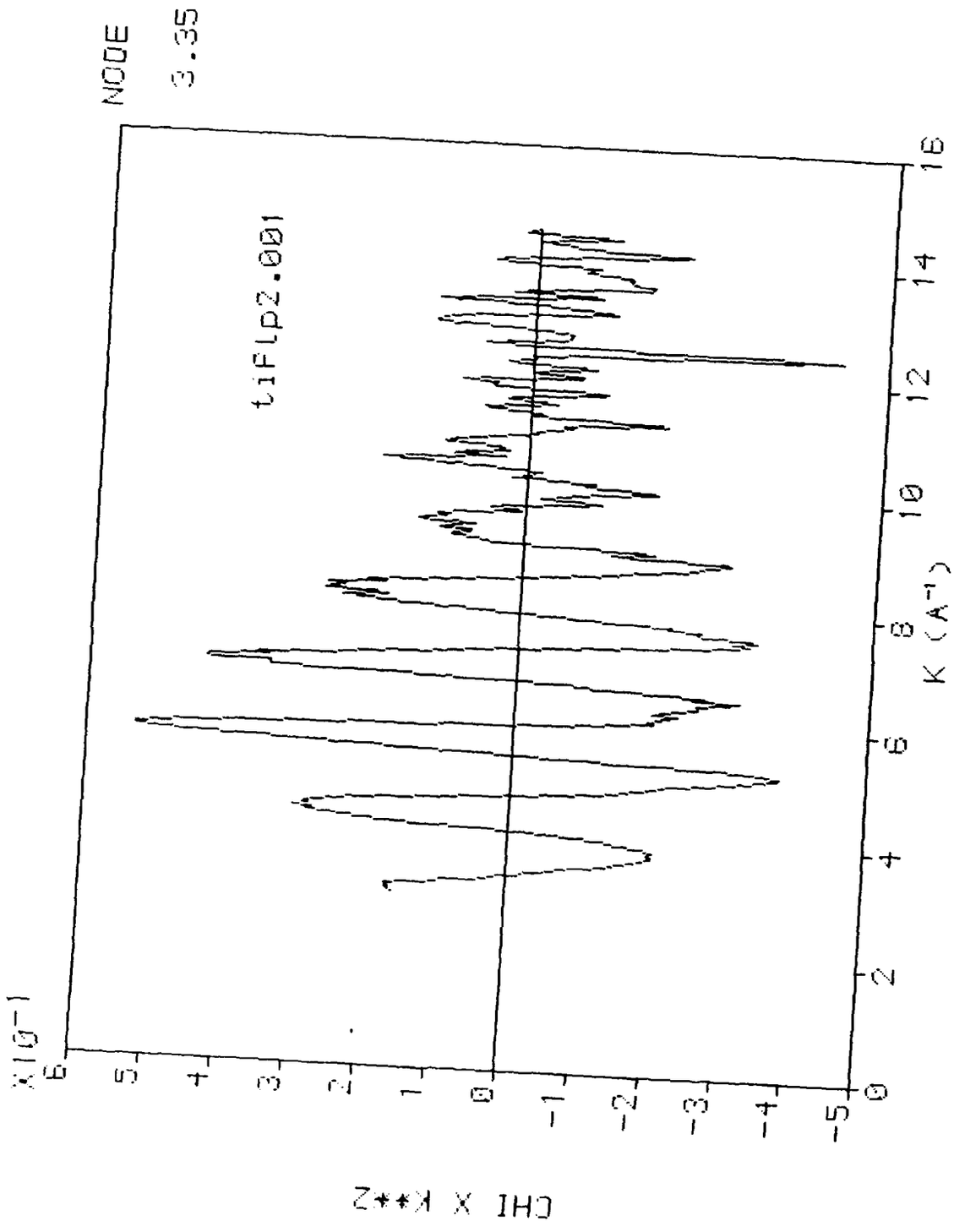

INNERPOTENTIAL DETERMINATION E0= 4957.5
tiFTp2.001
11.00
10.50
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
4850
4900
4950
5000
5050
5100

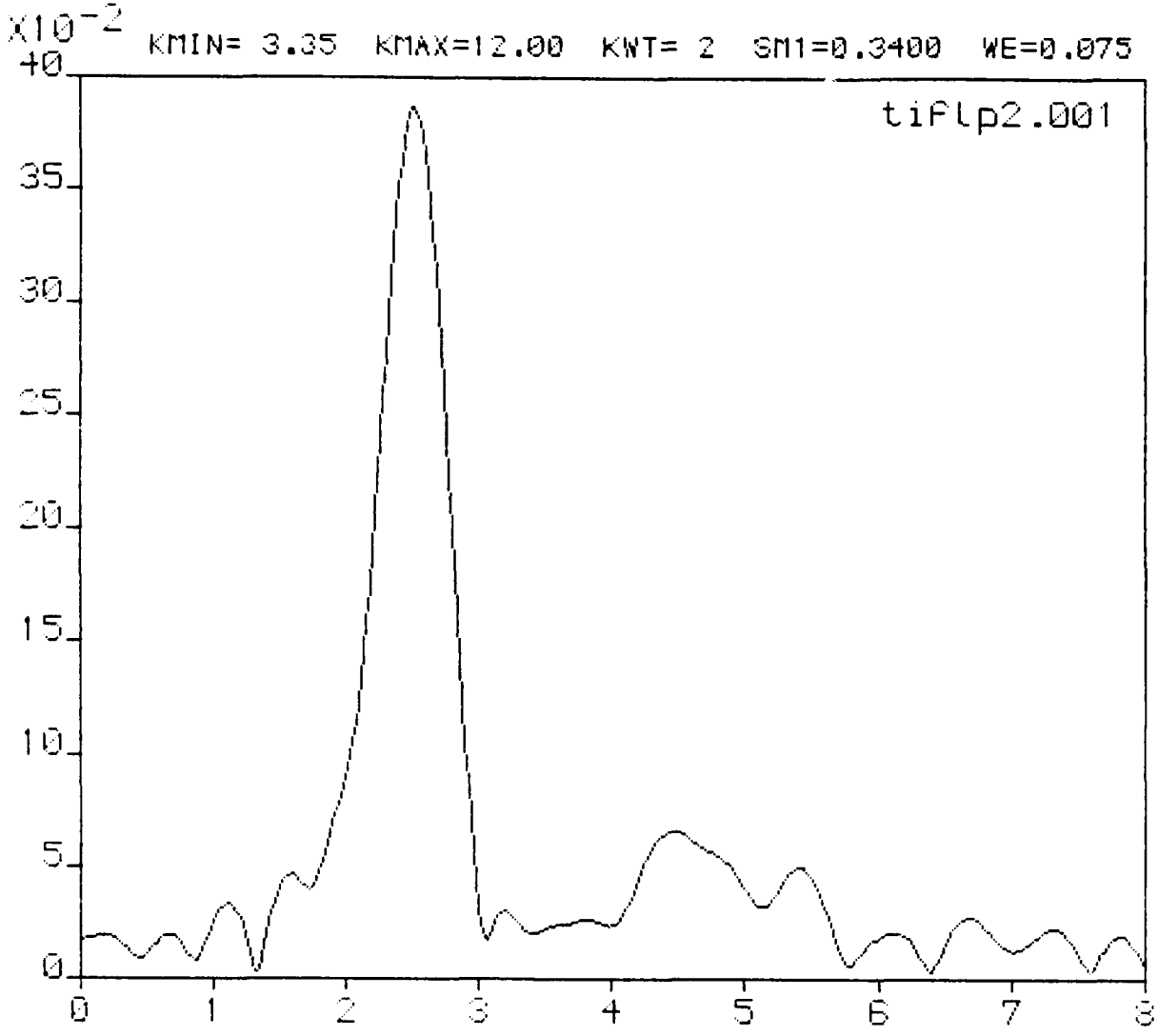

15.00
14.75
14.50
14.25
14.00
13.75
13.50
13.25
500
600
700
800
900
tiPlp2.001

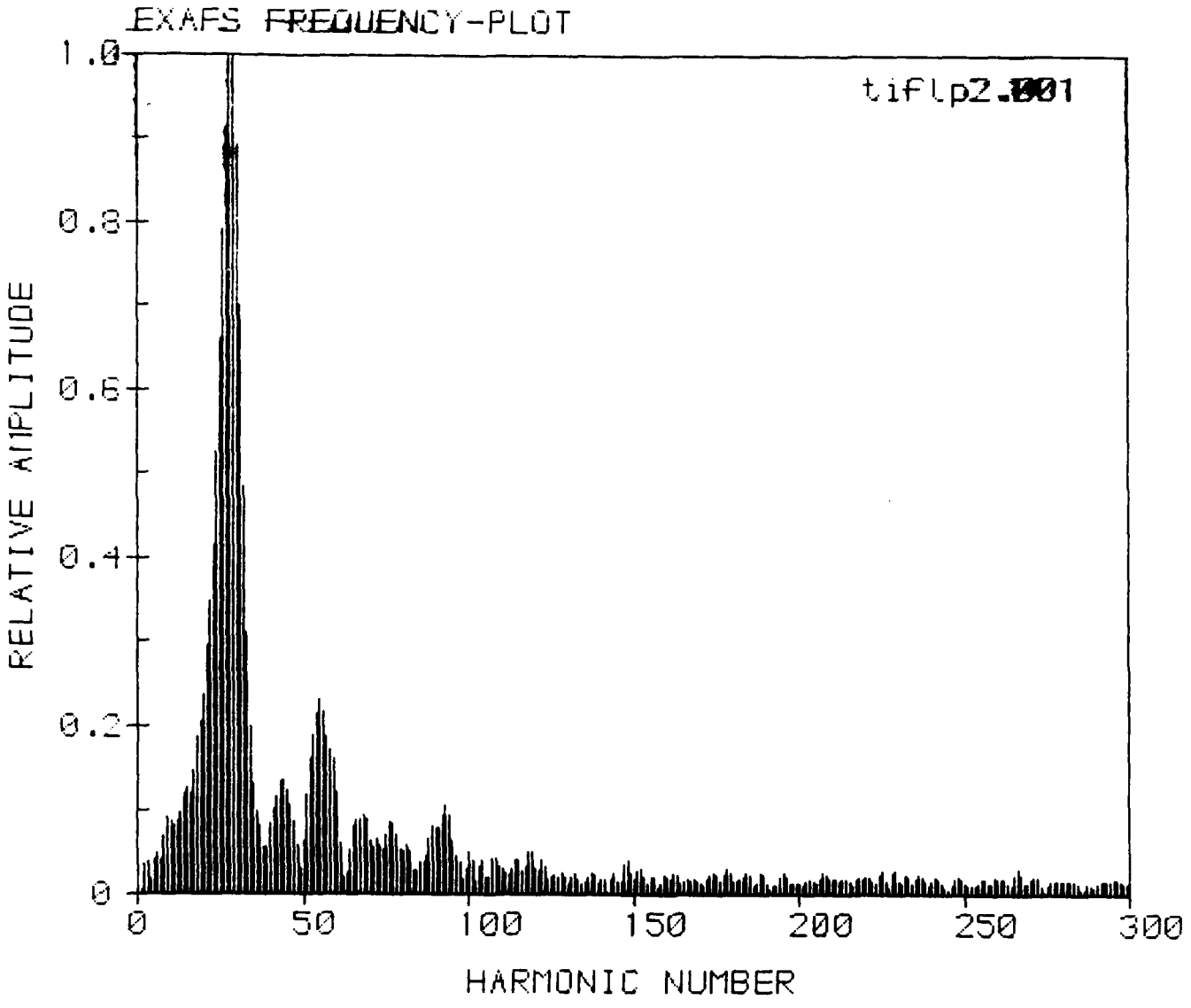

tiFlp2.001
14.50
14.40
14.30
14.20
14.10
14.00
13.90
13.80
13.70
13.60
13.50
13.40
550
600
650
700
750

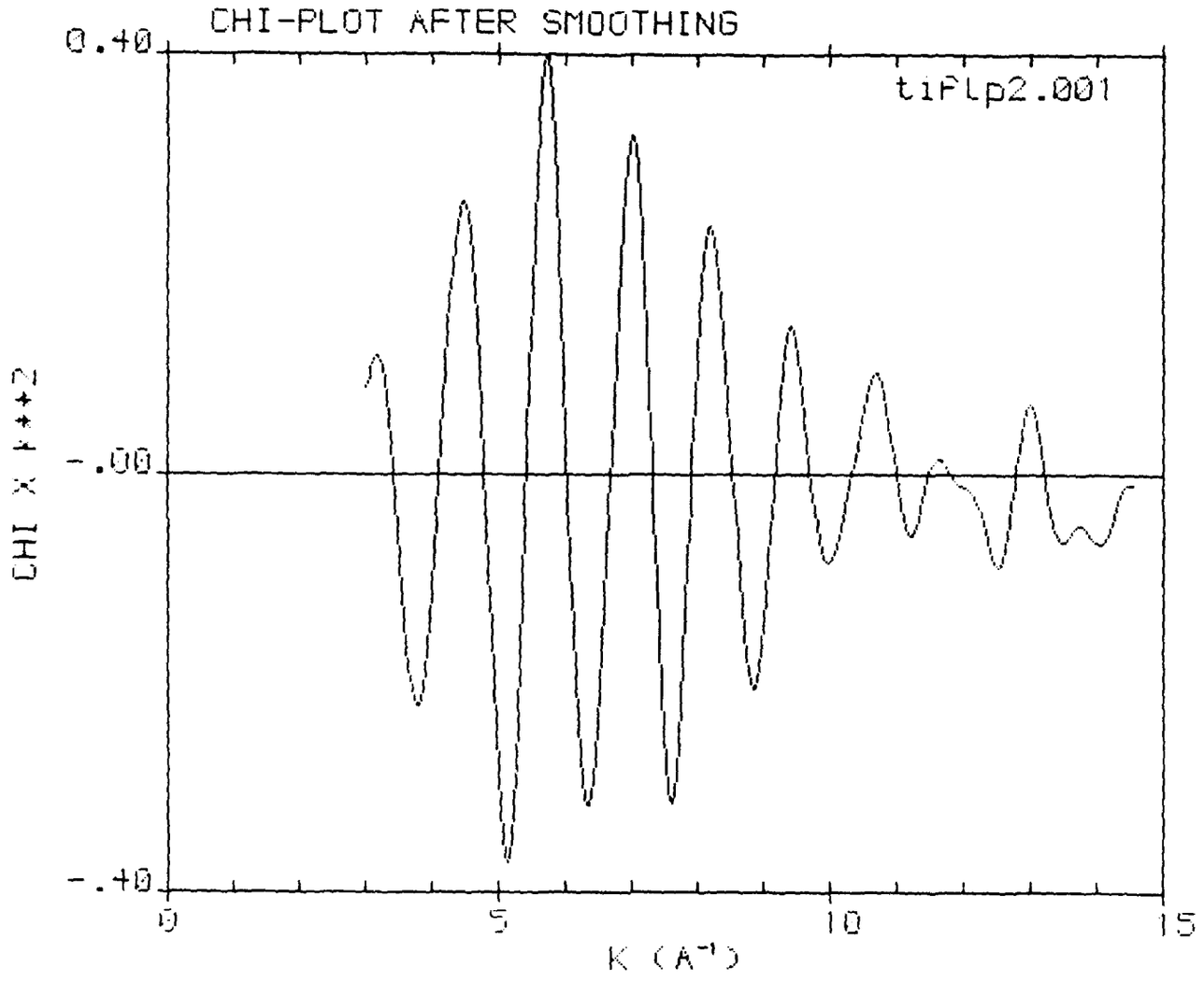

PLOT XMU + BACKGROUND
tiPlp2.001
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0
200
400
600
800
1000

MODE
3.33
DIFLD=0.001
X (FT)
CHI = F**2


NODE 3.35
tiFlp2.001
X10⁻¹
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
0
2
4
6
8
10
12
14
16
K (A⁻¹)
CHI X K**2


X10^-2
KMIN= 3.35 KMAX=12.00 KNT= 2 SM1=0.3400 WE=0.075
tiflp2.001
40
35
30
25
20
15
10
5
0
0
1
2
3
4
5
6
7
8


EXAFS FREQUENCY-PLOT
tiflp2.001
RELATIVE AMPLITUDE
1.0
0.8
0.6
0.4
0.2
0
0
50
100
150
200
250
300
HARMONIC NUMBER


CHI-PLOT AFTER SMOOTHING
tiFlp2.001
0.40
-.00
-.40
CHI X K**2
0
5
10
15
K (A-1)

TASK #15 : MOLD DESIGN/PART ANALYSIS

Thomas A. Elkins
OL-AC PL/RKAD
Edwards AFB, CA 93523-5000
(805) 275-5303, DSN 525-5303, FAX (805) 275-5144
E-mail : ELKINST@PL-EDWARDS.AF.MIL

ABSTRACT

In these times of diminishing budgets and manpower, understanding the behavior of liquid crystal polymers and the process of injection-molding is critical in minimizing the time and money spent in developing mold tools. The Phillips Laboratory has acquired software which works with our existing analysis tools to simulate the injection-molding process and optimize cooling line and runner geometry to minimize the cycle time and part warping, as well as indicate potential problems in the part before any actual machining is done.

INTRODUCTION

In 1987 the Phillips Laboratory (then the Rocket Propulsion Laboratory) purchased a software package called I-DEAS (Integrated - Design Engineering Analysis Software) from Structural Dynamics Research Corporation (SDRC). The package contains a series of modules which share a common product database, so finite element models may be developed from geometry created in the solid modeler, engineering drawings may be created in the drafting module from the solid model, test data may be input and stored with finite element analysis results, and so on. SDRC has added modules (families) to their package to enhance the capabilities of their product and enforce the move to "concurrent engineering." Also, the I-DEAS control, or master, module has an open interface so that users may add interfaces to external codes, a programming language to automate tasks or add capabilities, and a function library that allows users to write programs which can interface with the product database.

Currently, the Phillips Laboratory has the following families

GEOMOD	3D solid modeler
GEODRAW	Drafting
SUPERTAB	Finite element pre- and post-processor
MODEL SOLUTION	Linear statics solver
OPTIMIZATION	Design optimization
GNC	Pre- and post-processor for NC machines
PLASTICS	Mold filling, cooling, and optimization
TDAS	Test data analysis
SYSTAN	System dynamics solver

PLASTIC FLOW SIMULATION

The plastics analysis module of I-DEAS uses a finite element model which is created in the SUPERTAB module. The model of the part is created using thin-shell linear elements (either quadrilaterals or triangles); the mold exterior is modeled using plane strain elements; the parting lines and inserts are modeled with plate elements; the runner system is modeled with either cold- or hot-runner elements; and the cooling lines are modeled with cooling-line elements and/or baffle and fountain elements.

Once the model has been created, materials must be assigned to the mold, inserts, part, and coolant. This is where the database interface from task 9 comes into play. Next the process parameters are entered which include clamp direction, injection pressure, coolant temperature, coolant inlet pressure, cooling line connector geometry, mold temperature, ejection temperature, etc. One then selects the analysis method and number of iterations for the fill and cool calculations, and whether a data set is to be created for a warp and shrink analysis. Packing and holding data are then input as pressure and velocity profiles.

The software performs a cooling analysis first to estimate the maximum time it will take to fill the cavity and cool the part to the ejection temperature. It then performs a fill analysis using the estimated time and calculates the temperature of each element for input into the cooling solver, and so on. Even though the model is created from thin-shell elements, the software internally divides each element into 10, 16, or 24 (user-selectable) layers and performs the analysis on each layer.

When the analysis is completed, the user may read the results into the product database and use the post-processor to view various results, including an animation of the filling process. The software stores the results at various time steps from which the user may select. The following is a list of available results

Mold Filling

TIME-DEPENDENT	TIME-INDEPENDENT
Pressure	Ejection time
Layered strain rate	No-flow (freeze) time
Flux	Fill time (flow fronts)
Layered temperature	Sink mark magnitude
Bulk temperature	
Bulk velocity vector	
Solid layer thickness	

Mold Cooling

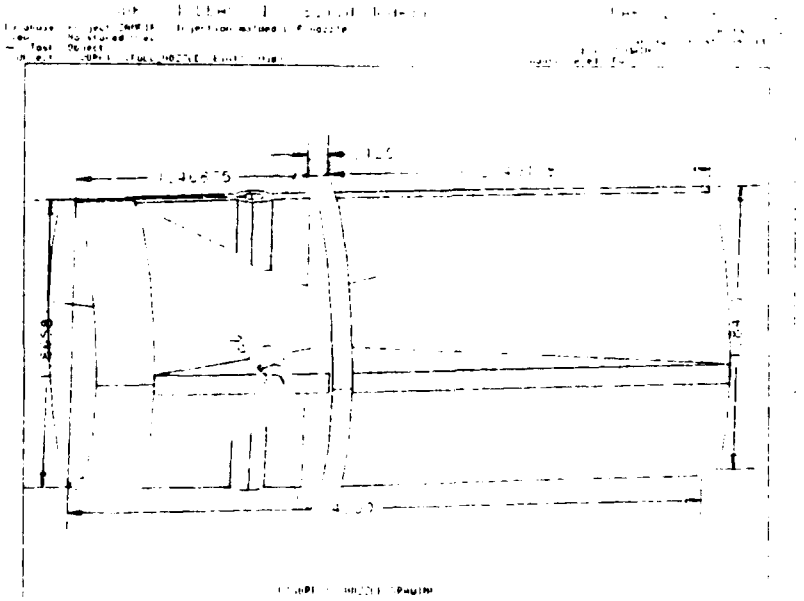
PART	WALL	SURFACE	COOLING LINES	MOLD EXTERIOR
Temperature	Temperature	Temperature	Reynold's number	Temperature
Flux	Convergence	Flux	Flux	Flux
Ejection Time			Pressure	
			Temperature	
			Film coefficient	

If the warp calculation was selected, the user simply changes modules to MODEL SOLUTION and executes a linear static analysis using the loadsets created by the plastics module. The user can then display deformations, stresses, and strains.

NOZZLE DESIGN

The first mold design under this task is a rocket nozzle which will attach to the Air Force Academy motor (also being injection-molded). Figure 1 is a drawing of the nozzle designed by Dr. John Rusek and Mr. Hieu Nguyen. The nozzle is 4 inches in length and 2 $\frac{1}{8}$ inches in diameter at the widest point, which is a circumferential rib. The leftmost part of the nozzle (to the left of the circumferential rib) will slip into the motor case and be pinned to the case. The motor case will rest on the lip of the circumferential rib.

The recommended lower limit to the size of an injection-molding part is $\frac{1}{8}$ inches, so that was used as the thickness of the longitudinal and circumferential ribs. Also, to reduce the possibility of sink marks, ribs should be between 60 and 70% of the nominal wall thickness which would make the nominal wall about $\frac{3}{16}$ inches thick.

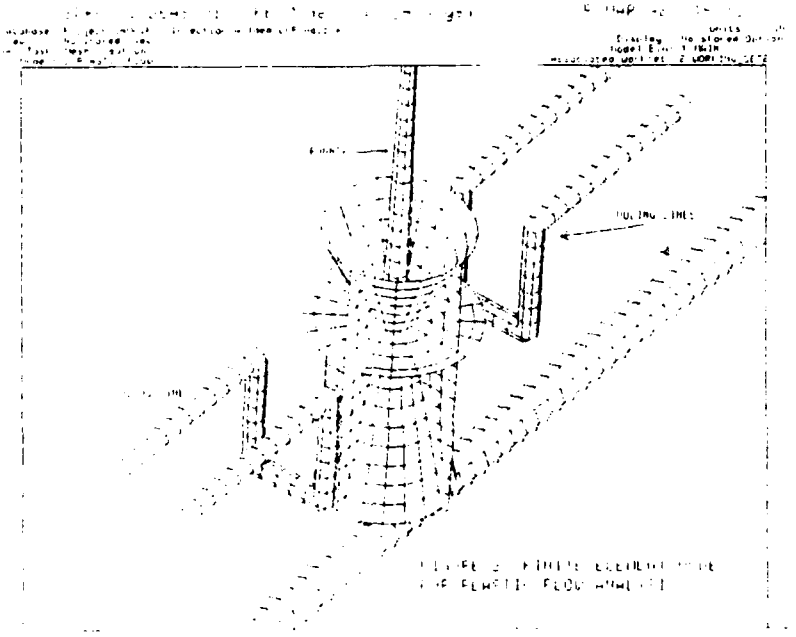


MOLD DESIGN

The overall dimensions of the nozzle are roughly equivalent to the dimensions of the 2x4 motor case. Mr. Chris Frank from McClellan AFB suggested using the same mold base for the nozzle, thus eliminating the cost of having a new mold base made up; the core and cavity pieces could be machined in-house. If this works out the same mold base could be used to make either the 2x4 motor case or the Academy nozzle.

