

2

AD-A212 853 RT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

2a. SECURITY CLASSIFICATION AUTHORITY			1b. RESTRICTIVE MARKINGS			
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution is unlimited			
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR-89-1239			
6a. NAME OF PERFORMING ORGANIZATION University of Massachusetts		6b. OFFICE SYMBOL (if applicable)		7a. NAME OF MONITORING ORGANIZATION AFOSR/NC		
6c. ADDRESS (City, State, and ZIP Code) Amherst, MA 01003			7b. ADDRESS (City, State, and ZIP Code) Building 410 Bolling AFB, DC 20332-6448			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR		8b. OFFICE SYMBOL (if applicable) NC		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F49620-87-C-0027		
8c. ADDRESS (City, State, and ZIP Code) Building 410 Bolling AFB, DC 20332-6448			10. SOURCE OF FUNDING NUMBERS			
			PROGRAM ELEMENT NO. 61103F		PROJECT NO. 3404	TASK NO. A2
			WORK UNIT ACCESSION NO.			
11. TITLE (Include Security Classification) (U) A Center for Advanced Electrical and Structural Polymers						
12. PERSONAL AUTHOR(S) Frank E. Karasz						
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day)		15. PAGE COUNT 44
16. SUPPLEMENTARY NOTATION						
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)			
FIELD	GROUP	SUB-GROUP				
19. ABSTRACT (Continue on reverse if necessary and identify by block number) See Back						
DTIC ELECTE S D SEP 27 1989 B						
89 9 27 041						
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED			
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr Donald R. Ulrich			22b. TELEPHONE (Include Area Code) (202) 767-4963		22c. OFFICE SYMBOL AFOSR/NC	

19. Electrical and optical properties have been investigated in which the main focus of attention has been the conjugated macromolecule, poly-p-phenylene vinylene, its analogues, derivatives, copolymers and blends. The potential of PPV as a conducting polymer has been amply demonstrated and more recently it has been shown that this polymer has relatively high third order non-linear optical characteristics and, of equal importance, can be fabricated into oriented films and into blends with silica glass which have optical transmittances commensurate with device fabrication. New advanced ultrastructural polymer blends have been developed. Second generation blends based on polybenzimidazole/polyimide blends have been studied in a third sub-program in collaboration with Celanese, Lockheed and GE, together with a new system based on polysulfane and polyimide blends. Both of these systems were investigated in terms of their macroscopic thermodynamic properties and their detailed molecular-level interaction. The use of several advanced spectroscopies have been developed into the latter sub-program.

The URI program has played a major role in education and in acquiring advanced instrumentation. About fifty graduate students and post-doctoral fellows have been supported and about \$1,400,000. of capital equipment for the U Mass and Wright State programs has been acquired. At both campuses the URI has had major impact.

AFOSR-TR-88-010

UNIVERSITY RESEARCH INITIATIVE

CENTER FOR ADVANCED ELECTRICAL
AND STRUCTURAL POLYMERS

AFOSR/DARPA F49620-87-C-0027

1 December 1986 - 31 October 1988

Frank E. Karasz
Department of Polymer Science & Engineering
University of Massachusetts
Amherst, MA 01003

Approved for public release;
distribution unlimited.

UNIVERSITY RESEARCH INITIATIVE

CENTER FOR ADVANCED ELECTRICAL AND STRUCTURAL POLYMERS

AFOSR/DARPA F49620-87-C-0027

1 December 1986 - 31 October 1988

Frank E. Karasz
Department of Polymer Science & Engineering
University of Massachusetts
Amherst, MA 01003



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

ACKNOWLEDGEMENT

The Principal Investigator would like to express his sincere thanks to Dr. Donald Ball, Director of Chemical Sciences, Air Force Office of Scientific Research, to Dr. Donald R. Ulrich, Senior Program Manager, Directorate of Chemical Sciences, to Dr. R. Keynolds, Director of Defense Science Office, to Dr. B. Wilcox, Assistant Director, Material Science Division, Defense Advanced Research Projects Agency, and to Drs. D. Squire and P. Parrish, Program Managers, for their unfailing cooperation, help and courtesy extended to him during the period of this grant.

CONTENTS

- I. TITLE
- II. PRINCIPAL INVESTIGATOR
- III. GRANT NUMBERS/DATES
- IV. FACULTY ASSOCIATES AND SENIOR RESEARCH PERSONNEL - UMASS
- V. JUNIOR RESEARCH PERSONNEL - UMASS
- VI. EXTRA-MURAL SUBCONTRACTORS
- VII. ABSTRACT OF ACCOMPLISHMENTS
- VIII. DESCRIPTION OF RESEARCH UNDERTAKEN
- IX. PUBLICATIONS

- I. TITLE: Center for Advanced Electrical and Structural Polymers
- II. PRINCIPAL INVESTIGATOR: Dr. Frank E. Karasz
Polymer Science & Engineering
University of Massachusetts
Amherst, MA 01003
- III. GRANT NUMBER: F49620-87-C-0027 December 1, 1986 - October 31, 1988
- IV. FACULTY ASSOCIATES: Professor K.H. Langley
Professor W.J. MacKnight
Professor M.F. Malone
Professor E.L. Thomas
Professor S.L. Hsu
Professor T.J. McCarthy
Professor R.B. Hallock
Professor E.M. Riseman
Professor K.D. Stephan
Professor A.P. DeFonzo
- SENIOR RESEARCH PERSONNEL:
- | | |
|------------------|---------------------|
| Dr. G. Banhegyi | Dr. N. Easwar |
| Dr. Z. Chai | Dr. K. Liang |
| Dr. S. Choe | Dr. G. Smyth |
| Dr. P. Cifra | Dr. J. Kim |
| Dr. W. Huh | Dr. Q. Bhatia |
| Dr. J. Grobelny | Dr. P. Pradere |
| Dr. K. Jeremic | Dr. Z. Xu |
| Dr. H. Lau | Dr. C. Chang |
| Dr. W. Liang | Dr. S. Pollack |
| Dr. H. Mattoussi | Dr. K. Lee |
| Dr. P. Musto | Dr. D. Madsen |
| Dr. S. Palmer | Dr. J. Chen (WSU) |
| Dr. G. Quin | Dr. M. Sinkys (WSU) |
| Dr. N. Segudovic | Dr. R. Miller (WSU) |
| Dr. G. Shy | Dr. Y. Gur |
| Mr. L. Wu | Dr. T. Bleha |
| Dr. A. Sikora | Dr. H. Fischer |
| Dr. S. O'Donohue | |
- V. JUNIOR RESEARCH PERSONNEL:
- | | |
|------------|---------------------|
| W. Nachlis | Y. Chang (WSU) |
| J. Simpson | K. Paulvannan (WSU) |
| Y. Guo | J. Peak (WSU) |
| G. Weaver | N. Akmal (WSU) |
| X. Hua | C. Jariwala (WSU) |
| R. Denton | L. Rider (WSU) |

VI. SUBCONTRACTORS: Profs. J.J. Kane; W.A. Feld - Wright State University,
Dayton, Ohio (WSU)

Mr. R. Lusignea - Foster-Miller, Inc., Waltham, MA

VII. ABSTRACT OF ACCOMPLISHMENTS

The URI Center for Advanced Electrical and Structural Polymers at UMass has sponsored programs in five thrust areas with the broad theme of new material development. Electrical and optical properties have been investigated in two thrusts in which the main focus of attention has been the conjugated macromolecule, poly-p-phenylene vinylene, its analogues, derivatives, copolymers and blends. The potential of PPV as a conducting polymer has been amply demonstrated and more recently it has been shown that this polymer has relatively high third order non-linear optical characteristics and, of equal importance, can be fabricated into oriented films and into blends with silica glass which have optical transmittances commensurate with device fabrication. New advanced ultrastructural polymer blends are the subject of a third thrust. Second generation blends based on polybenzimidazole/polyimide blends have been studied in a third sub-program in collaboration with Celanese, Lockheed and GE, together with a new system based on polysulfone and polyimide blends. Both of these systems were investigated in terms of their macroscopic thermodynamic properties and their detailed molecular-level interaction. The use of several advanced spectroscopies have been developed in to the latter sub-program. The novel architecture and characterization thrust contained several imitations pertinent to this theme. Studies of the novel "double diamond" structure observed in block copolymers have been conducted by Professor Thomas and extended to new systems, and temperaturc/molecular weight regimes, which Professors Kane and Feld have synthesized new heteroatomic low molecular and high molecular weight