PROCESS SIMULATION

A finite element model of the nozzle was generated in I-DEAS and a copy was made so that a structural analysis could also be performed. Cooling lines were added based on sketches from Mr. Rich Griffin at Hill AFB and a runner and gate system were modeled. The drawings from Hill did not provide enough information to accurately model the mold or runners, nor was there sufficient data about the injection molding machine at Hill AFB to properly set up the process parameters; however, this was just a first attempt to see how the software worked. Figure 2 shows the finite element model.



Material selection turned out to be a problem, because there were no LCPs in the supplied database; however, this was only a test of the software, so the materials were not that critical. The materials selected were PBT for the part, 414 Stainless for the mold, and water for the coolant. The default process parameters were selected for this test.

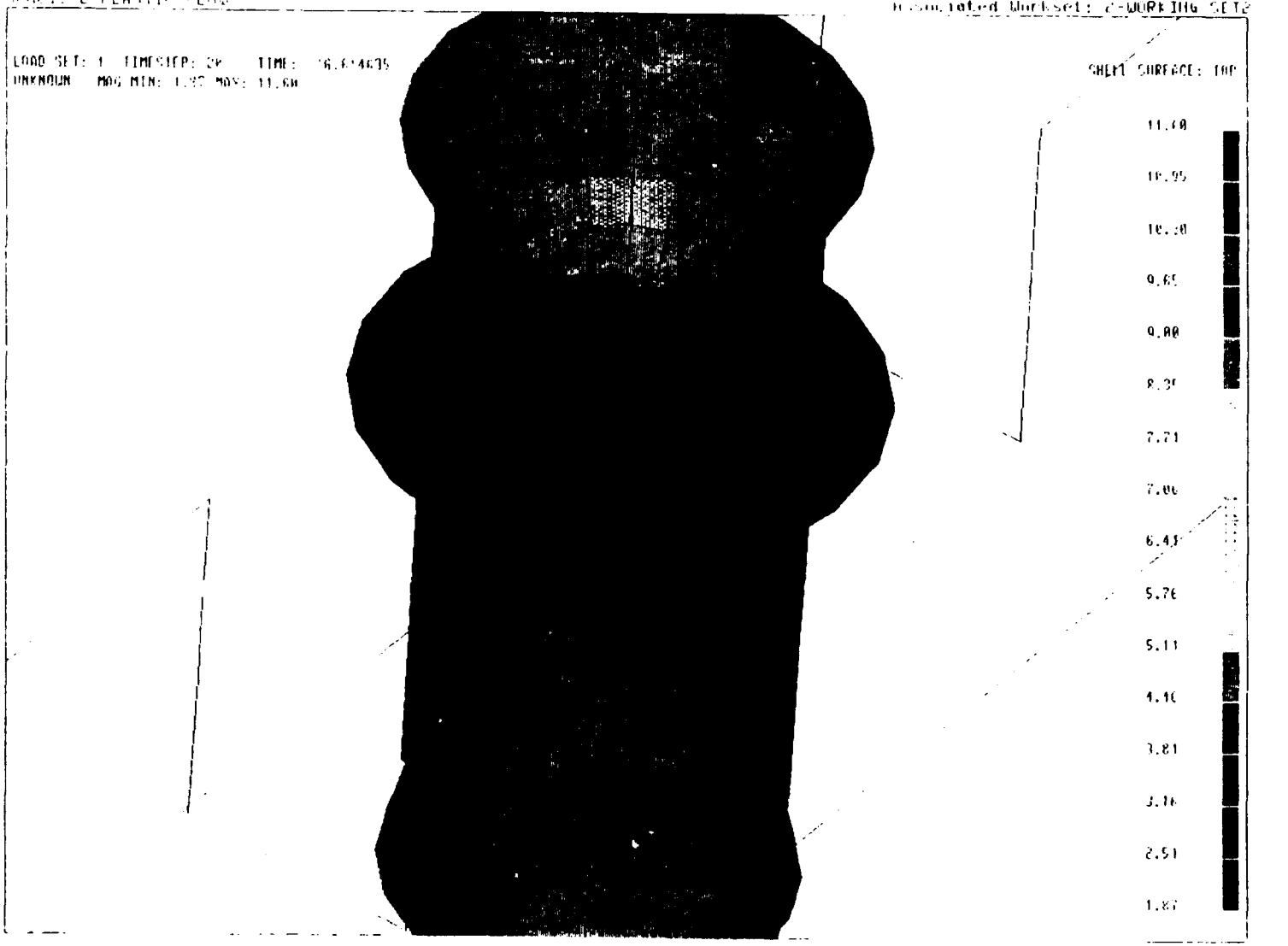
After submitting the job, the user may request updates as to how the analysis is progressing. The following is an excerpt from the status display.

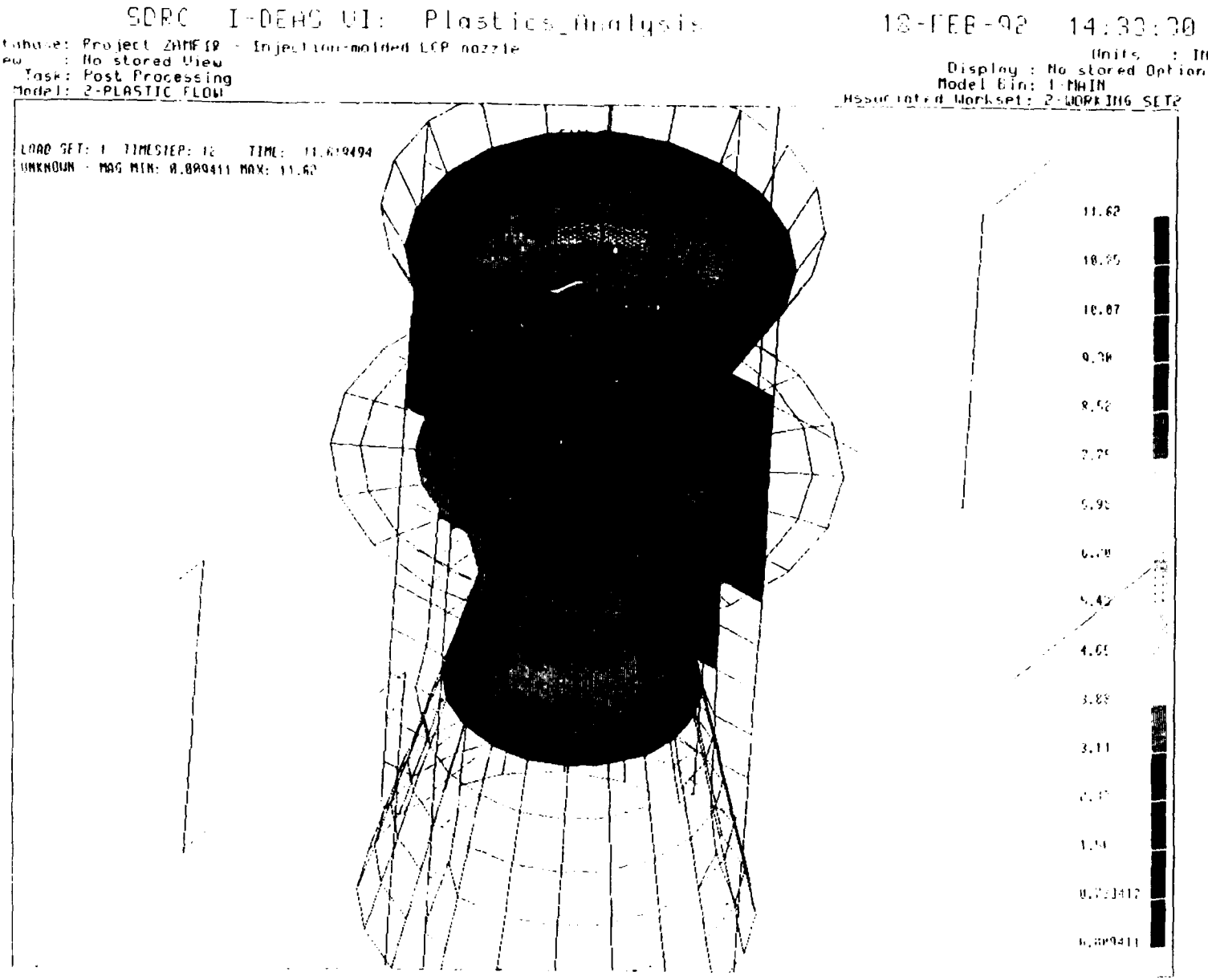
```
Step status at 00:46:00 --- Mold Cooling --- Started 18-FEB-93 00:00:19

Current iteration = 3                        Total CPU time = 00:38:16
Plastic calculation complete                 00:00:36
Fourier forward transform finished           00:00:48
Circuit calculation complete                 00:00:10
Mold:  Matrix and known vector formed        00:00:13
Mold:  Linear system of equations solved     00:00:50
Fourier inverse transform finished           00:00:26
Writing to the print file finished           00:00:05
```

```
Restart file write and other tasks finished  00:00:01
MOLD COOLING STEP COMPLETE -------------------------

Partial results for iteration 3 :
Ejection time =                          11.6146 seconds
Maximum deviation = 1.0339 C             Root-mean-square error = 0.8347 C

...
(3,10) 2-Fill.  ERROR: (CVDRVR) Miscellaneous at timestep 70
Short shot; remaining steps in coupled analysis not executed

Step status at 01:03:44 ---- Mold Filling ---- Started 18-FEB-92 00:46:08

Performing a NONISOTHERMAL COMPRESSIBLE analysis
Timestep = 70 Process time = 11.619 Total CPU time = 00:16:50

Percent filled                           = 71.6593 per cent
Fill time (requested)                    = 16.0000 seconds
Number of nodes filled                   = 362 out of 576 nodes
Ejection time (computed)                 = 11.6195 seconds
MOLD FILLING STEP COMPLETE -------------------

Pressures (RUNNER1):  16.3 MPa (inlet), 3.4 MPa (gate (min))
Flow rate (RUNNER1):  4.09E+03 mm**3/sec (inlet)
Temperatures:  258C (melt), 264C (max), 221C (Bulk (min))
```

FILL/COOL RESULTS

The next two pages show some of the results which may be displayed on the screen. The first one is from the cooling analysis showing the estimated time it would take for each element to reach the ejection temperature (in this case 150°F). The picture shows that the ribs reach the ejection temperature rather quickly, but the throat/gate region approaches 12 seconds. The second picture is from the fill analysis and shows what elements of the model were filled in the time calculated by the cooling analysis. The software was smart enough to realize that the flow froze before completely filling the mold.


LOAD SET: 1 TIMESTEP: 20 TIME:
UNKNOWN MAG MIN: MAX:
Units :
Display : No stored Options
Model Bin: 1-MAIN
Associated Workset: 2-WORKING SET2
SHELL SURFACE: TOP
11.60
10.95
10.30
9.65
9.00
8.35
7.71
7.06
6.41
5.76
5.11
4.46
3.81
3.16
2.51
1.87


SDRC I-DEAS UI: Plastics_Analysis
18-FEB-92 14:33:30
Database: Project ZAMFIR - Injection-molded LCP nozzle
View : No stored View
Task: Post Processing
Model: 2-PLASTIC_FLOW
Units : IN
Display : No stored Option
Model Bin: 1-MAIN
Associated Workset: 2-WORKING_SET2
LOAD SET: 1 TIMESTEP: 12 TIME: 11.619494
UNKNOWN - MAG MIN: 0.009411 MAX: 11.62
11.62
10.85
10.07
9.30
8.52
7.75
6.98
6.20
5.43
4.65
3.88
3.11
2.33
1.56
0.7813412
0.009411

STRUCTURAL ANALYSIS

One other possible use of the nozzle is to test the ablation properties of the liquid crystal polymers as molded and with a CVD coating. A structural analysis of the nozzle was performed on the second copy of the finite element model. The model was restrained at the four pin locations and a pressure load was applied to the element faces of the nominal wall. Material properties were input from supplier's data sheets, which assume isotropic material behavior.

A simple one-dimensional equilibrium flow calculation using the TDK code provided the pressure profile which was used. TDK prints data at user-specified area ratios (area at point of interest divided by the area at the throat) which were calculated by finding the area of the circle defined by the centroid of each "ring" of elements. For this analysis gaseous Hydrogen (GH_2) and air were selected as propellants, and the chamber pressure was set at 2000 psi. Figures 5 - 8 show the load profiles calculated by TDK. Figure 9 shows the finite element model with pressure loads and restraints.

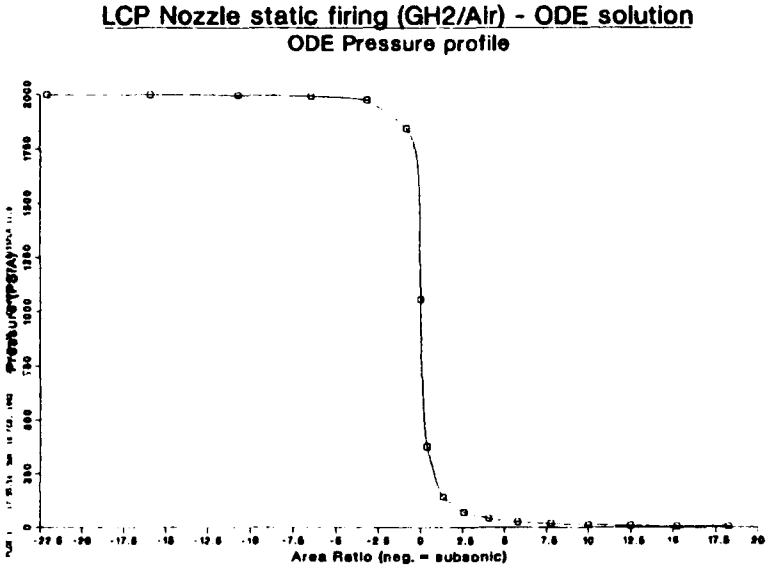


Figure 5. Pressure profile from TDK

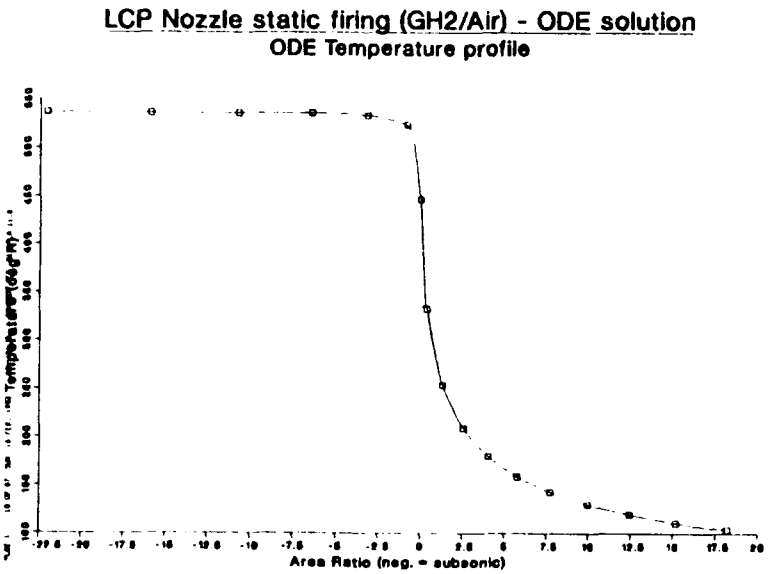


Figure 6. Temperature profile from TDK

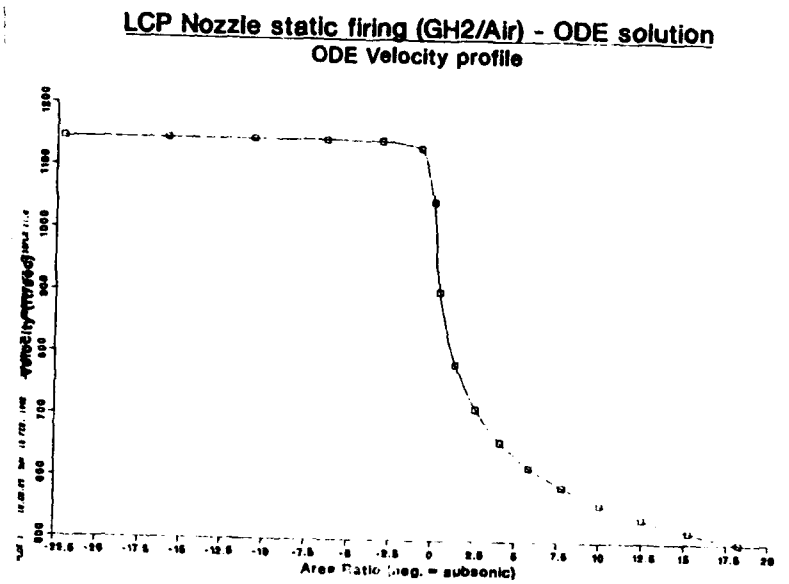


Figure 7. Sonic velocity through the nozzle

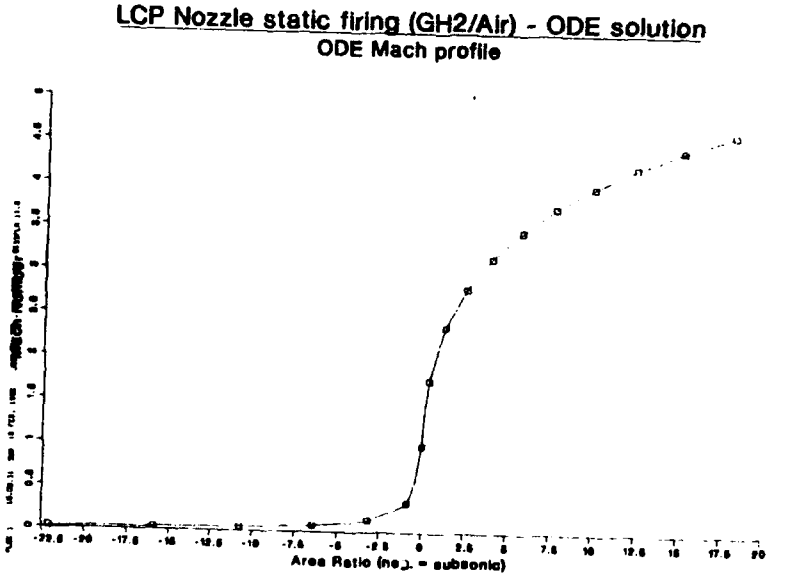


Figure 8. Mach profile from TDK

STRUCTURAL ANALYSIS RESULTS

The last two pages show the displacement magnitude and maximum principal stress. According to the results of the finite element analysis, even assuming isotropic material behavior and believing the manufacturer's data, the nozzle appears to fail at the pin bosses due to the nozzle inlet flaring out and buckling the support ribs. Tests done by Mr. Chris Frank also show that simply pinning the part will not hold.

CONCLUSIONS

The software does show promise that a part and mold could be designed and tested without actually building the tools. A better approach to testing the software would be to model the 2x4 motor case mold using the real numbers from Hill AFB and comparing the analysis results to the real parts. Once the two match well enough, then a more thorough analysis of the nozzle mold will be in order. The material properties of these LCPs need to be verified so that a more accurate analysis can be performed. The software has optimization switches which will change the cooling lines and runner systems to minimize the cycle time and warpage as well as recommend structural changes to minimize the amount of material used without sacrificing strength.