molecules with applications in the structural and the optical areas in collaboration with Wright-Patterson Materials Laboratory. An A.I. processing thrust is described in which advanced computer vision technology has been applied to the specific case of spinodal phase decomposition of blends in real time to optimize processing parameters in terms of required mechanical properties. Processing also has formed the focus of the interaction with Foster Miller, Inc., who have collaborated in novel fabrication methodology applied to PPV, high temperature blends, and rigid-rod polymers.

Research in the five thrusts described above was dynamic; in many cases it has overlapped the boundaries of the sub-programs, and many of the faculty and researchers involved have participated in several of the areas described.

The URI program has played a major role in education and in acquiring advanced instrumentation. About fifty graduate students and post-doctoral fellows have been supported and about \$1,400,000. of capital equipment for the UMass and Wright State programs has been acquired. At both campuses the URI has had major impact.

VIII. DESCRIPTION OF RESEARCH UNDERTAKEN

1. INTRODUCTION

This report covers the first twenty three months of the operation of a Center for Advanced Electrical and Structural Polymers at the University of Massachusetts sponsored by the University Research Initiative.

The organization of this URI has been dynamic and has evolved over the two

years. The main themes are, in brief:

1. Research programs in the context of the overall theme have been organized into five thrust areas.
2. Faculty from five academic departments have been involved in cooperative sub-programs.
3. Two major extra-mural sub-contractors (Wright State University; Foster-Miller, Inc.) have been supported from the inception.
4. An intensive continuing interactions with numerous outside industrial/academic/government researchers has been maintained.
5. The educational aspects of the URI through the support of graduate students and postdoctoral fellows has been emphasized.
6. A broad program for the acquisition of state-of-the-art capital instrumentation has been organized.
7. Major cost sharing from the respective institutions, both direct and indirect, has been a central feature of the use of the substantial funds involved.

Some details of these items are presented below:

i. The research components of the UMass URI have been organized in five major thrusts or sub-programs:

Electrical and Magnetic Properties of Polymers

Non-Linear Optical Properties of Polymers

Advanced Ultrastructural Polymers

Novel Macromolecular Architecture and Characterization

and

New Processing Technology

Many URI participants are involved in more than one thrust; several research activities also embrace two or more thrusts; specific examples are given below.

ii. The overall organization (as of October 1988) is shown on the accompanying figure.

iii. Intensive outside interactions include those with Celanese, NASA Langley, Wright Patterson Materials Laboratory, G.E., Lockheed which have been specifically involved with URI sub-program. However at least forty other companies has maintained interactions with the P.I. and/or faculty associates and/or sub-contractors. Thus the dissemination of URI sponsored activities in the U.S. is extremely widespread.

iv. The list of senior and junior research personnel directly supported by URI given in Sections IV and V, above. However, the educational impact has been much broader, for example through the cooperative use of URI funded capital equipment and facilities.

v. A partial list of major state-of-the-art equipment acquisitions include:

Wide-angle X-ray diffractometer with two-dimensional detection

300 MHz solid state NMR

High resolution FTIR spectrometer

Image processing facility for electron microscope

UHF dielectric spectrometer

XPS spectrometer

Forced Rayleigh light scattering facility

PERSONNEL

UMASS

PSE

F.E. Karasz (P.I.)
S.L. Hsu
W.J. MacKnight
T. McCarthy
E.L. Thomas

PHYSICS

K. Langley
R. Hallock

COINS

E. Riseman
et al.

CHEMISTRY

P. Lahti

CHEMICAL ENGINEERING

M. Malone

ELECTRICAL ENGINEERING

K. Stephan

SUBCONTRACTORS

WRIGHT STATE UNIV

W. Feld
J. Kane

FOSTER MILLER

R. Lusignea
et al.

FIGURE 1: ORGANIZATION OF UMASS URI - October 1988

Polymer characterization facility at Wright State University
Thermogravimetric/Mass Spectrometer Analysis facility
Molecular interaction computation facility (on loan to WPAFB)
Dynamic mechanical relaxation spectrometer
Heat of mixing calorimeter

For most items listed URI provided total funding.

vi. The cost sharing aspect includes the provision of 10,000 ft² of new and renovated lab/office space for URI at UMass, and the award of an Academic Challenge Grant to Wright State University from the State of Ohio for the development of a polymer research facility which has resulted in the hiring of new polymer related faculty.

URI funding for the initial period has supported fully or in part research which has resulted in 80 publications which have appeared or are in press together with one patent application.

Brief summaries of research in the five sub-programs follow:

2. ELECTRICAL AND MAGNETIC PROPERTIES OF POLYMERS

The focus of this sub-program has been on poly-p-phenylene vinylene. We have pioneered the use of this material as an electrically conducting macromolecule; in the last twelve months attention has been paid to the optical - in particular the third-order non-linear - properties of PPV.

PPV is synthesized via a unique polyelectrolyte precursor route. This synthesis has several distinct advantages. First processing the polymer to form

one-, two- and three-dimensional forms is facilitated. Thus the water or alcohol soluble precursor polymer can be fabricated by more-or-less conventional solution processing technology. The resulting material may then be converted to PPV by straightforward thermolysis. However, during the latter reaction (at $\sim 200^{\circ}\text{C}$) the evolution of volatile products and of residual solvent produces a transient plasticization which permits a controlled deformation (e.g. uni- or bi-axial orientation) to be imposed on the system. This has been explored in detail.

We have undertaken numerous studies of PPV. Selected examples are summarized below.

a. X-Ray Photoelectron Spectroscopy and Photoconductivity of PPV (Karasz)

The electronic structure of neutral and electrochemically doped poly (p-phenylene vinylene) (PPV) have been examined by XPS spectroscopy. The C(1s) core level spectra of doped PPV indicate that the positive charge is not uniformly distributed over the polymer matrix. The electron population is lower on a fraction of carbon atoms centers resulting in a dopant-related component structure displaced 1.6 eV from the C(1s) peak towards higher binding energies. MO calculations for low molecular weight analogues of the PPV backbone with dopant simulating perturbations of the valence orbitals, suggest that dopant coupling involves rearrangement of polymer and dopant orbitals to yield an energetically favorable structure of localized defects. In the valence region the XPS spectra of neutral PPV shows the influence of the condensed polymeric phase. Calculated XPS valence level spectra on the base of states derived from the tight binding model of the conjugated chain have been found to be essen-

tially consistent with experiment. In the 25 mol% doped material, the XPS peaks close to the Fermi level are similar to those of neutral polymer matrix and the detected hole states are more consistent with a disordered molecular solid than a one-dimensional metal. The photoconductivity of poly (p-phenylene vinylene) films have also been investigated between photon energies of 6 eV and 0.6 eV, and in the temperature range of 100K - 400K.

The photoconductivity threshold at 2.45 eV coincides with the absorption edge. Carrier generation appears to be an extrinsic process where photons create excitons rather than unbonded electron-hole pairs. Free charge carriers are not produced until the excitons interact with the film surface. Measurements of transient photocurrent have shown that only the holes are mobile with a mobility of about $10^{-4} \text{cm}^2/\text{Vs}$ at room temperature. The mobility is thermally activated and typically dispersive.

b. Processing of PPV (Karasz, FMI)

A continuous process has been developed to produce oriented PPV in a reproducible and controllable manner. This work has involved scale-up of the PPV precursor polymer synthesis, development of continuous or semi-continuous solvent casting operations, and the development of a continuous film stretching operation. The web stretching device exploits the temporary plasticization effected by the rapid evolution of volatiles accompanying thermal elimination of the precursor polymer. In this process, precursor film is passed over a heated roller where it is softened and stretched before passing over a second heated roller which is proceeding at a faster rate. The draw ratio is determined by the ratio of the speeds of the two rollers. The total line speed is determined

by the speed of the second roller. The temperature of the first heated roller determines the degree of plasticization (rate of volatilization). Other factors which affect processing behavior are the contact angle between the film and the first heated roller and the distance between the rollers.