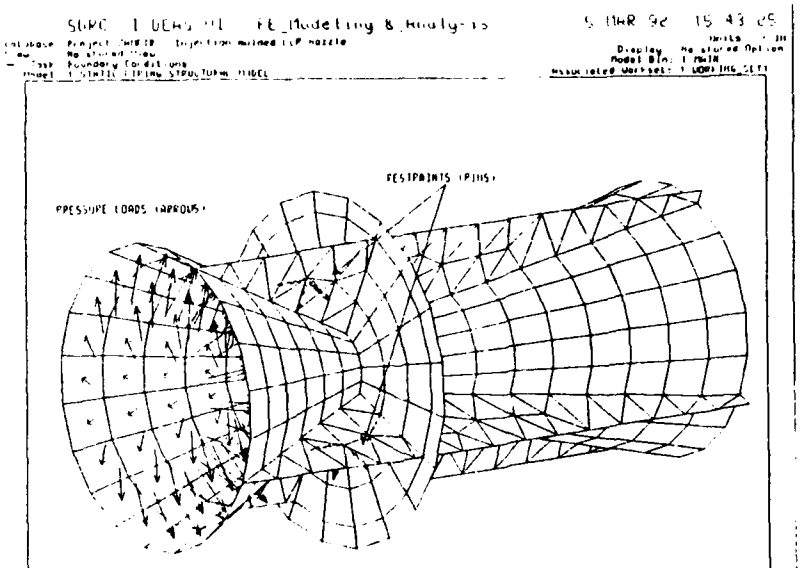
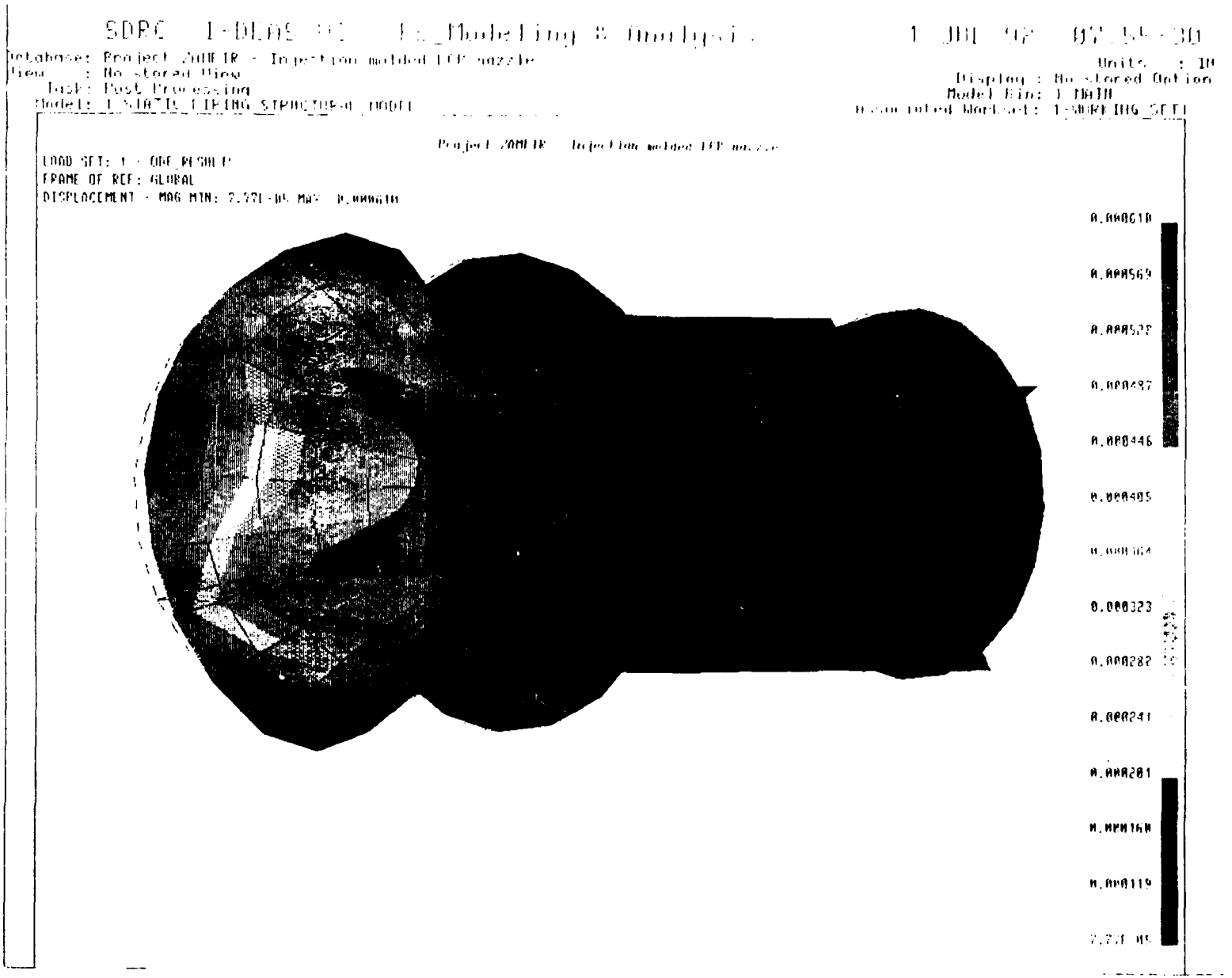
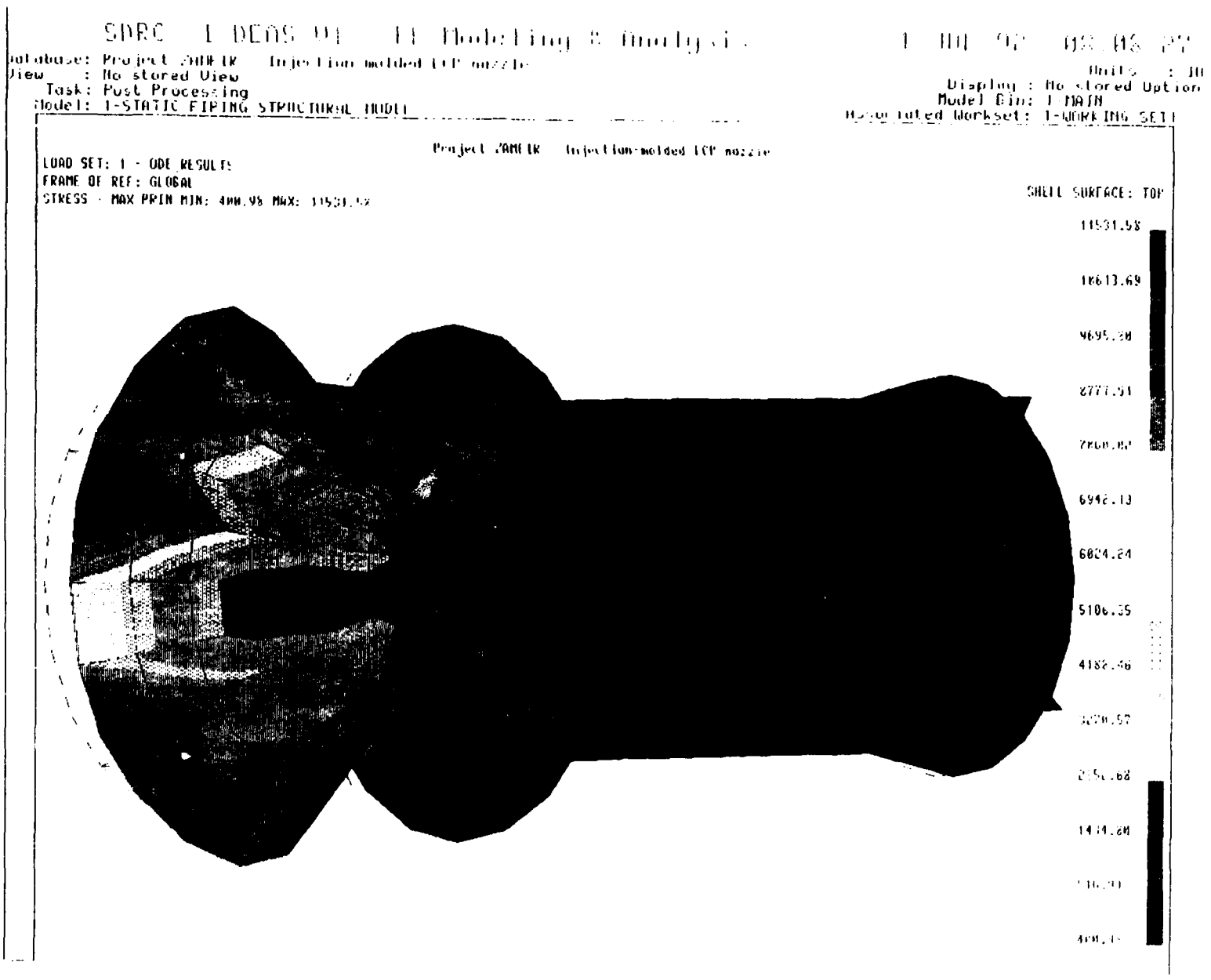


FIGURE 9 FINITE ELEMENT MODEL FOR STRUCTURAL ANALYSIS


Units : IN
Display : No stored Option
Model Dir: 1 MAIN
LOAD SET: 1 - ONE PSI LP
FRAME OF REF: GLOBAL
0.000610
0.000569
0.000528
0.000487
0.000446
0.000405
0.000323
0.000282
0.000241
0.000201
0.000119


Project :ANNEK Injection-molded ICP nozzle
LOAD SET: 1 - ODE RESULTS
FRAME OF REF: GLOBAL
SHELL SURFACE: TOP
11531.58
10613.69
9695.80
8777.91
7860.02
6942.13
6024.24
5106.35
3370.57
1634.80

APPENDIX 1 : ANIMATION

The animations shown at the symposium were all generated in-house using a combination of commercial software and utilities developed in-house. The following is a description of the animations that were shown and some of the steps involved. Except where noted, all animations and drawings were generated by Mr. Tom Elkins.

Spinning Phillips Lab Shield

Shield model was created using Wavefront's Advanced Visualizer by Mr. Russ Leighton at Phillips Laboratory. The gold texture on the back of the shield was actually an image of flames that was mapped to the object as a texture. The shield rotates 360° in 100 frames.

Project Zamfir Shield

Image was generated "by hand" using Deluxe Paint III on an Amiga 2000. The "motto" is a perversion of the motto of the U.S. Naval Academy (*ex scientia tridens* - from knowledge, seapower), and does represent the feelings of the author!

Nozzle Coming Out Of Drawing

The original drawing was scanned into the Amiga using a Sharp color scanner. The image was then converted from the Amiga's ILBM format to the run-length encoded (RLE) format used by Wavefront, and then converted into a texture map. The image was then mapped to a simple square and placed in front of the nozzle model. The nozzle model was generated completely in Wavefront using the actual dimensions. The "camera" was positioned so that the drawing completely obstructed the nozzle from view. The drawing was then animated moving back, passing through the model, and at the same time the camera was rotated. The length of the animation was 100 frames.

Spinning Nozzle

The model of the nozzle was modified to make a cut-away view of the interior, and was then animated rotating 360° about all three axes in 100 frames. The final animation was too large to fit on the Amiga, so the animation was recompiled using all odd-numbered frames, which is why the movement was jumpy.

Injection-molding Simulation

The model of the mold tool was based entirely on conversations with Mr. Chris Frank, Mr. Rich Griffin, and hand-drawn sketches of part of the mold. The nozzle model was used here as well.

Animation Procedures

All of the models were generated using the MODEL module of Wavefront's Advanced Visualizer. Materials and texture maps are created using Wavefront's MEDIT (Material EDITor) and then applied to the object in MODEL. Motion paths are created in Wavefront's PV (PreViewer) and objects are then assigned to a motion path. Individual frames are rendered using Wavefront's IMAGE module with shadows, reflections, and antialiasing turned off to speed up the rendering. After each frame is rendered, it is converted from Wavefront's RLE format to a 24-bit Amiga ILBM format using a program developed by Mr. Russ Leighton. The 24-bit image is copied to an Amiga 2000 and converted to a 4-bit compressed NTSC video image using commercial software. After all the images have been rendered, the animation is compiled using a commercial program on the Amiga which employs a delta compression method. The animation is then played back on the Amiga and each frame is decompressed to (in real time) to a true NTSC video image using commercial hardware. The output of the decompression hardware is connected to the video-in jack of a standard VCR and recorded. The background music was playing on the Amiga as the animation was playing, taking advantage of the Amiga's multitasking operating system. The audio output jacks of the Amiga were connected to the audio input jacks of the VCR.

Most of the process described above has been automated using unix scripts and programs developed by Messrs. Russ Leighton and Tom Elkins.

For More Information

I-DEAS

Structural Dynamics Research Corporation (SDRC)
Software Products Marketing Division
2000 Eastman Drive
Milford, OH 45150-2789
(513) 576-2400
They do offer discounts and special programs for Universities.

Wavefront

Wavefront Technologies
530 East Montecito St., Suite 106
Santa Barbara, CA 93103
(805) 962-8117

The software was about $ 35,000, but they do offer less expensive products as well; in fact, their Personal Visualizer comes with some unix workstations. They also offer a Data Visualizer which has some incredible capabilities for viewing complex datasets. One may also see the capabilities of the Advanced Visualiser by watching TV and movies such as Star Trek: The Next Generation, Lifesaver commercials, "Total Recall" (the X-ray screen), and many TV lead-ins to news, sporting events, and movies.

Compressed NTSC Video Images

The product is called DCTV (Digital Composite TeleVision)
Digital Creations
2865 Sunrise Blvd., Suite 103
Rancho Cordova, CA 95742
(916) 344-4825

Injection Molded Rocket Components

Christopher L. Frank

Advanced Composites Program Office
Sacramento Air Logistics Command
McClellan Air Force Base, Sacramento CA. 95652

ABSRACT

In September 1989, an informational meeting was held at McClellan AFB to discuss the Advanced Polymer Components (APC) project under the direction of Dr. John Rusek of the Air Force Astronautics Laboratory (AFAL) with the Advanced Composites Program Office (ACPO). A co-operative effort began between the AFAL and the ACPO to rapidly build a number of rocket motor and rocket engine parts using a new type of plastic, Liquid Crystal Polymers or LCPs. Plastic material had not been used for these type of applications before and a good deal of information had to be generated. The AFAL wanted to quickly establish an Air Force-staffed plastic motor program and came to the ACPO for the expertise needed to design the molds and develop the processes to produce these motors. By May of 1990, the timetable was set, and design and analysis had begun. Molds were built, and on Aug 28, 1990, less than 6 months from concept, the first eleven injection molded plastic solid rocket motor cases were fired. Seven of these cases survived the firings. The initial success of this project convinced the AFAL to continue working with the ACPO in this area. The use of plastic case designs for solid rocket motors will contribute greatly to the ultimate goal of a low-cost lightweight interceptor. This paper will highlight the work to date, present test data and process information.

Liquid Crystal Polymers (LCPs) have a number of intriguing properties that could prove very beneficial to the field of rocketry. The most significant of these are, high strength fiber formation (fibulation), resistance to extreme temperatures, impact tolerance, and ease of molding highly detailed parts.

Figure 1 shows a typical solid rocket motor schematic. The various mechanical parts and solid fuel contribute to the total weight of the motor. If this total weight can be lowered, through the use of new engineering polymers like the LCPs, increased payloads, increased fuel capacity, or smaller rocket sizes may be realized. Beyond decreasing rocket motor weight the LCPs may also lower manufacturing costs, as various parts may be more efficiently manufactured by the use of injection or compression molding. For the purpose of this paper we will be primarily concerned with the motor case, though other components are currently under development including a low pressure nozzle.

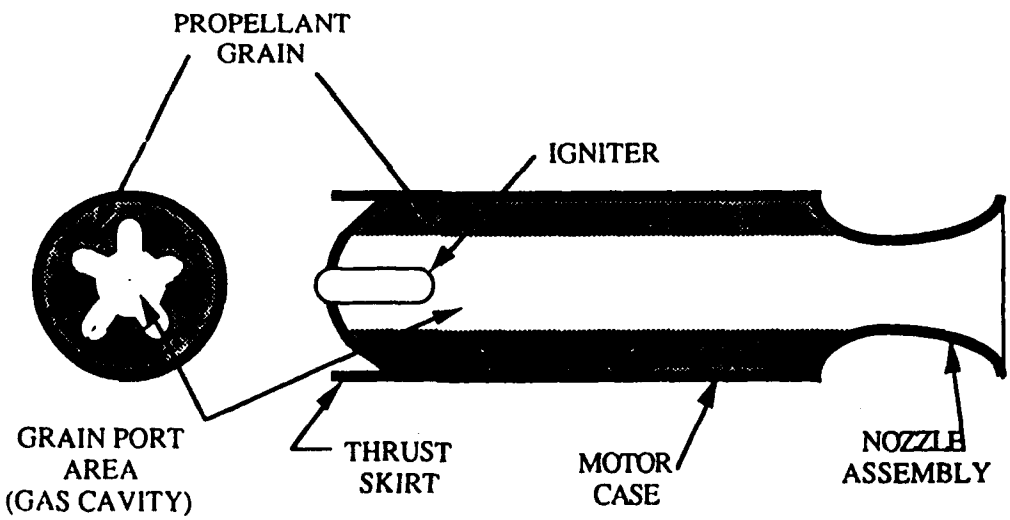


Figure 1
Generic Solid Motor Design

The 2X4 motor for testing solid propellants was suggested as one of the first prototypes. This case is used for testing the formulation and burn rates of solid rocket fuels. Currently the 2X4 motor cases are made of D6AC steel and are individually machined. They are reusable but require though cleaning and inspection. The size of the case is 2" inside diameter and is 4" long, thus the name 2 by 4 motor.(Fig 2)

The manageable size of this case, the varied fuel types possible, and the fact that an instrumented test fixture and test program were already in place for the 2X4 made it an ideal candidate to become a test bed for these new materials.

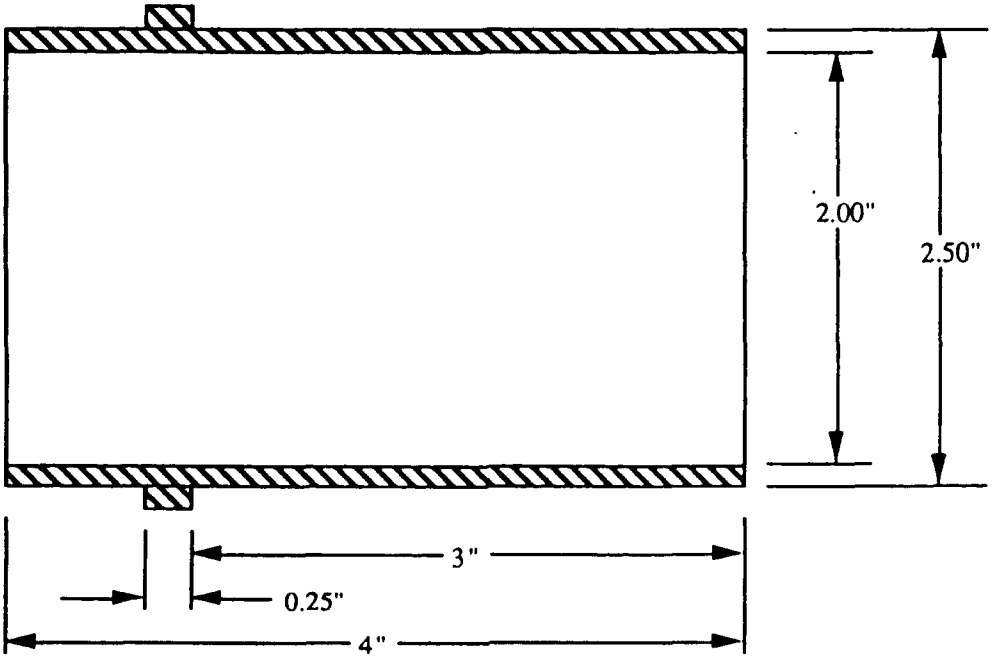


Fig.2
2X4 Test Motor Case

Fibulation is a well documented characteristic[1] of LCPs and so it is one of the APC goals to exploit this attribute. The use the injection molding grades of materials allowed us to capitalize on the natural tendencies of polymer alignment. Injection molding induces most plastics to flow in manner that causes the polymers to align near the wall where drag is high which induces shear. In the same flow the polymer in and near the center of the flow is random and much less aligned. The polymer associated with the wall forms a oriented region of strength in the direction of the flow, a sort of skin. The polymer in and near the center remains in it's random state and forms a sort of core (Figs 3&4).

[1]Liquid Crystalline Polymers
Nation Materials Advisory Board
Commission on engineering and Technical Systems
National Research Council NMAB-453 1990

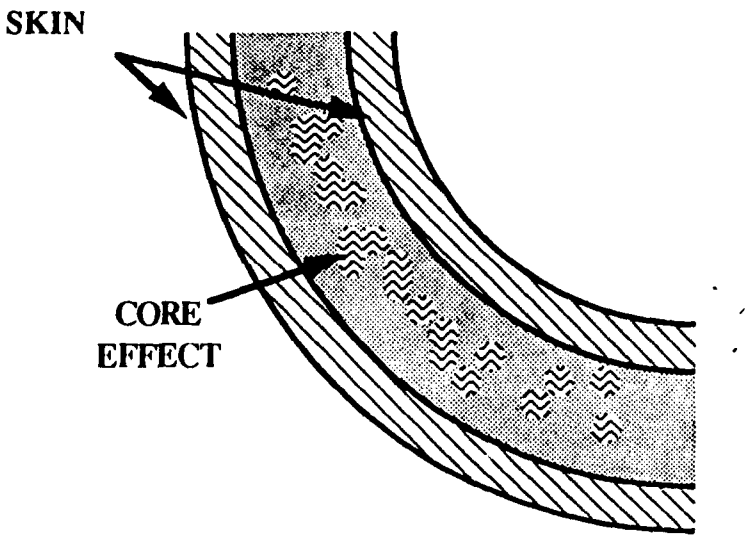


Fig. 3
Typical Section View of Flow

The effect of the flow through a passage causes the alignment of the polymer. The result is that the wall becomes stronger due to the alignment but ordinarily only in the direction of the flow. The flow in these molded rocket motor cases was all longitudinal so we can expect the circumferential strength to be lower than that over the length, and that is what was observed during initial testing.

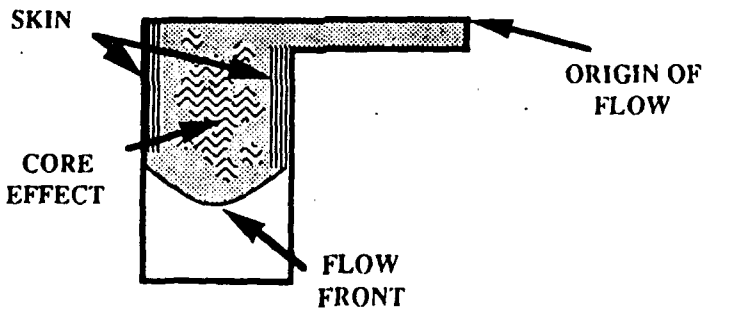
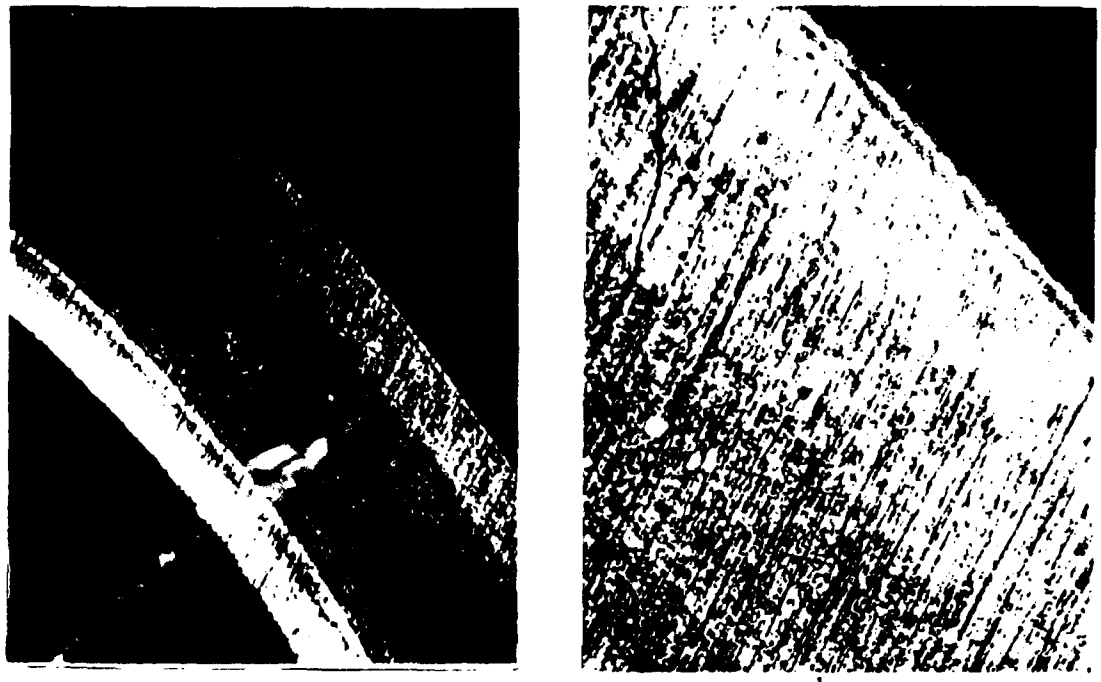


Figure 4
Section of Flow

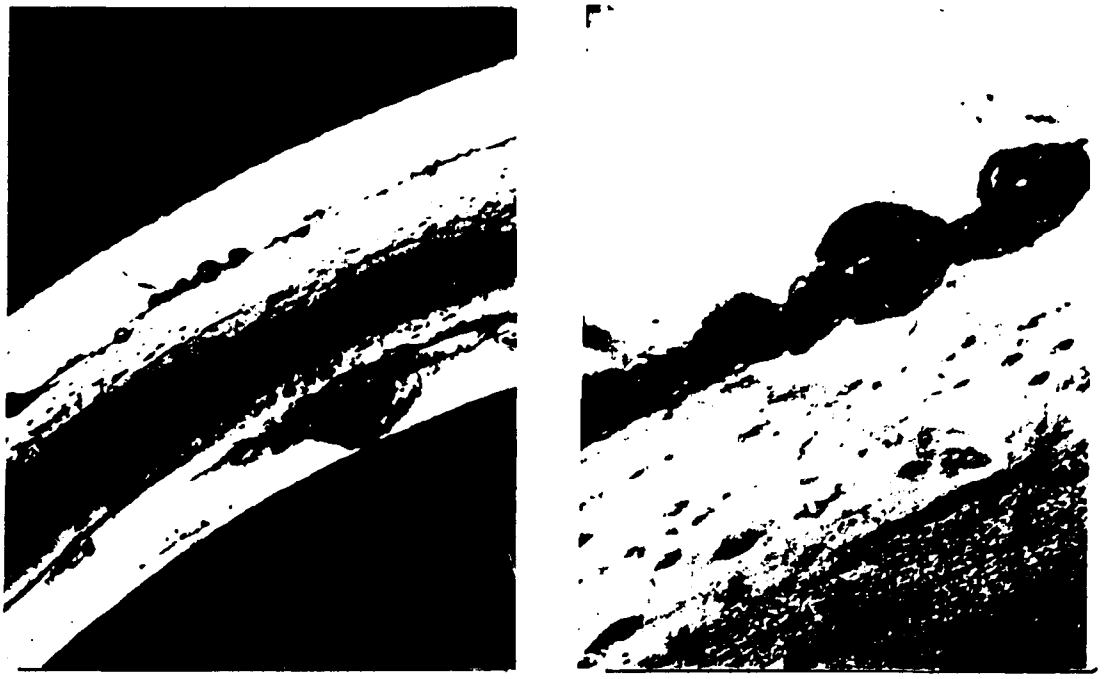
This skin and core effect enhances the fibrous formation of the LCPs. In figures 5a and 5b, the skin and core effect is quit visible and can often be seen with only minor polishing.



a b

Figure 5
Photo of Vectra A-950 Case

The skin and core effect can actually become so pronounced that during cooling of the molded article or under small loads the core pulls away from the skin due to the large differences in strength associated with alignment. In figures 6a and 6b, the failures between the skin and core are also quit visible.



a b

Figure 6
Photo of Xydar SRT-300

Initial testing of the cases consisted of loading the test cases with solid fuel and firing them in the instrumented test fixture. Once the tests were complete and results proved favorable the next design phase began. This next step was to design a simple flight article and test it. The flight article would be a motor known as the academy motor. This motor is a fairly simple design the current motor is made of a paper phenolic tube that is plugged with a wood blank at one end and has a graphite nozzle pinned in the other end. To redesign this motor posed only two design problems, first, end containment and second, attachment of the nozzle. The containment was accomplished by designing a domed end (Fig. 7).