Under a given set of processing conditions a processing window relating roll temperature to draw ratio can be established. A further goal of this work has been to describe the deformation sustained by the material as it is oriented. A full description of the deformation (strain tensor) during the process has shed light on the mechanism of orientation in this novel process. The correlation of molecular orientation with key properties such as electrical conductivity rests on the assumption that the deformation (and hence orientation) is homogeneous throughout the film. Molecular orientation has been measured using infrared dichroism. To use IR dichroism successfully as a probe of molecular orientation one must possess a system with strong, narrow and well-separated absorbances. The dipole transition moments of these absorbances in PPV makes angles with the molecular axis (chain direction) which are both well defined; PPV represents an ideal system for dichroism studies.

c. PPV Blends (Karasz)

Poly(phenylene vinylene)/poly(ethylene oxide) blends have been prepared under a variety of conditions to yield highly conducting materials (100-300 S/cm) upon either chemical or electrochemical doping. Accelerated doping rates and enhanced conductivities relative to those of pure poly(phenylene vinylene) were observed for blends over a wide range of compositions, and have been attributed to improved dopant transport as a result of

blending. The electrical properties of the doped materials have been related to the chemical compositions of the blends and the morphologies observed using optical microscopy.

The blends of electroactive PPV and electroinactive PEO can be prepared by casting from common solvents for PEO and the PPV precursor. The phase separated morphology of the blends consists of large spherulitic structures, micron-size disordered phases, and sub-micron dispersed phases, depending on the blend composition and casting conditions.

In light of the results obtained in this investigation, we can divide the morphological and electrical behavior of the PPV/PEO system into three distinct composition regimes. At extremely low PPV content (less than 10 wt %) a spherulitic morphology is formed which resembles pure PEO; the PPV constituent in this regime does not form a continuous phase and although it may be effectively doped, the macroscopic conductivity remains insulating or at best lightly semi-conducting (up to 10^{-3} S/cm). The second regime extends from 10 wt % to 60 wt % PPV and is characterized by a spherulitic morphology in which the PPV domains are excluded into interfibrillar regions forming a highly connected network. Materials in this range can be doped very quickly to high conductivity (>100 S/cm). The third regime consists of materials containing greater than 60 wt % PPV. Materials in this region are flexible and tough containing highly dispersed PEO domains in a PPV matrix. In this region the PEO constituent is still effective in accelerating chemical doping, however it is less effective in accelerating electrochemical doping. Electrical conductivities in this regime reach a maximum greater than 200 S/cm, Figure 4.

A second series of PPV containing blends with an inactive carrier species has been obtained using inorganic silica polymers using sol-gel polymerization techniques. These have proved to be extremely effective materials from a non-linear optical property point of view. They will be discussed in Section 3, below.

d. Poly 2,5-dimethoxy phenylene vinylene (Karasz)

Poly(2,5-dimethoxy phenylene vinylene), PDMPV, has been efficiently electrochemically cycled between the doped and undoped state. The electrical conductivity, σ , of perchlorate-doped PDMPV depends markedly on the doping level, y , and follows approximately the relationship $\sigma \propto y^4$. EPR has been used to characterize the magnetic properties of PDMPV. Nascent PDMPV is devoid of spins whereas a narrow ($<0.5G$), intense signal evolves upon doping. The line narrowing and the dependence of line width upon doping level is accounted for by three dimensional spin exchange. Electronic absorption spectra taken in situ during electrochemical doping of PDMPV show absorption bands at 6.05, 4.11, 4.84 and 3.70 eV due to localized molecular states, and a broad band at 2.43 eV, which may be described in terms of an exciton model. Upon electrochemical doping two additional bands appear at 1.77 eV and 0.62 eV.

e. Electrical Conductivity (Hallock)

The temperature dependence of the D.C. electrical conductivity of PPV which has been doped with AsF_5 has been investigated. We find spectacular agreement with the conductivity model based on variable range hopping for thin film samples which have been aged by exposure to air. Under other circumstances, the conductivity obeys a temperature dependence which has not been previously

reported, $T^{1/2}$, and calls for a new model of such conduction. Observations from 4.2 K to room temperature have been completed for a variety of doping conditions and a variety of "aging" conditions. All the studies have been carried out with material drawn by Foster Miller Corporation. The work was predominantly with stretched material made with various values of the draw ratio, λ . The in-plane conductivity parallel to the stretch direction as well as the conductivity perpendicular to the stretch direction were measured.

For this sample we can also test for agreement with the three dimensional variable range hopping model. We observe that the agreement with the model is limited; the agreement is not nearly as good over the full temperature range as that seen in aged samples of lower conductivity. From the studies of the temperature dependence of the conductivity which we have done to date we conclude that for low conductivity samples (no matter how the conductivity reached those low values) we generally observe the conductivity to obey the variable range hopping model. High conductivity samples which retain their conductivity even after exposure to air demonstrate a conductivity which has a temperature dependence which is not consistent with the variable range hopping picture over the full temperature range of the studies; rather, the dependence appears to follow a $T^{1/2}$ law.

f. Microwave Properties of PPV (Stephan)

Although a heavily doped sample of PPV is primarily an absorber at microwave and millimeter wavelengths, a small fraction of the incident energy is transmitted if the sample is thin enough. The resulting power transmission coefficient, although very small (typically $<10^{-3}$) can be measured with preci-

sion by an automatic network analyzer. By itself, the transmission coefficient is insufficient to allow calculation of both the index of refraction n and the absorption coefficient α . However, for the doped materials under study the entire absorption can be attributed to the conduction mechanism, and assuming a nominal value for n leads to an estimate of the equivalent microwave conductivity of the sample.

Waveguide measurements of doped PPV samples having thicknesses of 14 μm and 37 μm were performed in the 18-26 GHz range. Data taken initially showed an average conductivity in the 40-80 $\text{ohm}^{-1}\text{cm}^{-1}$ range, which is consistent with DC measurements on other similarly treated samples. In addition, an effort to develop open-resonator techniques for the measurement of low-loss polymer films was initiated with the URI program. The open-resonator technique, although potentially much more precise than the waveguide technique for low-loss materials, requires large, flat samples if diffraction and scattering are to be avoided. We have been working at two different frequency ranges: 35 GHz and 94 GHz. While our instrumentation is in place for 35 GHz, the samples must be at least 5 cm in diameter. An undoped PPV sample this size was measured, but losses were so high that the measurement precision was severely degraded. The value of n obtained (2.4) could be in error by as much as $\pm 50\%$. A machine-stretched undoped sample was also studied and although its narrow dimension prevents a measurement at 35 GHz, it is large enough to use at 94 GHz where smaller sample sizes are useable.

g. Mechanistic (Lahti, Karasz)

A reaction mechanism involving base attack on the precursor disulfonium

xylylene to form a ylide, with subsequent E1cB 1,6-elimination of a thioether to generate the actual monomer (a terminally substituted para-xylylene), followed by dimerization and radical propagation has been postulated. There are four points of special interest in the polymerization chemistry: ylide formation, xylylene formation, mode of propagation, and absence of true termination steps. The aim has been to accumulate instrumental and chemical evidence bearing on each of these four aspects.

It is believed that an anionic addition process is the most likely mode of propagation. Evidence for a radical mechanism is lacking, and experiments with meta- α,α' -bis(dialkyl sulfonium) xylenes indicate that the propagation does not proceed by S_N2 (ylide displacing a thioether at another site). Evidence favoring anionic propagation is the fact that acid terminates the reaction (note that acid should also terminate monomer xylylene production). It has been shown that benzaldehyde present at initiation prevents polymerization, but apparently assumed that was due to reaction with monomer precursor; no attempt at using it as an end-capping agent to terminate propagation by a chain-end ylide has been reported.