Fairly low pressures are involved, approximately 700 psi in the chamber at maximum thrust. The resulting load on the nozzle attachment is about 2000 pounds. The nozzle attachment required some testing to determine the proper pin diameter to allow the plastic to carry the load. This test was accomplished with a simple test fixture (Fig. 8) that could be pinned into the cases. The results of these test are the following table.

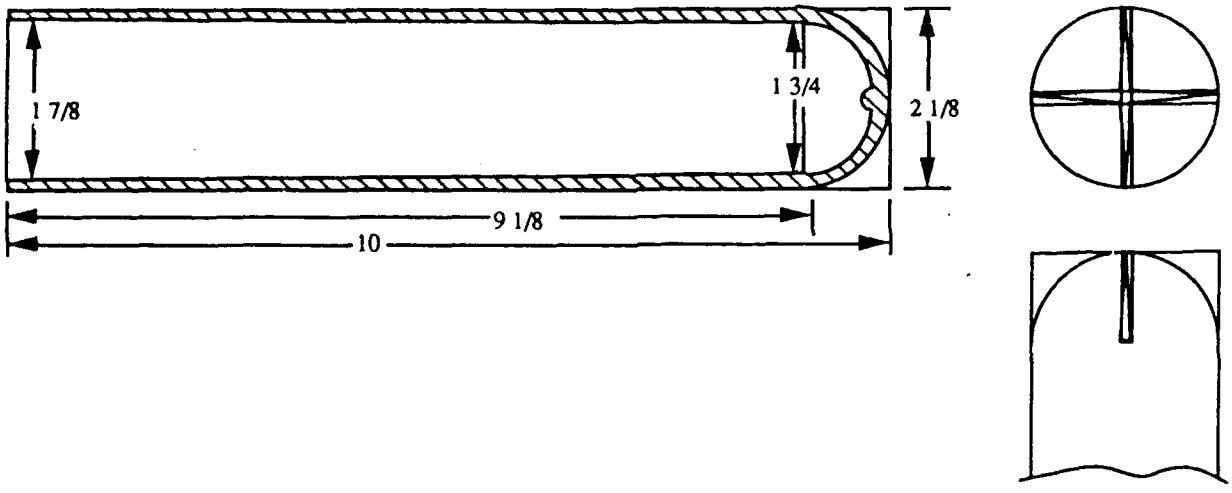


Figure 7
Academy Motor

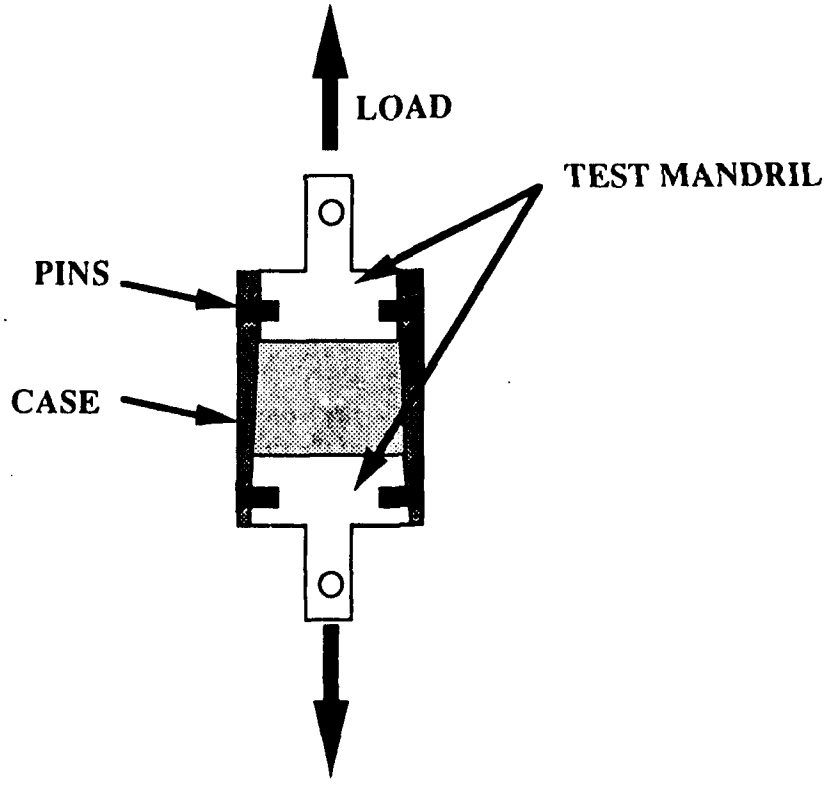


Figure 8
Test Fixture for Pinning

As the test showed the larger diameter pins have been chosen for the design. Although the pinned values are very close to the load values

they are considered to be with acceptable limits due to the use of an additional adhesive to attach the nozzle (Fig.9).

An interesting observation about the failures is that the rivets began to bend prior to failure of the LCP. Photos of these failures were not available at press but will be presented at the Thermoplastic Review. Also based on the type of failure the stronger LCPs exhibited and the bearing failure of the rivets further work with a new test fixture will be conducted.

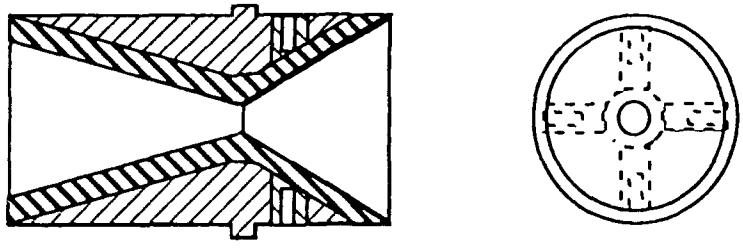


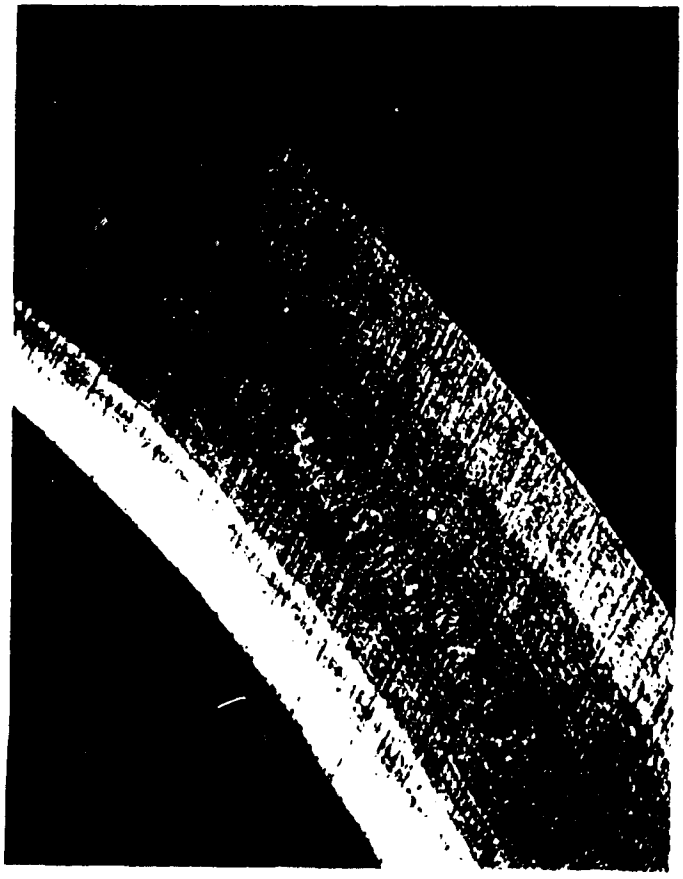
Figure 9
Academy Motor Nozzle

During a recent end burn test a plastic motor case was exposed to a 5000 degree flame at 50 psi for over 30 seconds. This type of condition can cut plate steel when using an oxy-acetylene torch.(See Video presentation) As more applications are attempted and more testing of this material is accomplished the total potential of LCPs may soon be realized.

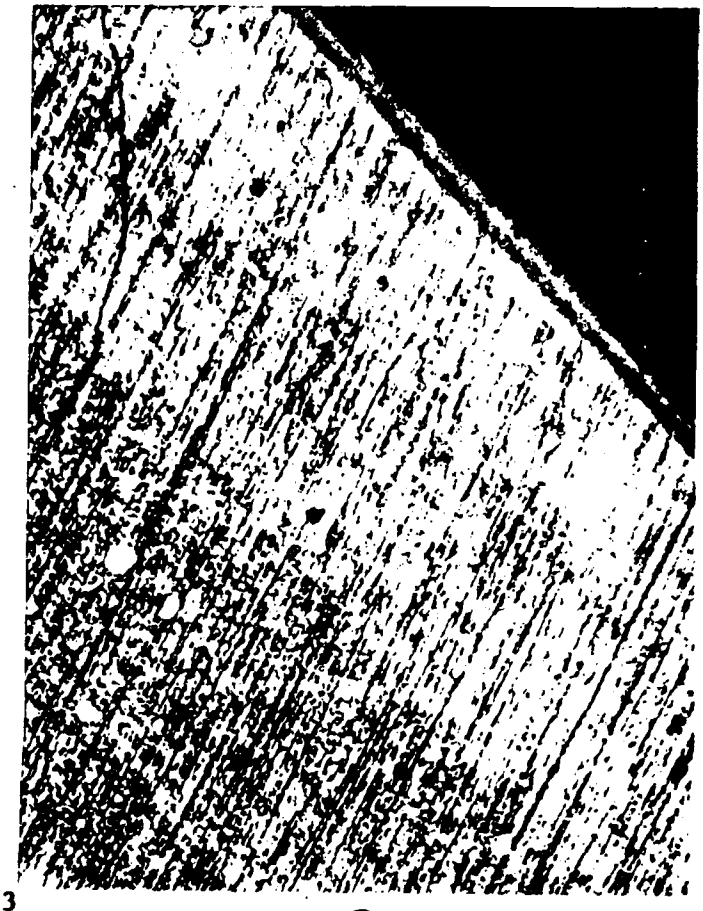
Material	Number of Rivets	Rivet Dia.	Distance of Hole From End	Max Load
Vectra C-130	4	0.125	0.3125	1007 Lbs.
Vectra C-130	8	0.125	0.5625 & 0.3125	2300 Lbs.
Vectra A-625	4	0.125	0.3125	1260 Lbs.
Vectra A-625	4	0.125	0.5625	1304 Lbs.
Vectra A-625	4	0.125	0.5625	1435 Lbs.
Vectra A-625	8	0.125	0.5625 & 0.3125	2615 Lbs.
Vectra A-950	4	0.125	0.5625	1470 Lbs.
Vectra A-950	4	0.125	0.5625	1600 Lbs.
Vectra A-950	4	0.1875	0.5625	2100 Lbs.
Vectra A-950	4	0.1875	0.5625	2050 Lbs.
Vectra B-950	4	0.125	0.5625	1850 Lbs.
Vectra B-950	4	0.125	0.5625	1400 Lbs.
Vectra B-950	4	0.1875	0.5625	2070 Lbs.
Vectra B-950	4	0.1875	0.5625	2250 Lbs.
XYDAR SRT-300	4	0.125	0.5625	1150 Lbs.
XYDAR SRT-300	4	0.1875	0.5625	1240 Lbs.
XYDAR SRT-300	4	0.1875	0.5625	1350 Lbs.
XYDAR SRT-500	4	0.1875	0.5625	1290 Lbs.
XYDAR SRT-500	4	0.125	0.5625	2244 Lbs.
XYDAR SRT-500	4	0.1875	0.5625	1290 Lbs.
XYDAR RC-210	4	0.1875	0.5625	1500 Lbs.
XYDAR RC-210	4	0.1875	0.5625	1627 Lbs.
XYDAR RC-210	4	0.1875	0.5625	1490 Lbs.

SRT 300

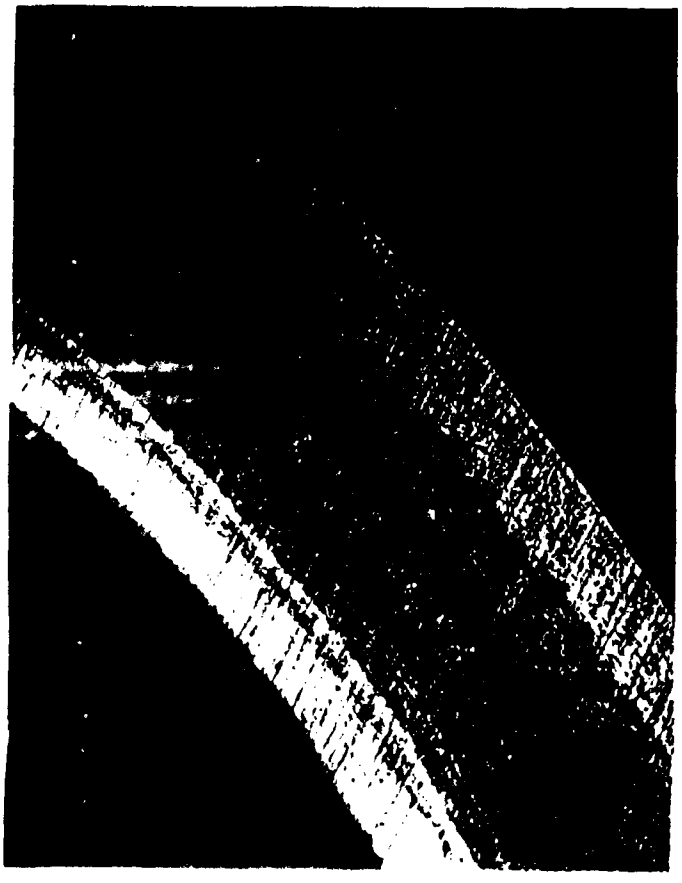
SRT 300

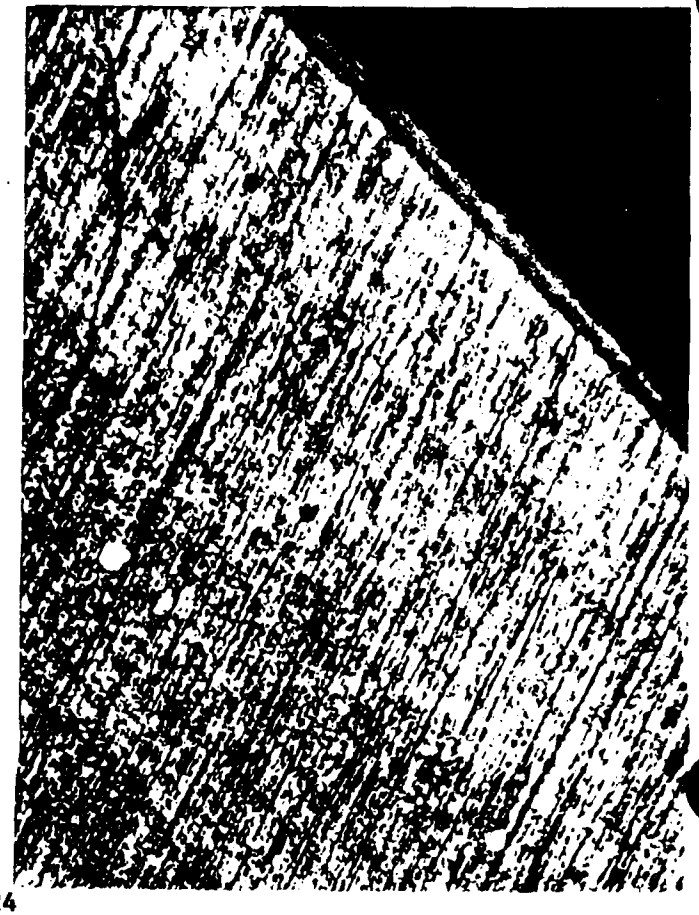


950



960





University of Lowell, Department of Plastics Engineering

The work being performed by Dr. Nick Schott and Dr. Rob Nunn at the University of Lowell, MA falls under the Macroscopic Material Properties task. Lowell has begun a research effort to injection mold test specimens and perform mechnical properties tests. Drs Schott and Nunn will develop recommended injection molding processing parameters for several Liquid Crystal Polymers. Room temperature mechnaical properties tests will be conducted to establish baselines for the material property database. The mechanical properties test will determine longitudinal tensile properties, Isotropic compressive properties, and longitudinal flexural modulus.

"Propella: Compatibility and Low Temperature CVD"

Dr. E.J. Wucherer
UDRI, OLAC PL/RKFC
(805) 275-5759, wuchere@pl-edwards.af.mil

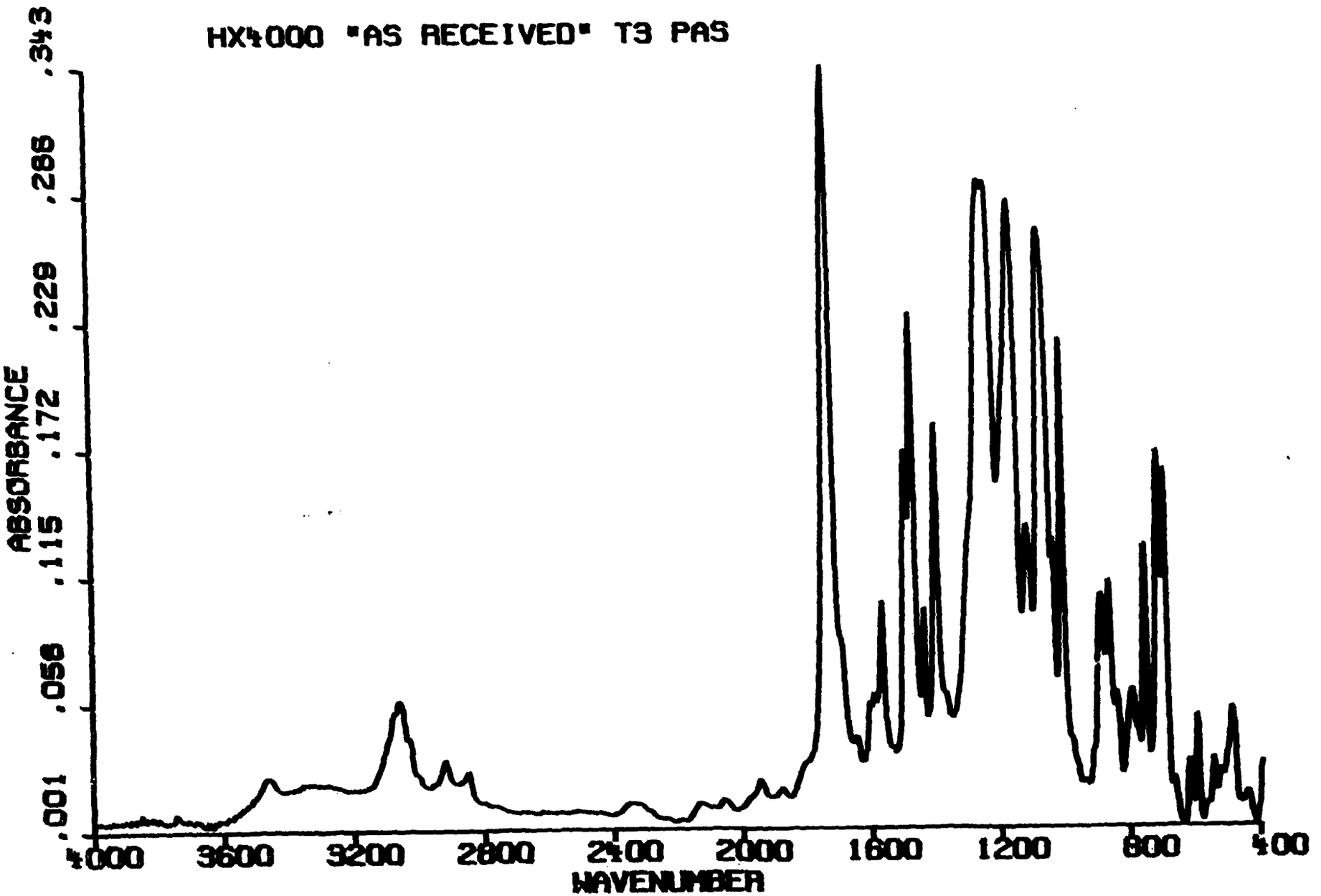
"Monomethylhydrazine (MMH) and Nitrogen Tetroxide (NTO) Compatibility with Liquid Crystal Polymers"