Other work also found an increase in viscosity-average molecular weight with the addition of equimolar amounts of base and monomer precursor to reaction mixture that has already gone to completion. In other words, a true termination of chain growth is absent. This is also consistent with an anionic mechanism for chain growth, since living polymers typically propagate by anionic mechanisms.

h. Deuterium NMR (Karasz)

The simulation of deuterium quadrupole echo NMR spectra has provided data which support an empirical two component Gaussian distribution of crystallite orientations in PPV. The narrow component of the distribution has a width at the $1/e$ points of 9.5° while the broader component has a width of 30° . Spectra show evidence of phenylene ring tilt relative to the crystallite c axis, though the angle, 7.7° , is less than the 9.1° predicted for the stilbene-like PPV crystal structure. This smaller tilt provides evidence for chain disorder within PPV crystallites.

The observed chain distribution is similar to the Kratky distribution predicted for pseudo-affine deformation ($\lambda=3.3$) and the orientation function, $f=0.95$ is somewhat less than that usually obtained from infrared measurements with protonated films. Infrared dichroism measurements of these films agree with the NMR data, so it is possible that these films are less ordered than similarly prepared protonated material. In general a direct comparison of infrared dichroism data and NMR data has benefited the interpretation of results of both methods.

The precision which has been obtained in the simulation of the narrow component of the PPV line shape has resulted from the particular geometry of the phenylene ring. The 60° orientation of C-D bonds relative to the ring axis places these bonds close to 54.7° , the "magic angle", relative to the magnetic field. At this angle the magnetic field is highly sensitive to small changes in the orientation distribution. Also, the spectrum of an oriented ring is completely different from the Pake doublet line shape of an isotropic distribution, making it possible to characterize the broad component of the distribution

separately from the narrow component.

This study of deuterium NMR results have conveniently provided information about chain order and structure from a material with rigid phenylene rings. Many high performance polymers contain rings which can be isotopically labelled, and these methods are potentially applicable to the study of structure of these materials as well.

3. NON LINEAR OPTICAL POLYMERS

The basis for these studies has been the PPV series of polymers, its derivatives and copolymers, and blends of these with inactive carrier species.

Our strategy has been to cooperate in this sub-program with FMI in research on the important processing step of these materials and with Professor Prasad (SUNY Buffalo) in the actual measurements of the characteristic optical parameters. Results from these interactions are then used to modify or emphasize particular points in the sub-program.

Thus PPV films made by a specially designed apparatus capable of applying uniform extension under carefully controlled conditions has been found to be amongst the most optically active polymers yet produced. In the stretch direction, values for $\chi^{(3)}$ of 5×10^{-10} have been observed. Biaxially oriented films have also been produced (by two techniques) which have also high $\chi^{(3)}$'s. Preliminary results of these experiments have recently been published [Polymer, 1988] or are in press.

While PPV has now been proven to have a high intrinsic $\chi^{(3)}$, the practical problem of obtaining reproducible, low-loss, optical quality films has proved

difficult. We have now overcome this by using blends of PPV with intrinsically low loss silica glass. To accomplish this advantage has been taken of the fact that PPV is produced from a water-soluble precursor and that silica glass can be conveniently obtained by a low temperature sol-gel route. This serendipitous combination (again, in collaboration with Professor Prasad) has produced PPV/SiO₂ films which have very recently been demonstrated to have the desired combination of high $\chi^{(3)}$ activity and low scattering. [A patent application for this material was filed on February 20, 1989].

As has been indicated, PPV derivations have also been examined. These include the 2,5-dimethoxy derivative of PPV and copolymers of the substituted and unsubstituted materials. The production of adequate quality films of high orientation has again proved to be difficult, but has been achieved in a few cases.

4. ADVANCED ULTRASTRUCTURE POLYMERS (Karasz, MacKnight)

The basis for this sub-program has been the discovery that the high temperature polymer, polybenzimidazole (PBI), is miscible with a number of polyimides (PI) under certain conditions. In addition a second class of high temperature polymer blends, containing polyimides and certain polysulfones, has also been discovered.