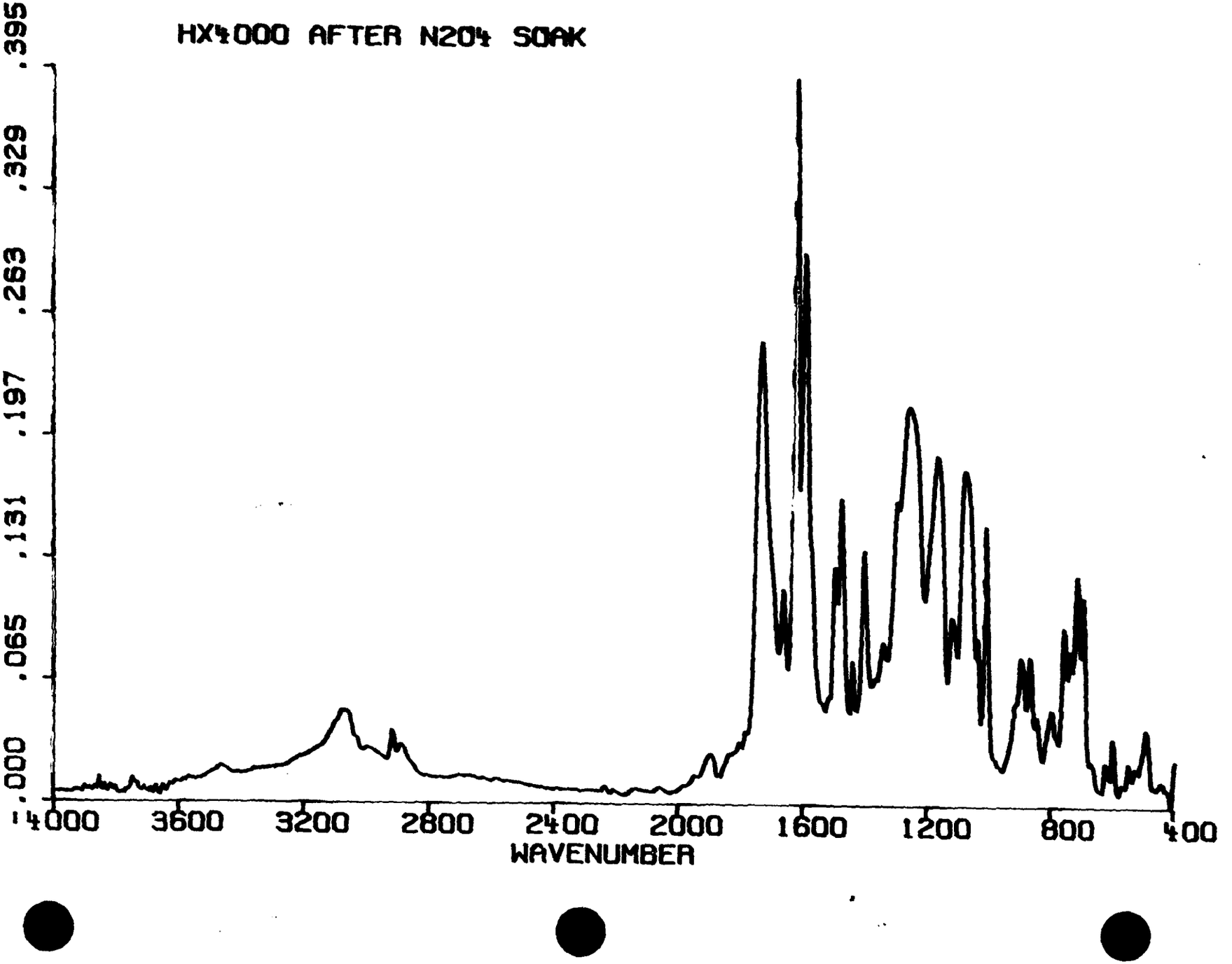
Thomas R. Hill
RKLC

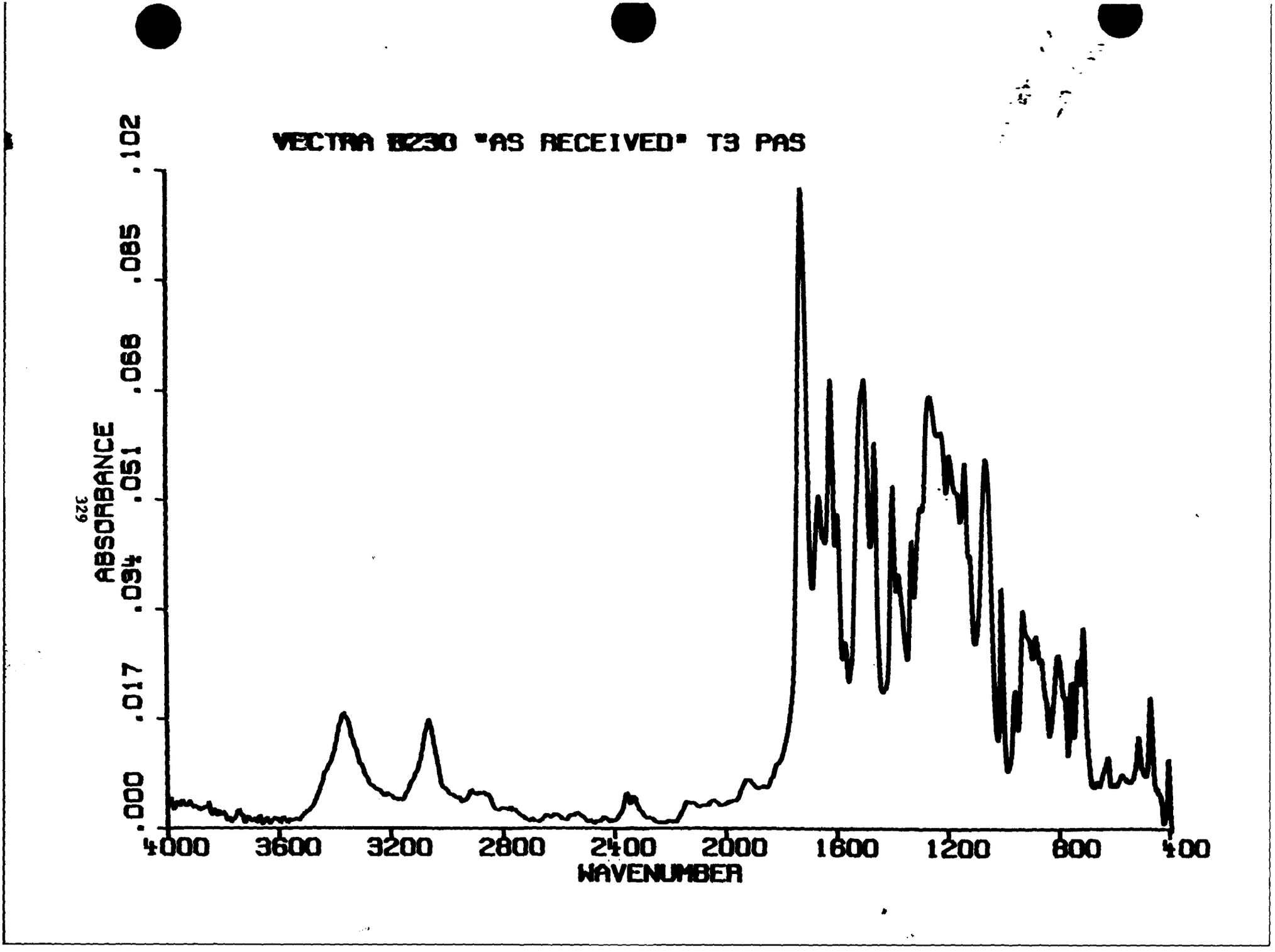
APC Symposium
21 February 1992

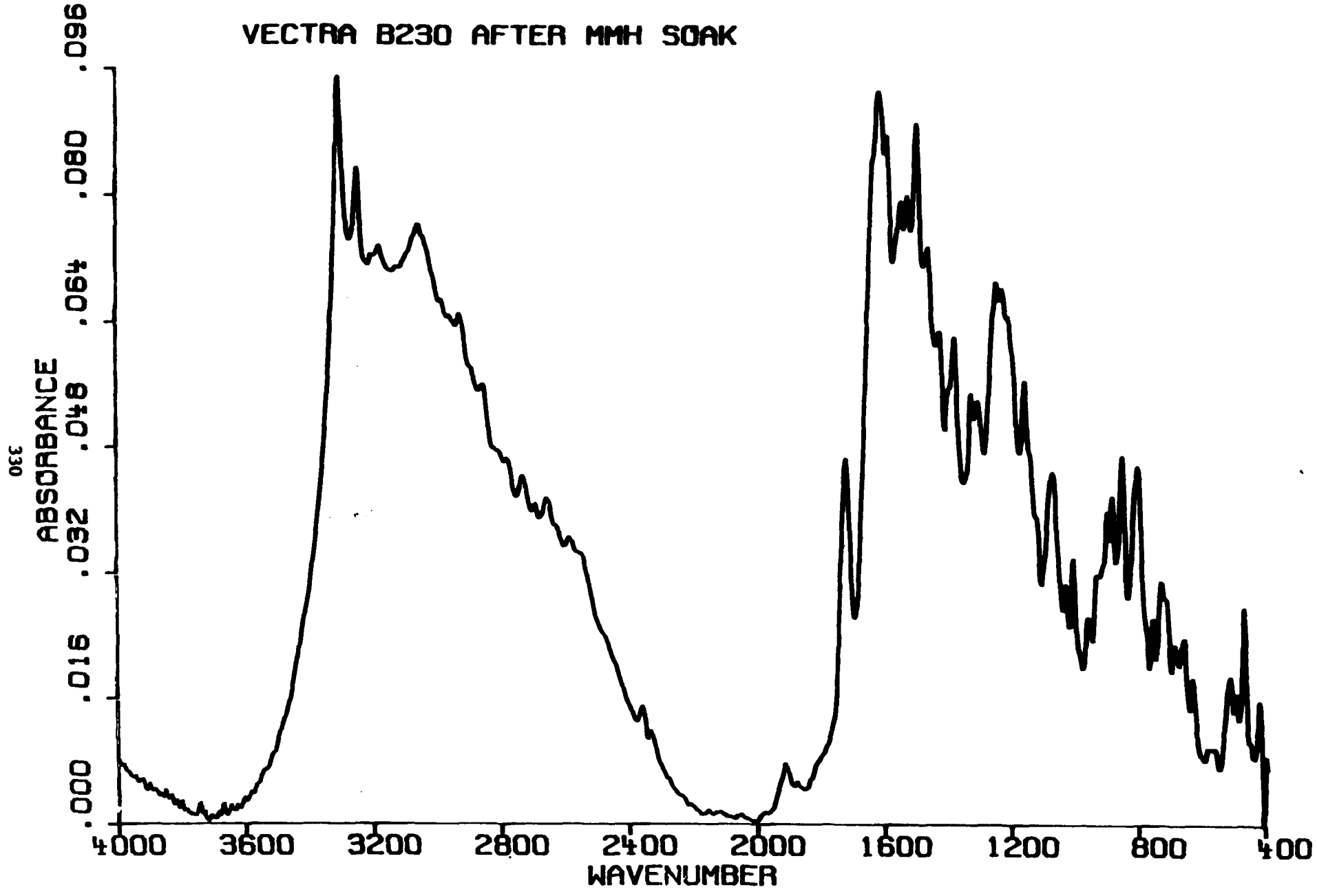
ABSTRACT: Tests conducted by Tom Hill indicated that many aromatic polyester based LPCs were incompatible with Monomethylhydrazine (MMH) and Nitrogen Tetroxide (NTO). The LCPs generally gained weight when exposed to NTO for 24h at RT, consistent with some sort of radical aromatic nitration process. Similar exposure to MMH resulted in severe sample degradation, presumably due to the formation of a hydrazide and resultant rupture of the polymer backbone.

Chemical Vapor Deposition has been used to coat some LCP samples with Aluminum films at 110C. Careful control of the sample preparation, surface pretreatment and deposition times are used to control the morphology of the metal film. Al coated Vectra substrates are resistant to attack by MMH, though film quality must be carefully controlled since any slight film defect can open a pathway for failure and substrate degradation. Several LCPs (esp HX-4000) are difficult to coat and may require mechanical roughening of their "skins" before they can be successfully coated.


HX4000 "AS RECEIVED" T3 PAS
ABSORBANCE
.001
.058
.115
.172
.229
.286
.343
4000
3600
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBER

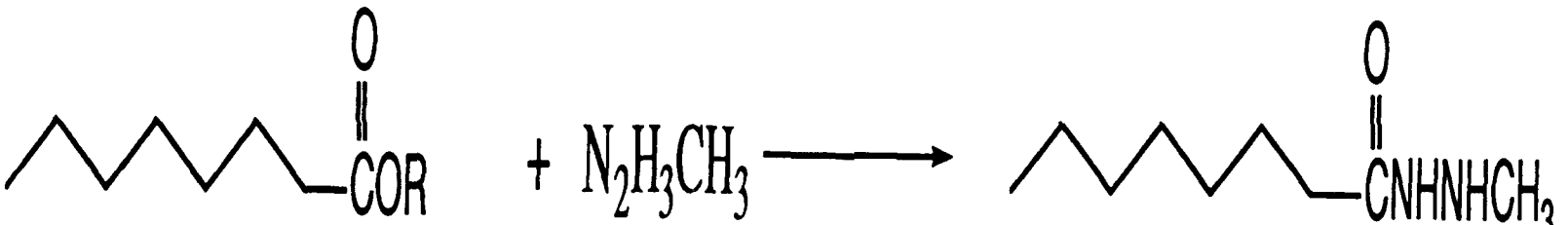

HX4000 AFTER N2O4 SOAK
ABSORBANCE
-.000
.065
.131
.197
.263
.329
.395
4000
3600
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBER


VECTRA B230 "AS RECEIVED" T3 PAS
ABSORBANCE
329
.000
.017
.034
.051
.068
.085
.102
4000
3600
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBER


VECTRA B230 AFTER MMH SOAK
ABSORBANCE
.000
.016
.032
.048
.064
.080
.096
4000
3600
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBER

COMPATIBILITY CHEMISTRY

MMH ATTACK UPON AN ESTER TO FORM HYDRAZIDE



+ ROH

A similar reaction occurred on an early Shuttle flight. N2H4 was leaking past a bearing seal into turbine oil reservoir. The hydrazine quickly reacted with the ester based oil to form a hydrazide which plugged the filtering system and delayed the launch.

MMH and NTO
Compatibility Test Reults

Material	Dimension Change		Weight Change		Color Change	
Vectra	MMH	NTO	MMH	NTO	MMH	NTO
A130	+.8%	+.016%	-16.4%	+.02%	Yellowed	Yellowed
A950	X	X	+7.5%	+.045%	NONE	Lightened
C950	X	X	-4.08%	+.04%	NONE	NONE
A625	-1.2%	NEG.	-3.2%	NEG	NONE	NONE
Ryton	+.4%	+.8%	NEG	+4.7%	NONE	1
HX-4000						
Beads	X	X	-53%	+14.2%	NONE	NONE
Solid Sample	-3.5%	+.1%	-61.3%	+2.33%	2	2
Sheet Samples Tested for Other Programs						
PBO +/-22	X	X	-13.1%	+8.4%	NONE	Darkened
PBZT +/-22	X	X	-22.7%	+30.9	NONE	Purpled
Vectra +/-45	X	X	-13.4%	+.05%	Yellowed	Browned

1 - Sample turned brown and decomposed
2 - MMH - Center of sample eaten away, surface cracked
NTO - Surface lightened and blistered

Low Temperature CVD

What:	Aluminum, nickel, copper or rhenium thin films.
Where:	On polymer, liquid crystal polymer, or polymer composite substrates.
Why:	Light weight, inexpensive, oxidation resistant, propellant compatible metals with known CVD processes.
Application:	Tanks, tubes, valves or structural materials (O atom resist).

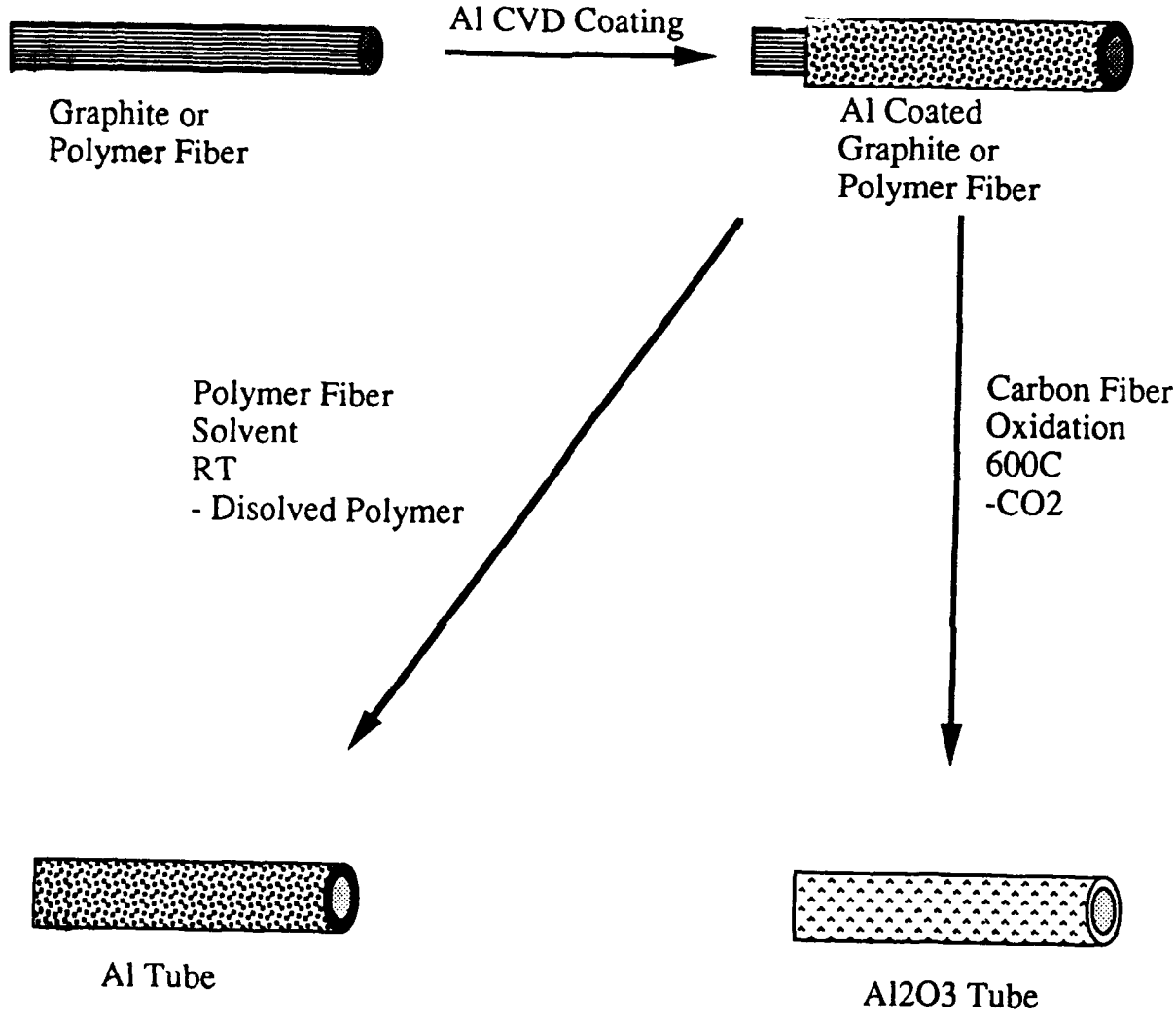
Aluminum Low Temp CVD

$$LiAlH_4 + HN(CH_3)_3Cl \longrightarrow AlH_3{\cdot}N(CH_3)_3 + LiCl + H_2$$

$$AlH_3{\cdot}N(CH_3)_3 \xrightarrow{110C} Al(s) + 3/2H_2 + N(CH_3)_3$$

$$\text{Vectra}^{TM} \xrightarrow[110C]{5\times10^{-5}\text{torr}} \xrightarrow[110C\ 30s]{TiCl_4} \xrightarrow[110C\ 30\ min]{AlH_3{\cdot}N(CH_3)_3} \text{Al-Vectra}^{TM}$$

Micro Tubes


Al CVD Coating
Graphite or
Polymer Fiber
Al Coated
Graphite or
Polymer Fiber
Polymer Fiber
Solvent
RT
- Disolved Polymer
Carbon Fiber
Oxidation
600C
-CO2
Al Tube
Al2O3 Tube

Al Coating Characteristics

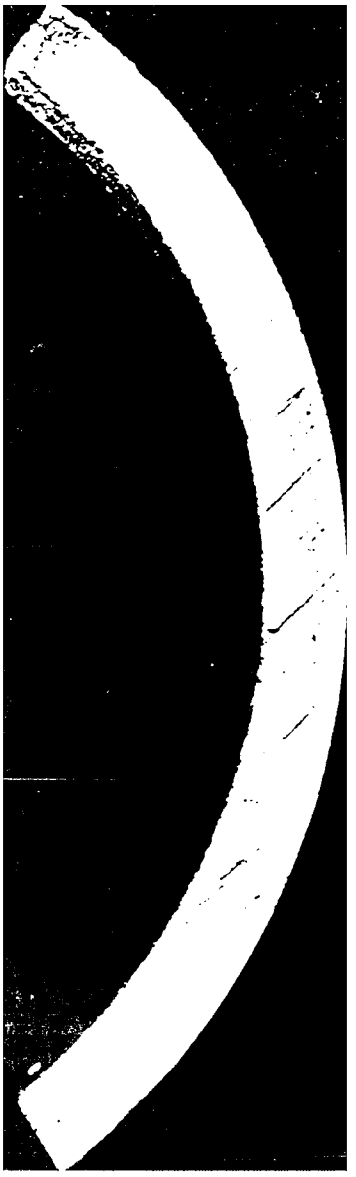
1. Nucleation and initial growth has a very fine grain resulting in a highly reflective surface.

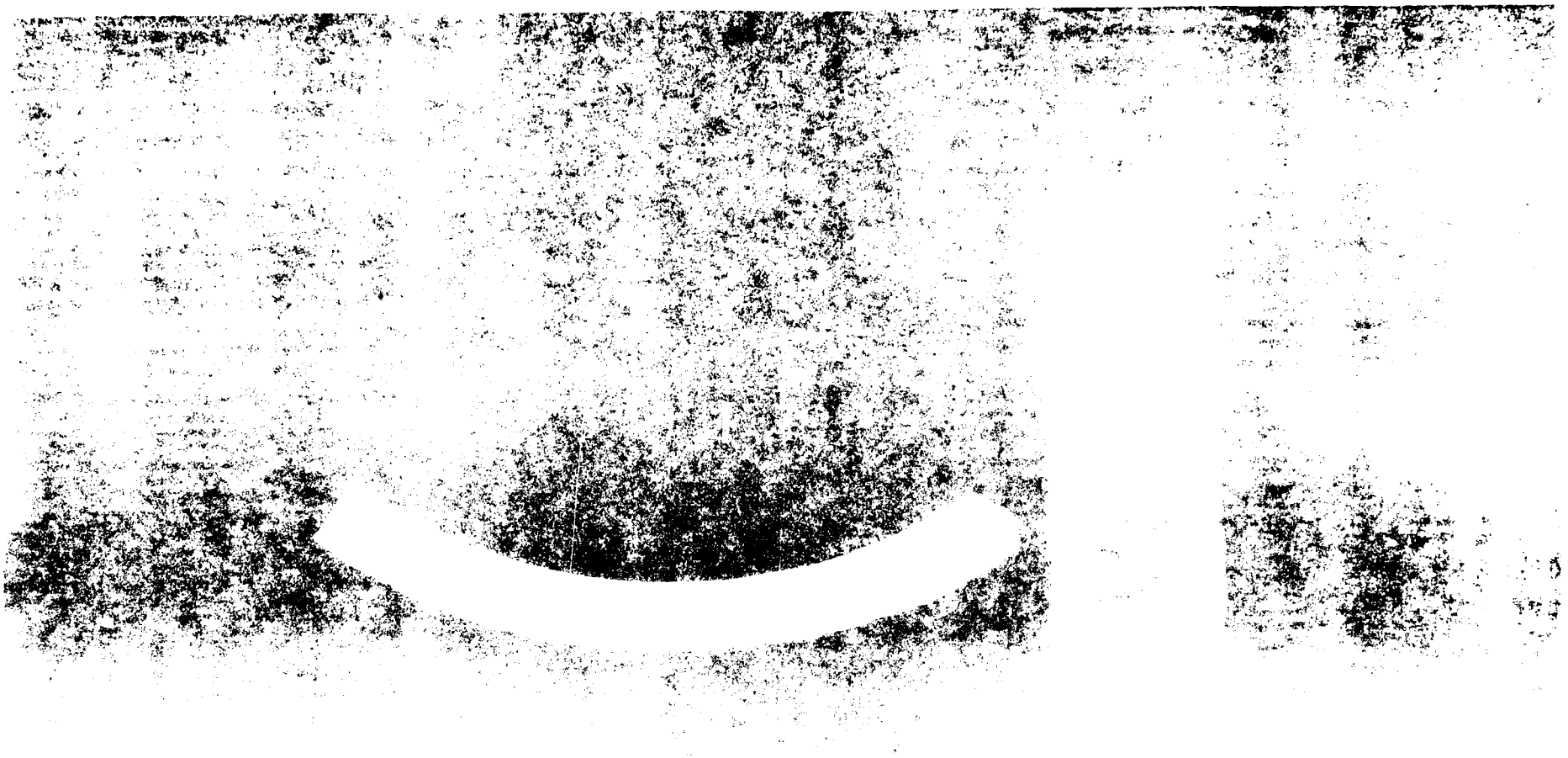
2. Growth proceeds on preferred crystalline faces, resulting in large (~1μ) grains.

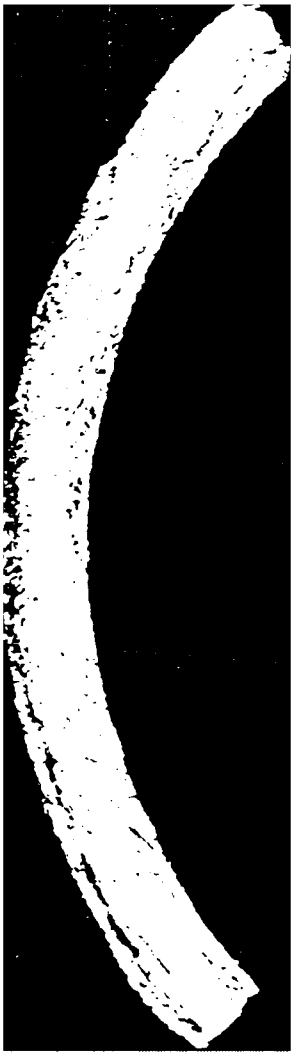
3. "Cobble stone" growth may not be the best sealant.

"Dunk" Testing

Substrate:	Vectra™ liquid crystal polymer.
Coating:	Aluminum, 4 x 1μ.
Sample:	Glass fiber filled injection molded cylinder cut into pieces approx. 1.5" x 0.38" x 0.19".
Propellant:	Monomethylhydrazine (MMH), propellant grade.
Test:	Samples immersed in MMH for 24h at RT.
Result:	Uncoated sample weight loss > 50%. Coated sample weight change ±2%.







Conclusions

1. LCPs are significantly attacked by propellants

2. CVD coatings can reduce (prevent?) degradation.

Current Problems

1. Can CVD coating prevent degradation?

2. Will coated components survive long term application in stressful environments?

2 x4 MOTOR DEMONSTRATIONS

TASK 19

The objective of this task is to determine if advanced polymers, specifically liquid crystal polymers, can be used as solid rocket case/insulation material. The tests performed in this task include solid rocket propellant to LCP bonding, LCP motor case strength, and the ablative properties of LCP's due to solid propellant exhaust.

The primary apparatus used for these experiments is a 2 in. diameter by 4 in. length cylindrical rocket motor case. Experiments done to determine if solid rocket propellant can be bonded to LCP cases showed that typical solid rocket propellants can be bonded to LCP materials with standard adhesives used in conventional rocket motor cases. The strength of LCP motor cases were determined by firing the motors at increasingly high pressures until the cases fail. Ablation properties of LCP's were studied using long duration (~ 14 seconds) motor firings where a section of each motor case is directly exposed to the high temperature (> 2800 K) solid propellant exhaust products.

FEASIBILITY OF ADVANCED POLYMERS FOR SOLID ROCKET MOTOR COMPONENTS

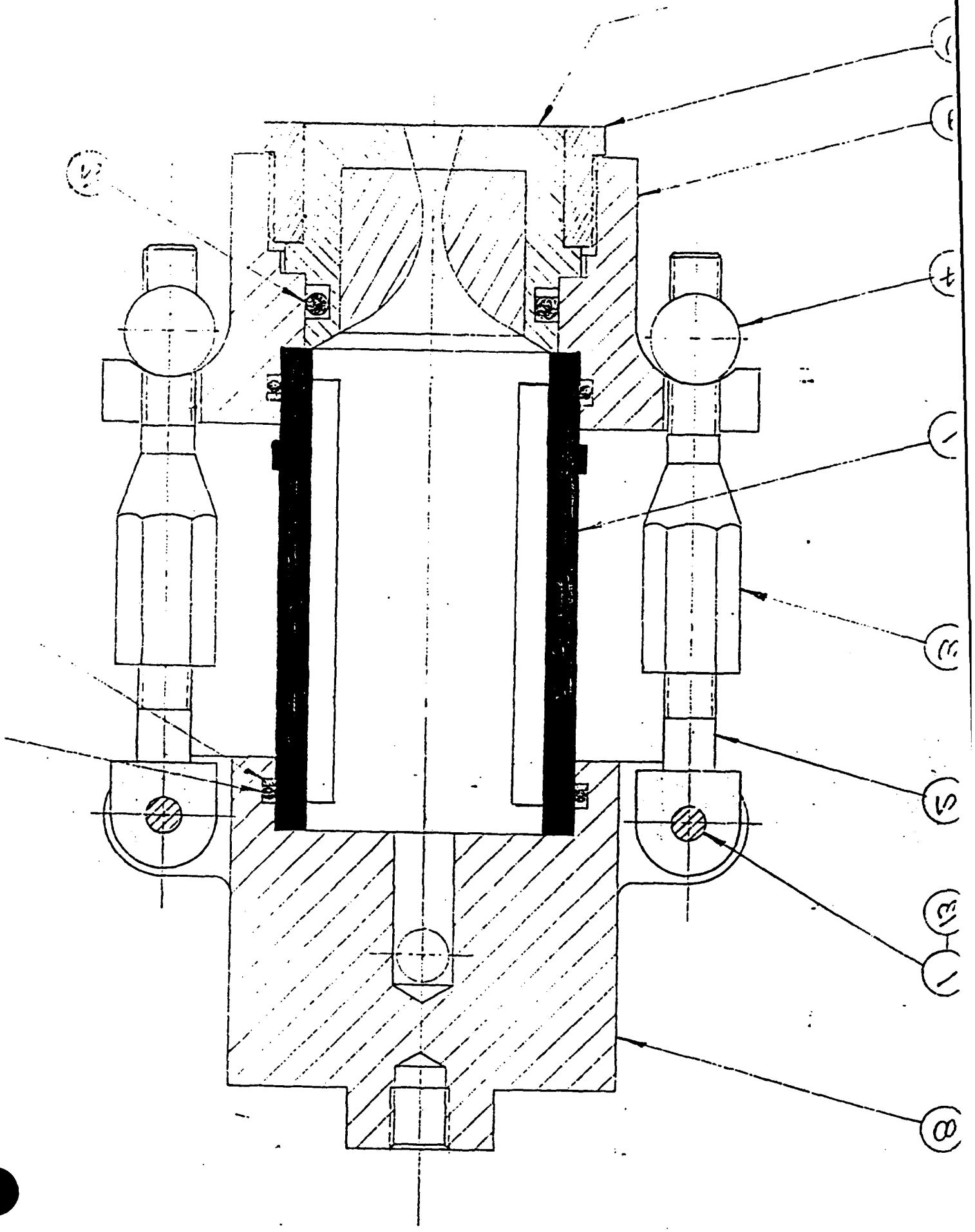
HIEU NGUYEN

- GOAL:
  - DETERMINE IF ADVANCED POLYMERS CAN BE USED AS SOLID ROCKET MOTOR CASE/INSULATION MATERIAL

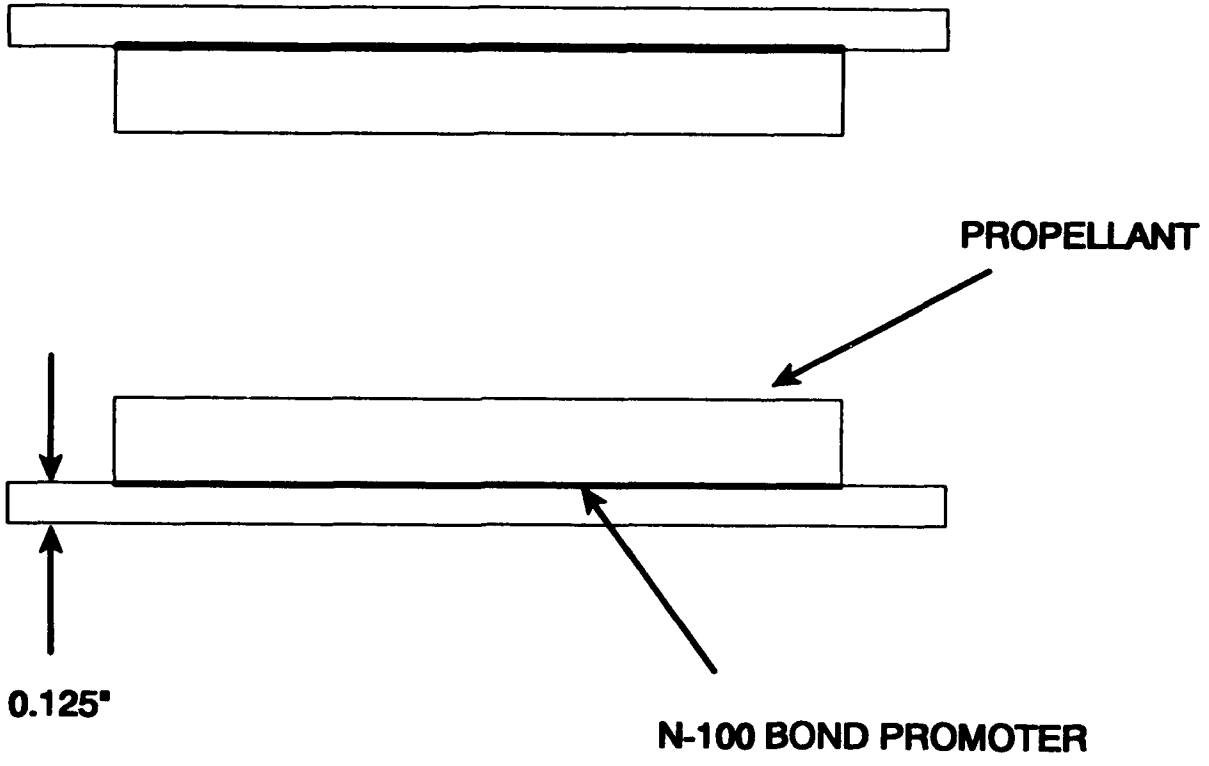
- APPROACH:
  - MANUFACTURE ADVANCED PLASTIC MOTOR CASES WITH SIMPLE CONFIGURATION (STANDARD 2IN. X 4IN.)
  - DETERMINE IF SOLID PROPELLANTS CAN BE BONDED TO THE CASES
  - TEST THE CASES:
    - BURST PRESSURE TESTS
    - ABLATION TESTS

2X4 TEST MOTOR CASES

- VECTRA C130
  HOECHST-CELANESE LCP WITH 30% CHOPPED GLASS FIBER
- VECTRA A625
  HOECHST-CELANESE LCP WITH 25% FLAKE GRAPHITE
- RYTON
  POLYPHENYLENE SULFIDE
  ENGINEERING PLASTIC WITH 30% GLASS FIBER
- VECTRA A950
  HOECHST-CELANESE LCP NEAT RESIN
- HX-4000
  DUPONT LCP

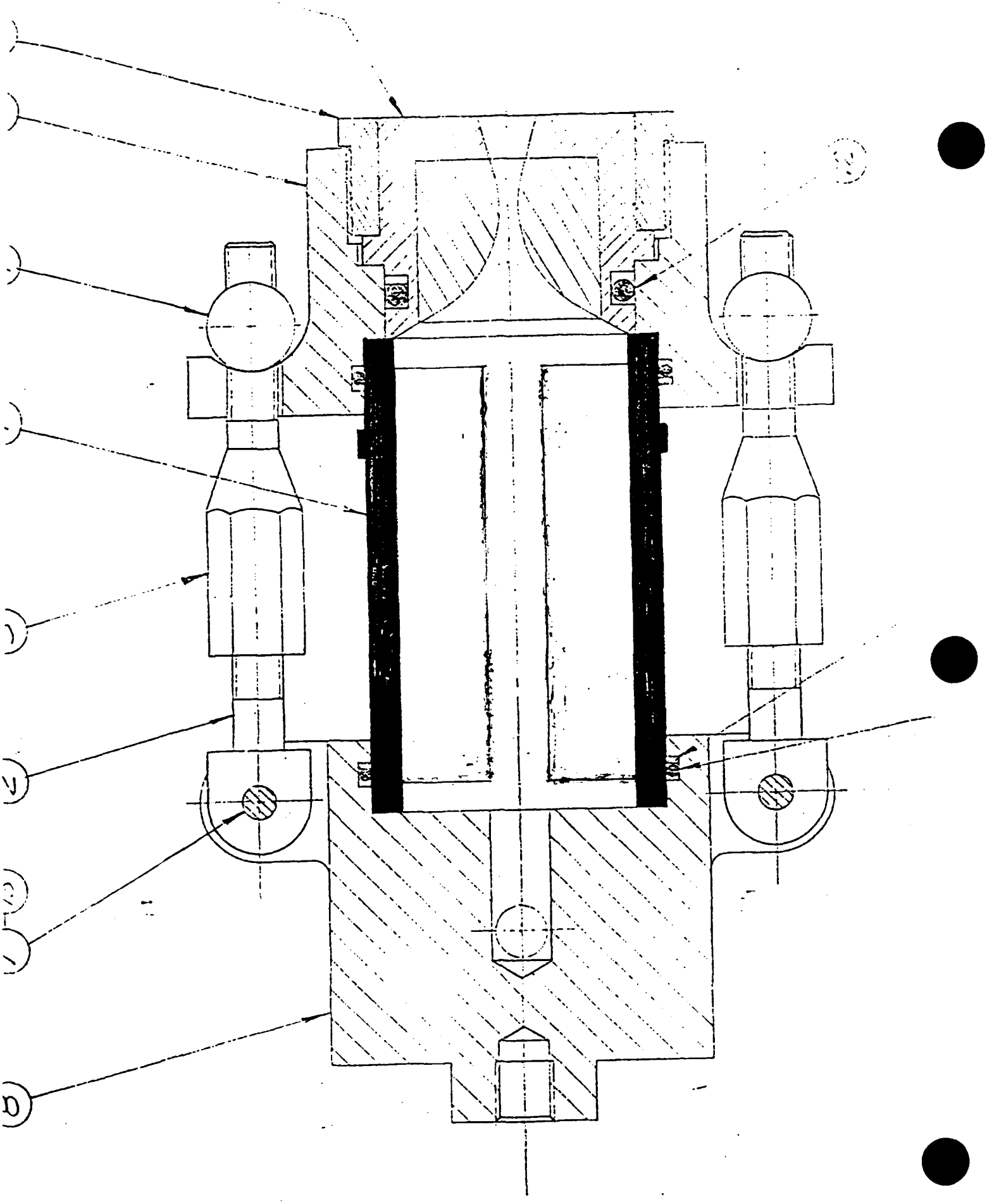


BURST PRESSURE TEST MOTOR CONFIGURATION

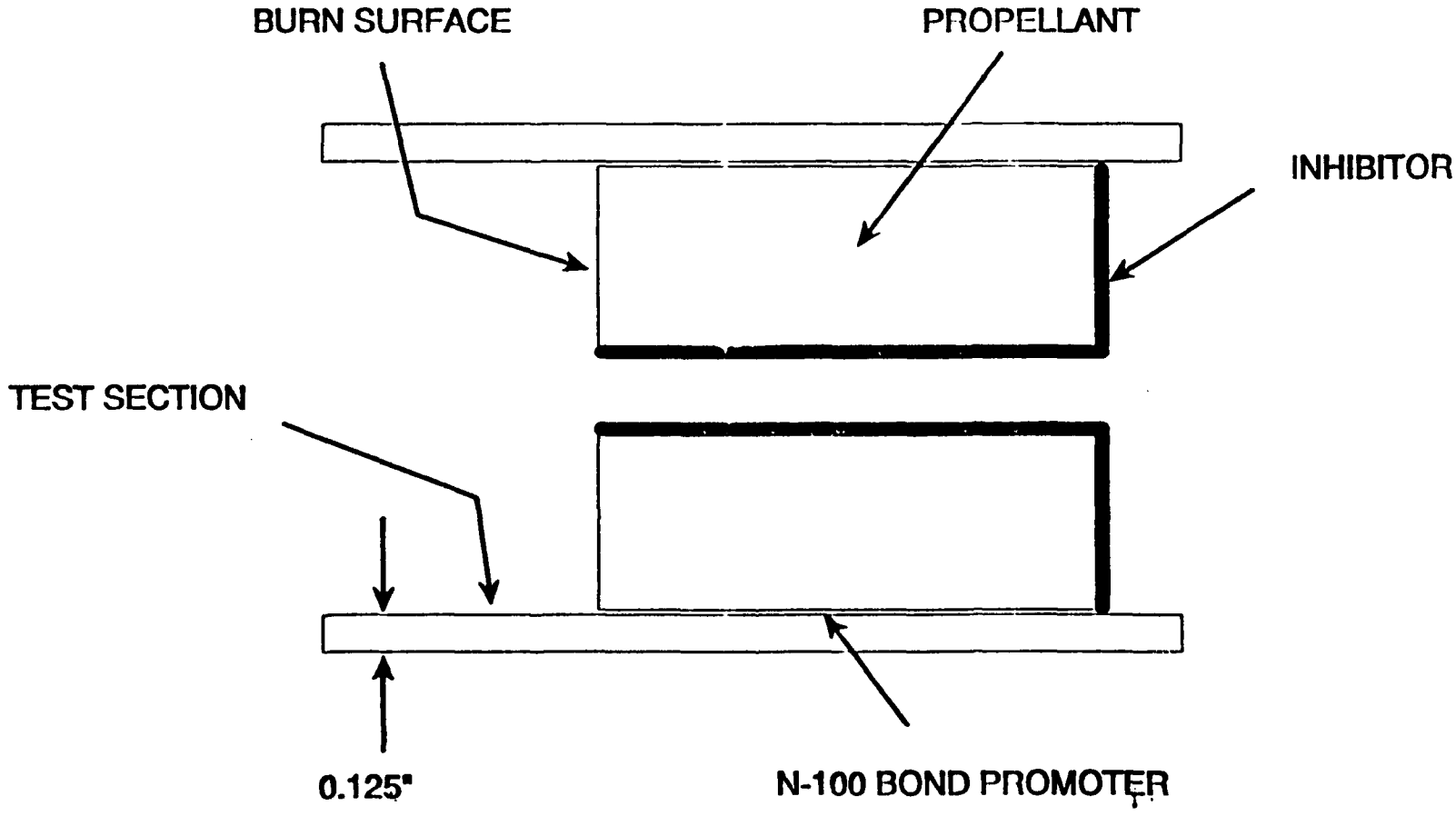


LCP 2X4 FIRINGS

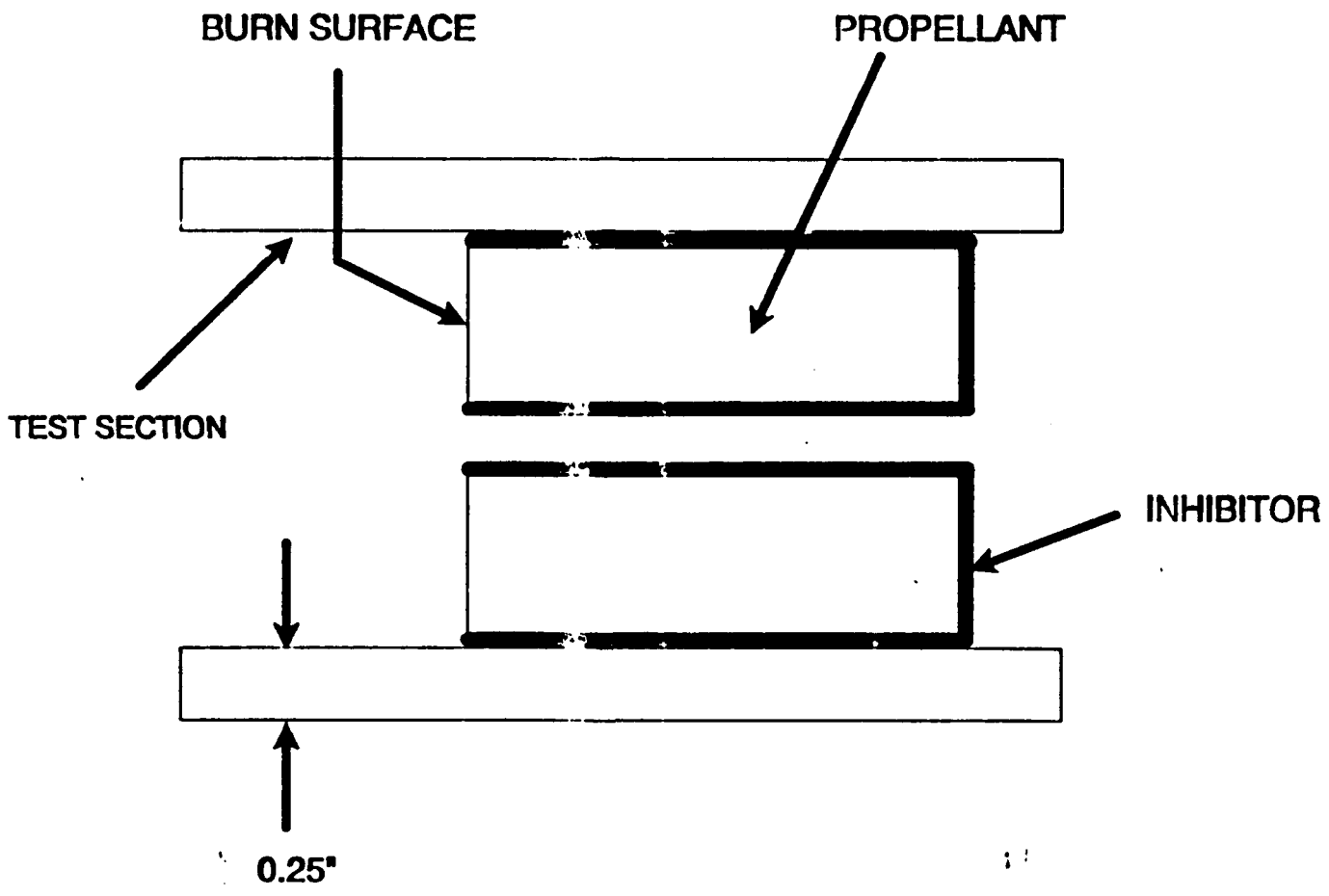
FIRING NUMBER	CASE MATERIAL	PEAK PRESSURE (PSI)	AVERAGE PRESSURE (PSI)	DURATION (SEC)	CASE/PROPELLANT BOND PROMOTER	COMMENTS
1	VECTRA C130	961	864	1.446	N-100	
2	VECTRA C130	1278		.070	NONE	FAILED ON IGNITION
3	VECTRA C130	1018	990	1.376	NONE	
4	VECTRA C130	1303		.059	N-100	FAILED ON IGNITION
5	VECTRA A625	966		.058	N-100	FAILED ON IGNITION
6	VECTRA A625	1019		.807	N-100	FAILED @ +.80 SEC
7	VECTRA A625	862	818	1.436	NONE	
8	VECTRA A625	913	876	1.419	NONE	
9	RYTON	316	269	2.346	NONE	
10	RYTON	753	727	1.578	N-100	
11	RYTON	745	713	1.605	NONE	



ABLATION TEST MOTOR CONFIGURATION
(EARLY DESIGN)



ABLATION TEST MOTOR CONFIGURATION



SUMMARY OF RESULTS

- PROPELLANT TO CASE BONDING
  - N-100 IS A SUITABLE BOND PROMOTER FOR THIN PROPELLANT GRAINS
  - CONVENTIONAL LINER RECOMMENDED FOR THICKER WEBS
- CASE STRENGTH
  - BURST PRESSURE TESTS (VECTRA C130, A625, RYTON) RESULTS AGREE WITH MACROSCOPIC ANALYSIS
- ABLATION PROPERTIES
  - VECTRA A950
    - MOTOR FIRING AT 300 PSI, 6 SEC DURATION TIME SHOWED LITTLE DAMAGE TO INSIDE SURFACE
  - HX-4000
    - MOTOR FIRING AT 300 PSI, 14 SEC DURATION TIME SHOWED MINIMAL DAMAGE

FUTURE PLANS

- ANNEAL HX-4000 MOTOR CASES
- TEST HX-4000 CASES
  - BURST PRESSURE
  - ABLATION

No-Deposit, No-Return Spacecraft

J. T. Kare
Lawrence Livermore National Laboratory, USA

In ground-to-orbit laser propulsion, a ground-based laser supplies energy to a small rocket vehicle. The laser energy heats an inert propellant, which is exhausted to provide thrust. The rocket can be both simpler and higher in performance than a conventional chemical rocket, and (with some designs) can be steered from the ground, by controlling the laser beam. However, to make economical use of the laser, a very large number of payloads must be launched -- up to 30,000 per year. The individual rocket vehicles must therefore be very inexpensive.

One laser propulsion technology, under development at LLNL, uses a high-performance heat exchanger to absorb the laser energy and transfer it to the liquid hydrogen propellant. HX (Heat eXchanger) vehicles basically consist of a liquid hydrogen tank, a flat metal heat exchanger, and one or more nozzles. The hydrogen is pressure-fed from the tank, at a typical pressure of 70 psi, and heated to 1000 to 2000 K in the heat exchanger. It is exhausted at a typical pressure of 25-30 psi.

If such vehicles are to be both feasible and economical, low-cost, light-weight components are essential. LLNL is developing a low-cost electroplating technique to fabricate heat exchangers. Advanced polymers, with their high strength to weight ratios, good thermal performance, and low fabrication cost, could be useful for other parts. In particular, blow-molding might allow cheap fabrication of meter-scale liquid hydrogen tanks with better performance than aluminum tanks. Other structural components, and perhaps even "hot" parts such as nozzle skirts, might be made by injection molding. The very short working life (5 minutes) and low operating stresses of these parts would allow operation at the very edge of their mechanical and thermal limits. A potential future advantage would be that such plastic parts could be recycled in space, either as thermoplastics or as a simple stockpile of carbon and hydrogen.

A near-term demonstration of HX technology is planned, using a 50 kW laser and a 10 cm diameter heat exchanger. This "bottle rocket" will use liquid nitrogen propellant, and will need a 1 to 2 liter propellant tank. Fabrication of such a tank would be a good test of blow-molding techniques for advanced polymers.

KEY POINTS ABOUT LASER PROPULSION

- LASER PROPULSION VEHICLES ARE VERY SMALL
  - Typical payload is 10's to 100's of kg
  - Typical initial vehicle mass is 100's to at most a few thousand kg

- VERY LARGE NUMBERS OF VEHICLES ARE NEEDED
  - Minimum economical launch rate is of order 10,000 per year
  - Flat-out rate is 1 launch/15 minutes
    - That's 100 per day, ≈300,000 per year
    - Even at 20 kg each, that's 600 Tons of payload per year

- VEHICLE COST MUST BE KEPT VERY LOW
  - Goal for total cost per launch is <$250/kg ($100/lb)
  - Vehicle cost should be ≈1/3 of total
    - <$2000 per vehicle for a 20 kg payload
    - Almost certainly too cheap to bring down and reuse

- VEHICLE MASS IS ALSO CRITICAL FOR "HX" THRUSTER

POTENTIALLY PLASTIC PARTS in the HX Rocket

- Liquid Hydrogen Propellant Tank
- Structure and "Plumbing"
- Perhaps even "hot" parts, e.g., nozzle skirts
- Why?
    - Better strength-to-weight than low-cost competition (e.g., Al)
    - Extremely low fabrication cost in high volume
    - Minimum parts count and assembly effort
        - Molded-in ports, mounting flanges, etc.
        - Perhaps even "snap together" rocket parts

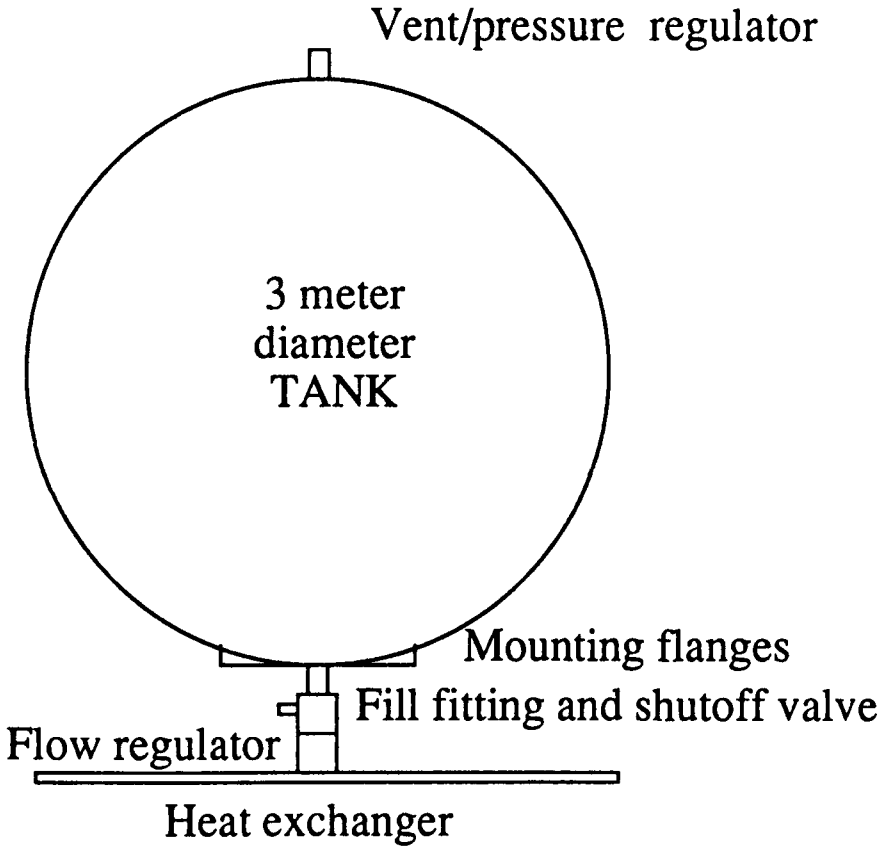
PROPELLANT TANKS -- First Use

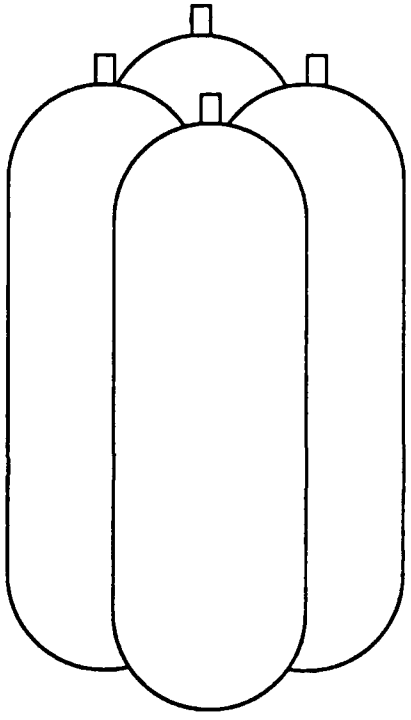
- Tank holds liquid hydrogen propellant at 30 degrees K
  - Tank pressure is nominally 70 psi
  - Tank volume is nominally 10 cubic meters
    - 2 - 3 meter diameter (if spherical; not a requirement)
    - Only 70 kg/m^3; tank is almost purely pressure loaded (a balloon)

- Competition (1) is an aluminum tank
  - Nominal wall thickness ≈1 mm
  - Nominal strength 50,000 psi (at density 2.7)
  - Nominal "figure of merit" ε = .085 (tank mass/propellant mass)

- Competition (2) is a fiber-wrapped aluminum (or plastic) tank
  - Potentially very light and strong; ε = .03 or so
  - But currently *very* expensive by these standards

PROPELLANT TANK CONCEPT





Multiple cylindrical tanks
are an alternative

OTHER APPLICATIONS

- General structure -- maximally lightweight molded parts
  - Aerodynamic shell/stray light shield
  - Payload supports
  - Central part of heat exchanger supports (up to T≈400 K)

- Plumbing -- lightweight cryogenic parts
  - Main flow regulator(s) at tank outputs
  - Pipes from tank to heat exchanger(s)
  - Low-temperature (100 K, 400 K) gas manifolds

- Nozzle extensions
  - Exhaust is 1250 K to 2000 K hydrogen, 30 psi at the throat
  - Low gas density and short (5 minute) operating time may allow, e.g., metal plated parts to survive uncooled

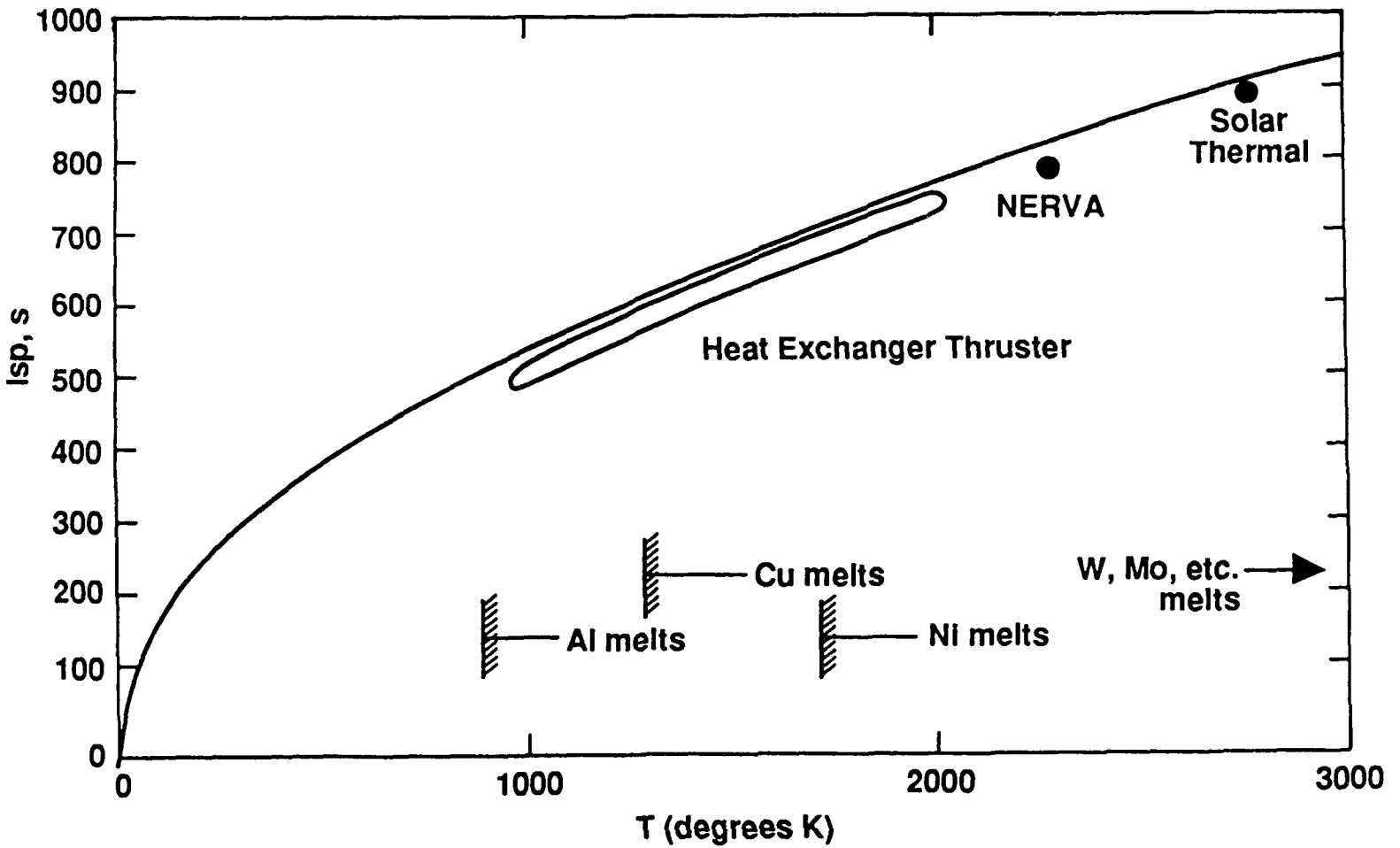


Figure 2: Ideal Isp vs. T for undissociated hydrogen

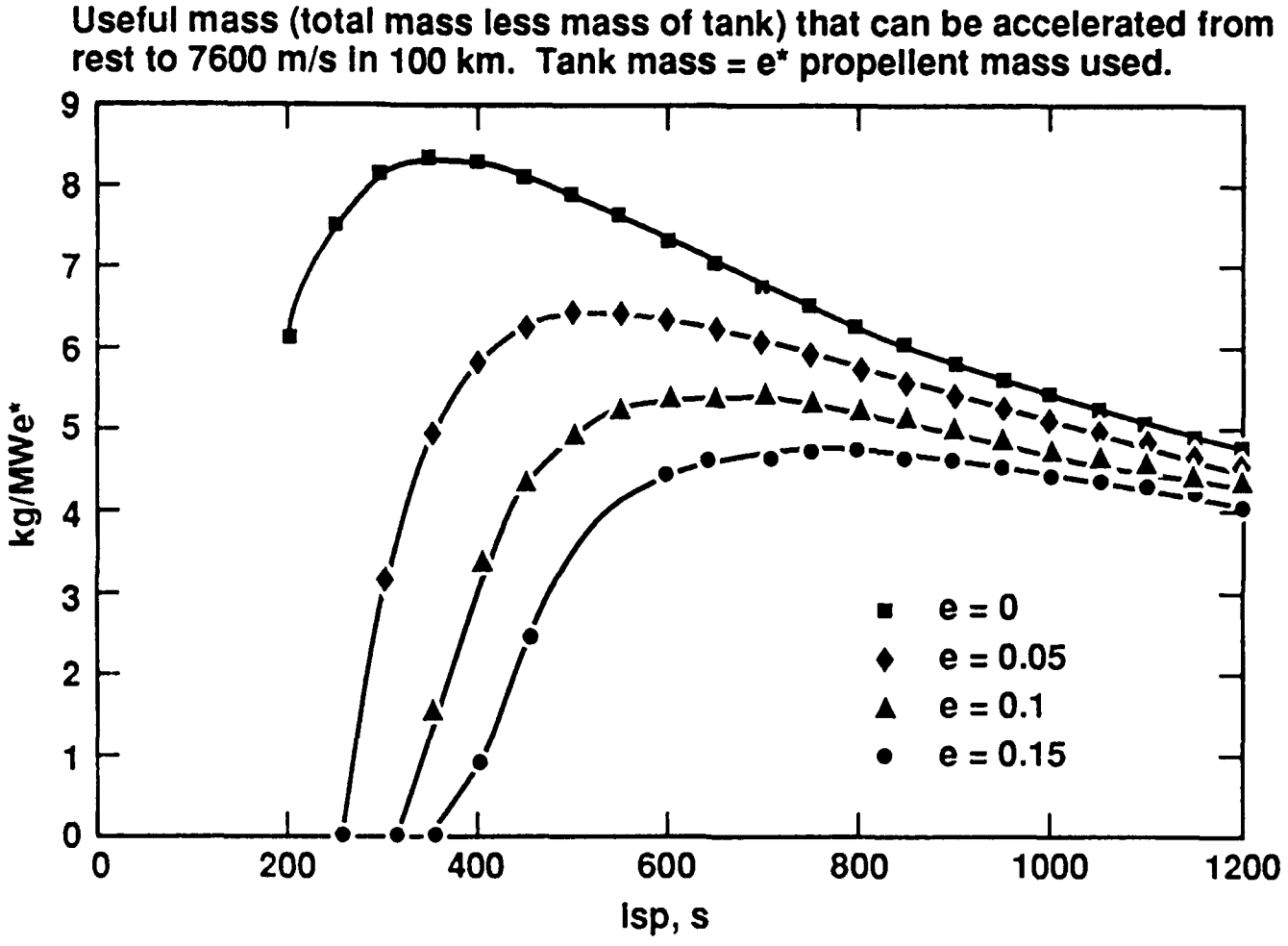


Figure 3: "Mass to orbit" vs. Isp and tank mass

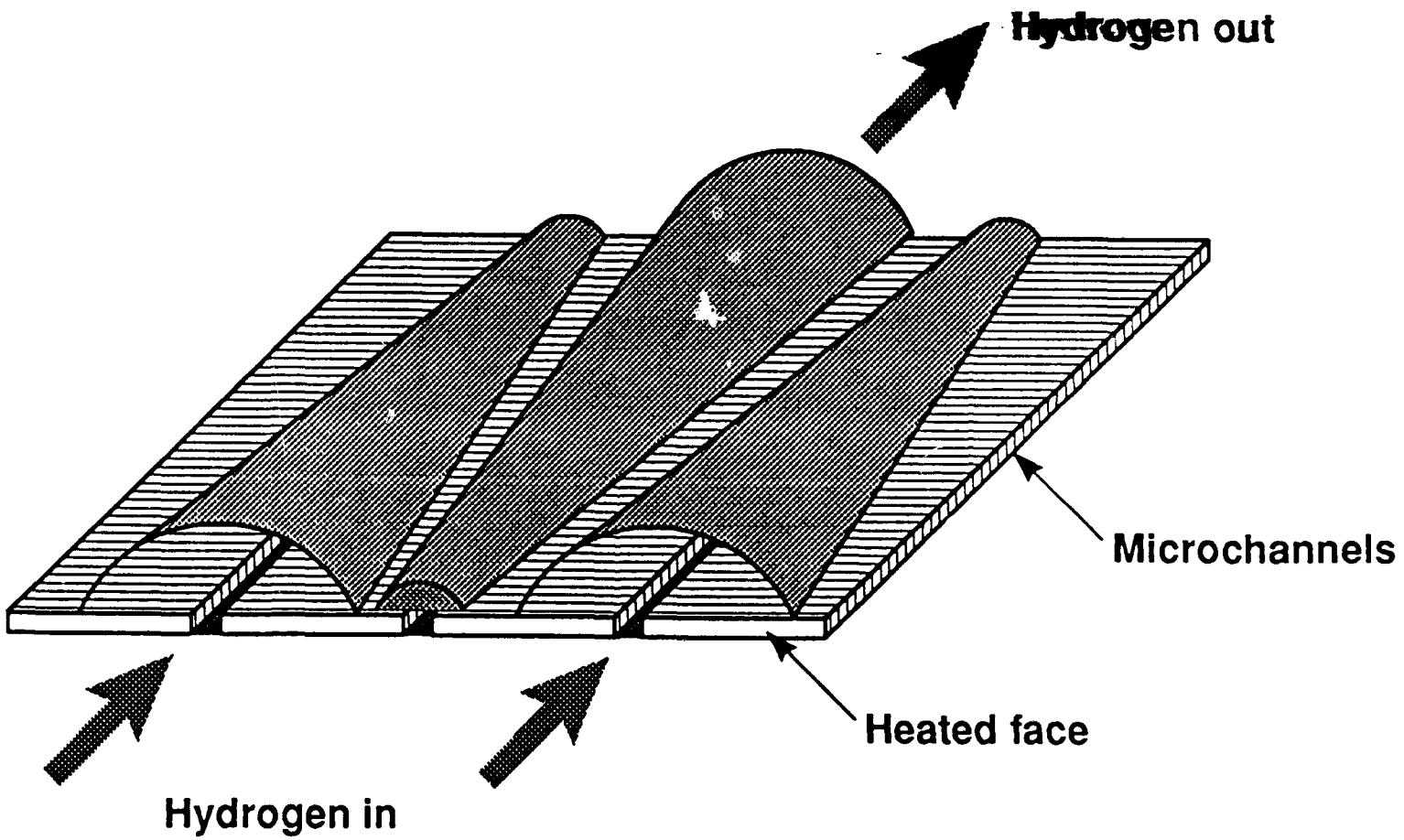


Figure 5. Heat exchanger assembly

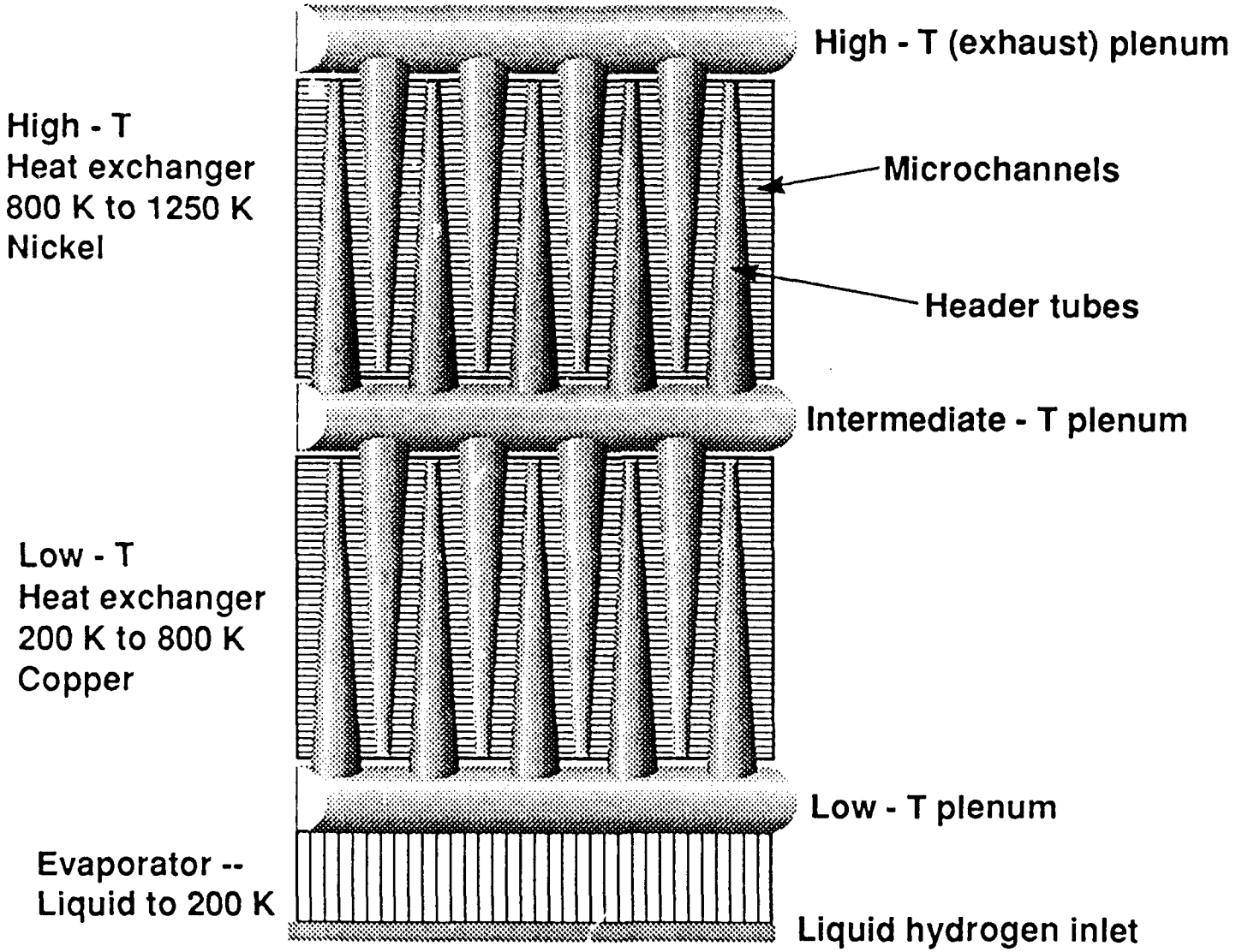
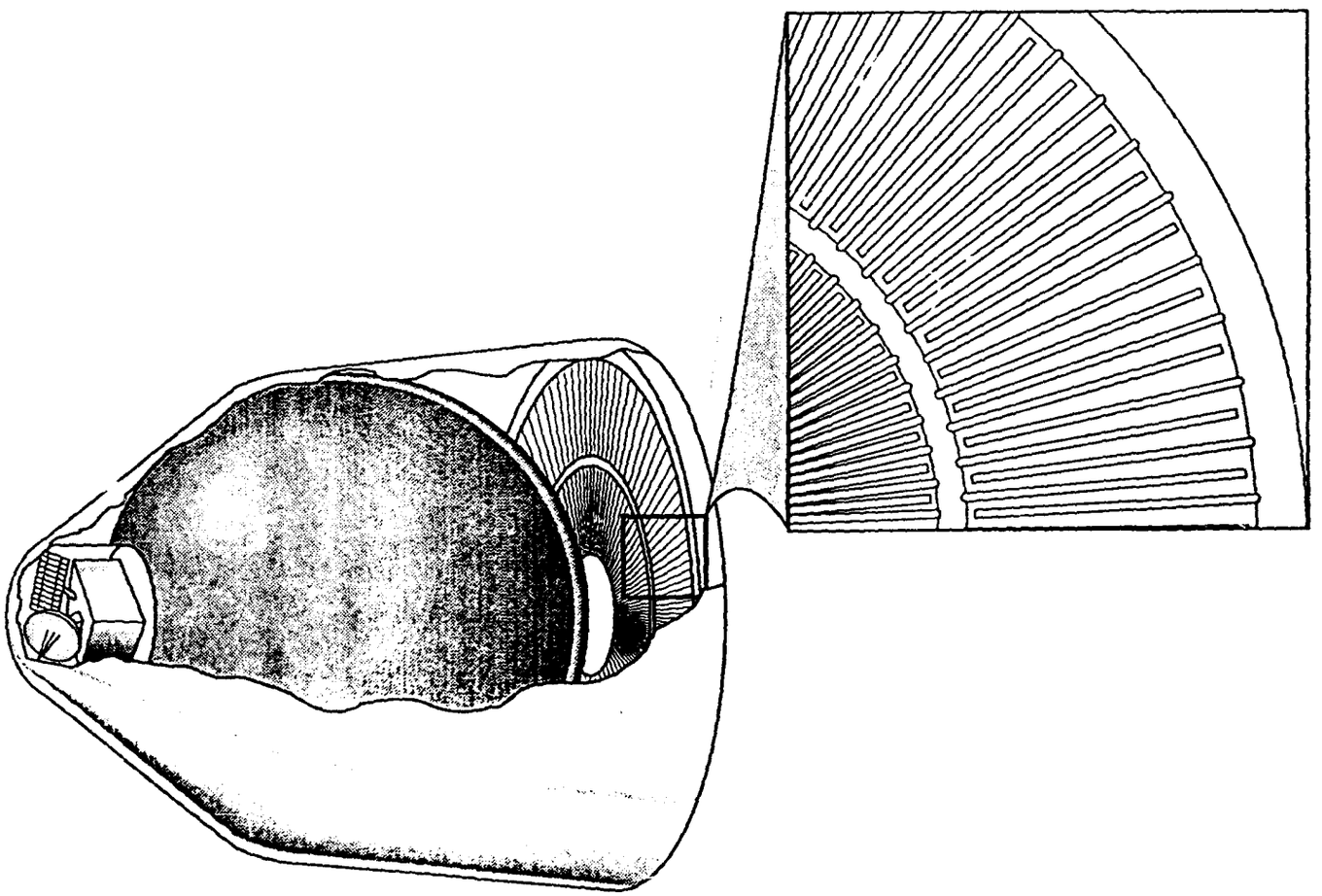
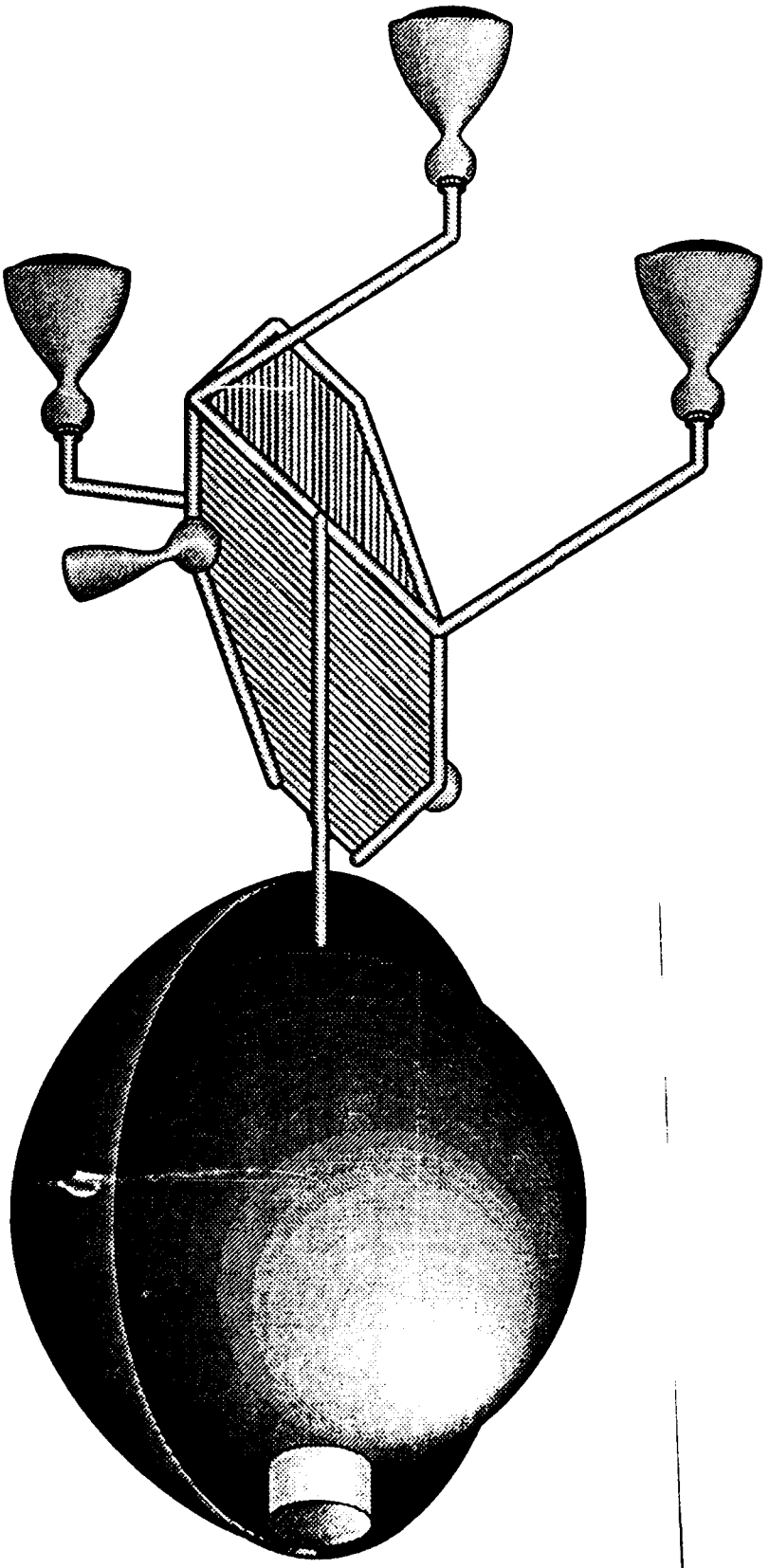
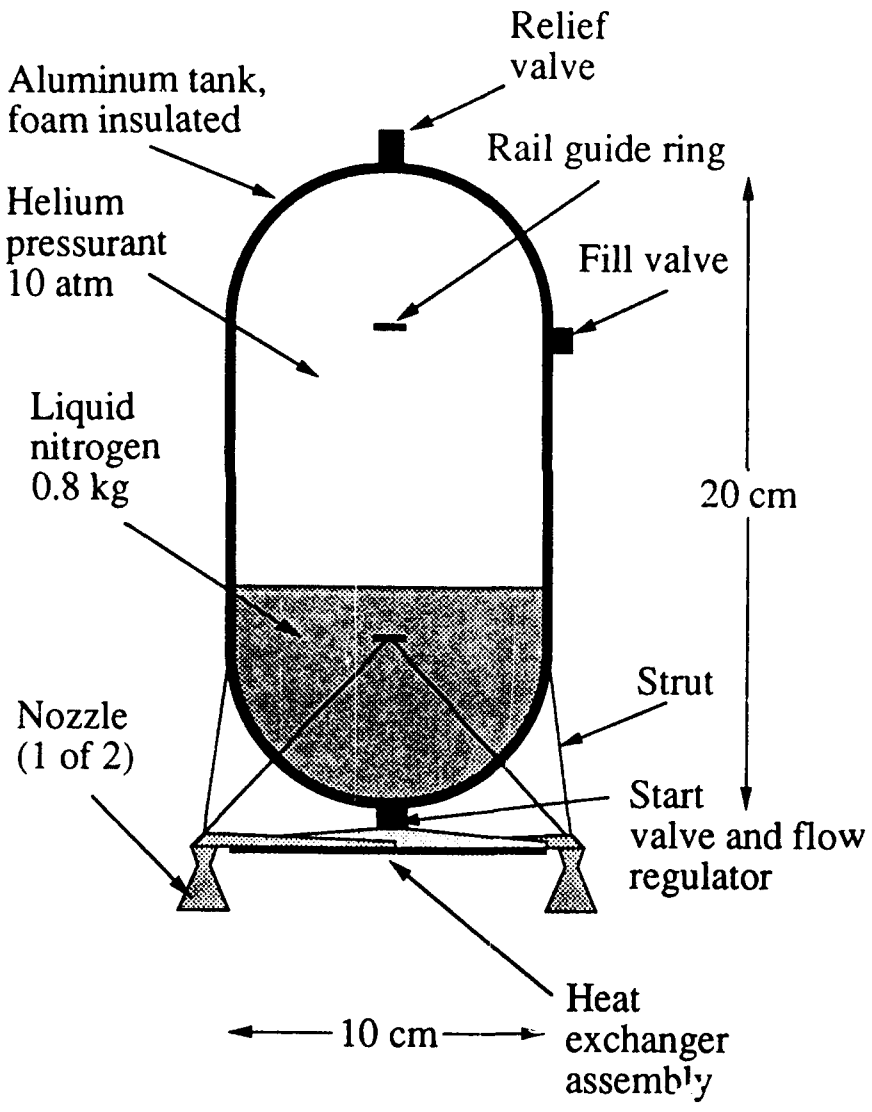


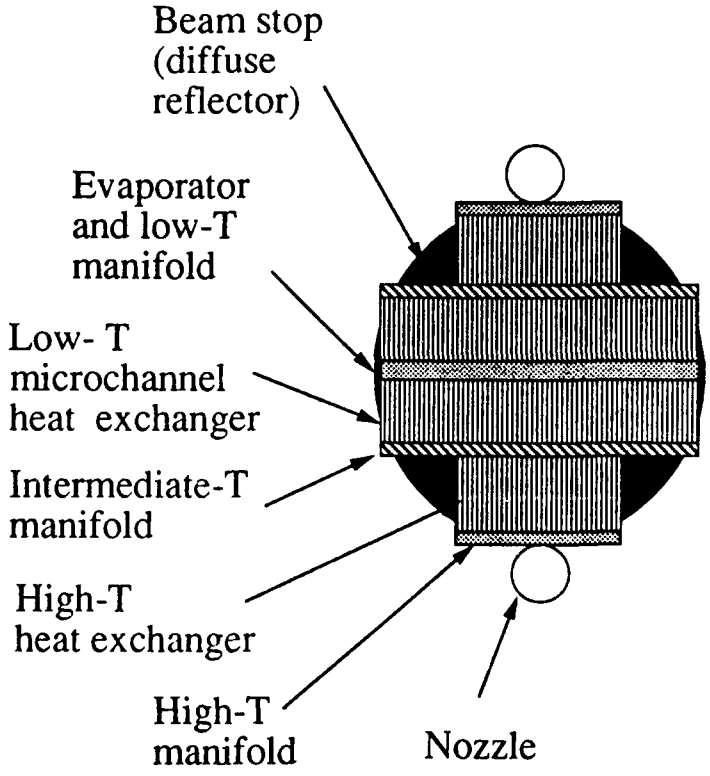
Figure 6. Multistage heat exchanger assembly
(Conceptual only -- not to scale)





50 kW Heat Exchanger "Bottle Rocket"





Bottom View

DEPARTMENT OF THE AIR FORCE
HEADQUARTERS OGDEN AIR LOGISTICS CENTER (AFLC)
HILL AIR FORCE BASE, UTAH 84056-5069

REPLY TO ATTN OF: OO-ALC/TIELM 3 Mar 92

SUBJECT: Interest in the APC Program

TO: AL/RKP (Dr Rusek/275-5430)

1. The purpose of this letter is to provide background information on my interest in the APC program, provide any applicable information and capabilities, and define any future requirements.

2. My educational background is a B.S.in Engineering Science and Mechanics. I am presently serving as an Air Force Captain at Hill AFB. My present job specialty is working in a laboratory environment performing failure analysis from a metallurgical viewpoint. I have had training and experience in advanced composite structures and injection molding processing.

3. My interest in the APC program originated as a funds manager at Hill AFB. My task was to program funds for injection molding projects and prototyping. My function is to act as a laison between the plastics shop and the funding people to insure the materials are available, work orders are accurate, and training for the plastic shop personnel is available. Hill AFB is one of two sites within the Air Force that has injection molding capabilities. McClellan AFB has a large injection molding machine managed by Mr Chris Franks. Hill AFB has a smaller injection molding machine capable of molding parts up to approximately twenty ounces, managed by Mr Rich Griffin. Several of the parts that were displayed at the recent APC Symposium were manufactured at Hill AFB. Currently my interest lies in developing an understanding of liquid crystal polymers (LCPs) and tying that to an Air Force application. Current projects include molding a thermoplastic radome for fighter aircraft.

4. Please call for specific information on the injection molding capabilities if you are interested or have a potential use. In addition, we have scanning electron microscopes (SEM) available for testing purposes in the metallurgical laboratory.

5. Future requirements will be to continue support of the APC program. Hill can serve as the distribution point of commercial grade quantities of LCPs for your research. Presently, we have on hand quantities of Zydar 300 & 500, HS4000, and Vectra.

6. If any questions, please contact the undersigned commercially at (801) 777-2874 or 775-2482 and DSN 458-2874 or 924-2482. Our FAX number is (801) 777-8049.

Steven B. Hardy

STEVEN B. HARDY, CAPT, USAF
Materials and Processes Engineer
Metallurgical Section
Technology and Industrial Support
Directorate

ADVANCED POLYMER COMPONENTS RESEARCH SYMPOSIUM

Mercer Engineering Research Center
1861 Watson Boulevard
Warner Robins, GA 31093

The primary focus on advancing the understanding and enhancing the physical properties of Liquid Crystal Polymers (LCP) is the pursuance of applications in the astronautics community. LCPs are prime candidates for space applications because of their high strength to weight ratio. However, the remarkable mechanical properties and thermal stability of LCPs also make them desirable candidates for a multitude of more common applications where weight savings are advantageous. These common applications range from military aviation to the private automobile.

Mercer Engineering Research Center is currently interested in the development of LCPs because of its applicability to military aviation. The design evolution of military and commercial aviation has gone from primarily aluminum structures to a heavy reliance on composite materials. This reliance has been primarily fueled by the increased strength to weight ratio of these composite materials. However, composite materials are not without their problems. Delamination, loss of strength due to aging, and structural integrity non-destructive testing are some of the problems inherent with composite materials. As our military and commercial aircraft design demands continually increase, new materials will be required to fulfill the dreams of these new designers. LCPs are prime candidates for these new materials.

While the aircraft industry is looking to the future and continually stretching material technology as it goes, there are still hundreds of older aircraft that could also benefit from this new technology. Because of high replacement cost, these older aircraft are being required to fly beyond their design life with added demands of more aggressive mission profiles. As a result, structural failures are becoming common place. Instead of just repairing the failures, upgrades to the design are generally warranted. The designers of these upgrades must keep abreast of new technologies that may provide an alternative with enhancements. This has inherent benefits to the user,i.e. increased structural integrity, lower weight, and better performance.

As the technology of the LCPs matures, the areas of its applications will become better defined. As space is an obvious environment for LCPs, other more down-to-earth environments and applications are logical extensions of this technology.

POC: Terry Fuchser, ph. (912) 929-6444

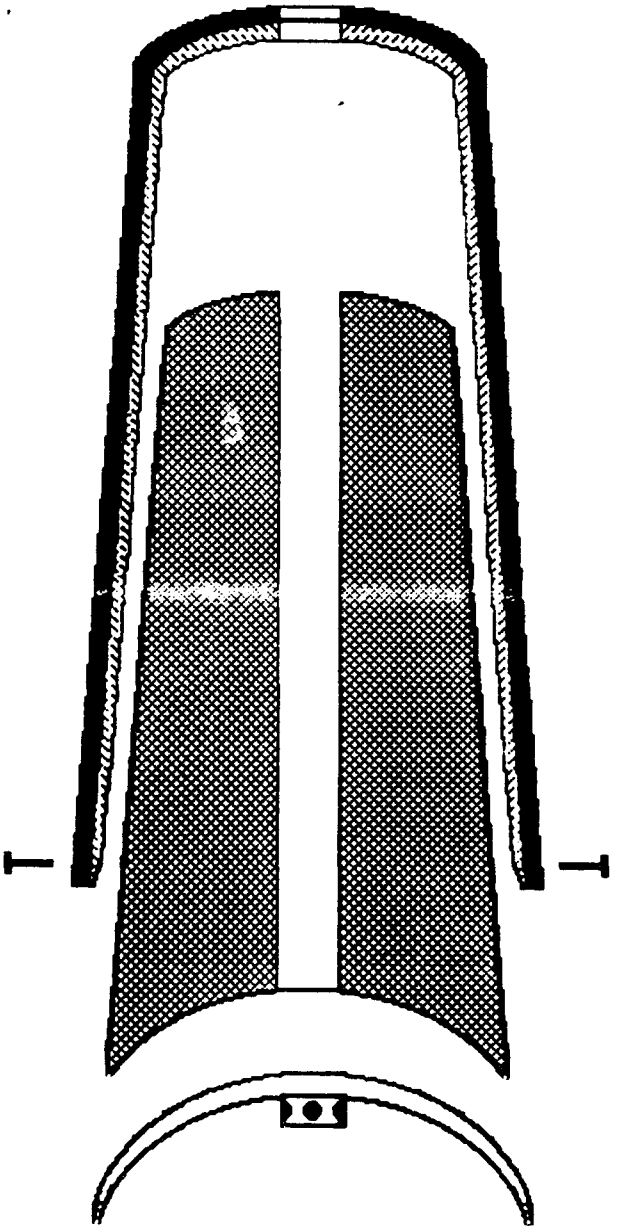
Kevin E. Mahaffy
OLAC-Phillips Lab
RKCC
Edwards AFB, Ca.
93523-5000
T(805)275-5450
F(805)275-5144

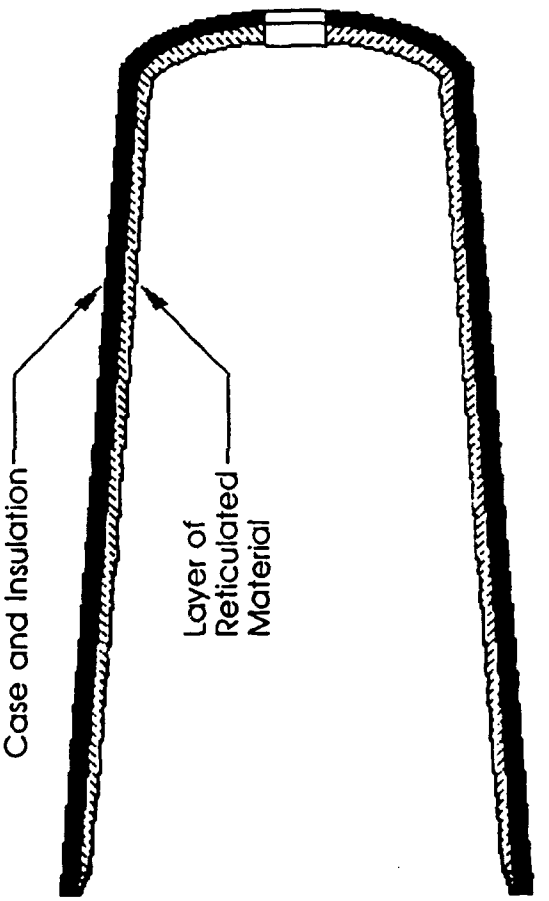
RETICULATED BOND LINE RESEARCH

The goal of the Reticulated Bond Line project is to create a strong and long lasting bond between the propellant and the insulation of the case wall. In this concept, the propellant, with a polymer binder, flows into the cavities of the open cell foam. The bond derives its strength from two sources. First of all, the greatly increased surface area of open cell foam over which chemical bonding can take place. Second, the propellant will polymerize around the ligaments of the foam. The inter-penetrating networks will add mechanical strength to the bond.

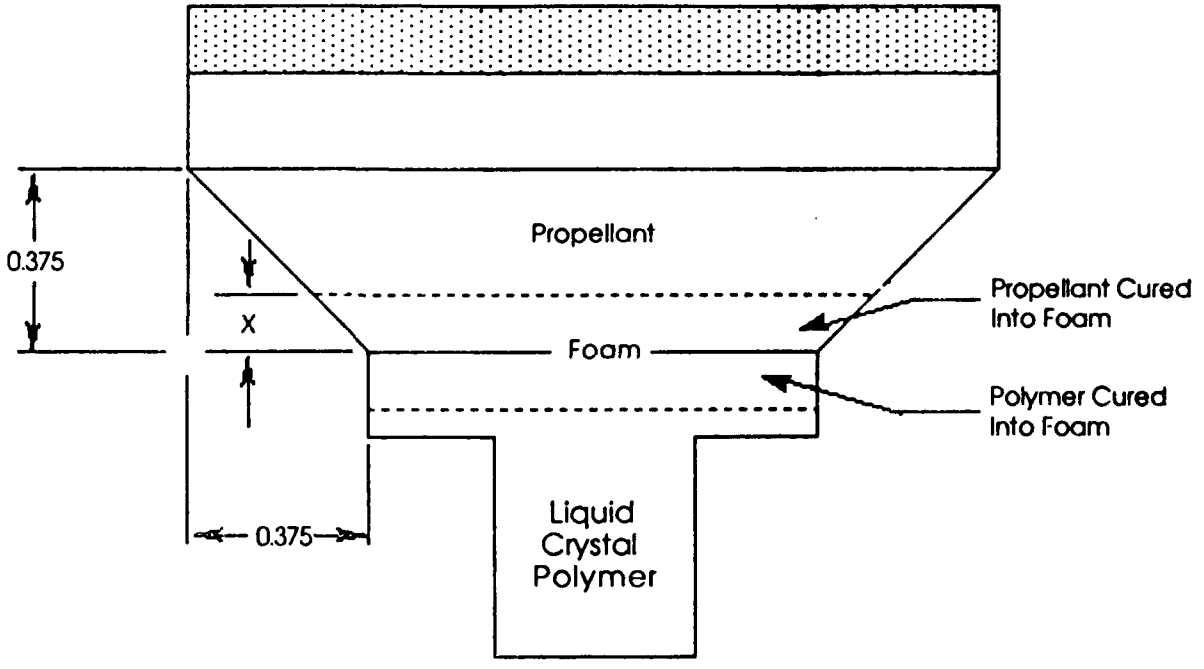
The primary technical problem is how to get a layer of open cell foam joined to a layer of solid insulative material. The preferred solution would take a material such as a Liquid Crystal Polymer(LCP) and form it into the shape of the missile case. The finished part would have a shell of solid LCP that transitioned continuously into an open cell foam.

Any suggestion of a possible technical approach to this problem would be welcomed.




Case and Insulation
Layer of Reticulated Material

RETICULATED BOND LINE



MTI CONICAL BOND-IN-TENSION SPECIMEN