The focus of the sub-program has therefore been the elucidation of the molecular bases for these unexpected miscibilities, the characterization of the blends, and the establishment of a theoretical basis for predicting other possible blend systems of interest.

a. Polybenzimidazole/Polyimides (Karasz, MacKnight)

An AFOSR/DARPA project (1984-87) at UMass led to the discovery of the miscibility of polybenzimidazole (PBI) and a series of polyimides. The molecular basis for the miscibility has been studied by means of FTIR and solid state NMR. An obvious possibility is the presence of hydrogen bond interactions between the relevant moieties in the two constituent polymers. This has been confirmed in the FTIR work. Model low molecular weight components have been used in the NMR study of interactions between imidazole and imide groups. In addition FTIR studies of deuterated PBI and PI's has shown the importance of these interactions.

These investigations have been closely coordinated with the development program for PBI/PI systems under way at Hoechst-Celanese. Interactions with other industrial research laboratories interested in this system, Lockheed and G.E. (Jet Engine Division), have been implemented.

Hydrogen bonded carbonyl and NH bonds revert to their corresponding positions in the pure polymers when thermally induced phase separation occurs. The phase separation temperatures are quantitatively consistent with the earlier results. Thus PBI and Ultem mixtures form what is apparently a single phase miscible blend when prepared from solution by either film casting or coprecipitation. However these studies show that over a rather wide range of compositions these blends revert to two phases, consisting essentially of the two constituents, when allowed to do so by heating to a temperature at, or close to, the blend T_g . Even outside this composition range where equilibrium behavior may be anticipated, thermal reversibility in terms of phase separation and

rehomogenization is not observed. This is presumably due to the highly viscous nature of the constituent polymers which cannot be compensated for experimentally by heating to a higher temperature because of chemical reaction. The thermal and spectroscopic measurements are in reasonable accordance with respect to this phase behavior; in addition the latter data provide persuasive evidence of extensive hydrogen bonding in the blends.

Results from ^{13}C solid state (magic angle) NMR of PBI/polyimide blends have provided positive evidence for miscibility, and they support the conclusion that miscibility is the result of a specific hydrogen bond between the phthalimide carbonyl of the polyimide and the imidazolic N-H bond of PBI. Blending of PBI broadens this resonance, principally in the downfield direction, and a downfield carbonyl chemical shift is consistent with the development of a fraction of carbonyl, N-H hydrogen bonds. PBI/polyimide blends are amorphous, and only a fraction of the carbonyls undergo hydrogen bond interaction. Only a fraction of the carbonyl resonances are shifted downfield.

Evidence for miscibility in this blend also comes from the measurement of T_1 through the ^{13}C CPMAS contact time. The T_1 associated with the polyimide changes from 14 msec to 10 msec upon blending with PBI. The values of T_1 for the PBI/Ultem 1000 blend are similar.

The URI-sponsored research has focused on the basic molecular characterization of these systems: the effect of variations in chemical structure, and the possible application of our copolymer theory to enhance and tailor miscibilities (in terms of LCST's) to optimize the materials. We have also been involved, as part of the collaboration, in developing solutions for problems

that have appeared in the development phase. The most important of these has been an emerging knowledge of the thermo-oxidative sensitivity of the PBI/PI blend. A basic research program to elucidate the nature of the degradative reactions involved has been set up.

b) PES/PI

Blends of an aromatic polyethersulfone, and a polyimide which is the condensation product of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 5(6)-amino-1-(4'-aminophenyl)-1,3,3'-trimethylindane, were studied by differential scanning calorimetry, dynamic mechanical analysis and rheological techniques. The blends are miscible over the whole range of compositions when cast as films or precipitated from solution in different solvents. After annealing above the apparent phase boundary the blends irreversibly phase separate indicating that the phase boundary does not represent a true equilibrium transition. A "processing window" was found for blends containing up to 20 wt % polyimide. Rheological measurements in this range of compositions indicated that blending polyethersulfone with polyimide increases the complex viscosity and the elastic modulus of the blends. For blends containing more than 10 wt % polyimide, rapid changes in the rheological properties were observed at temperatures above the phase boundary. These changes may be consistent with the formation of a network structure due to phase separation and/or crosslinking. Blends containing less than 10 wt % polyimide exhibited stable rheological properties after heating at 320°C for 20 min indicating the existence of thermodynamic equilibrium. A patent application has been filed.

5. NOVEL MACROMOLECULAR ARCHITECTURE AND CHARACTERIZATION

a. Monolayer Structures (McCarthy)

Polystyrenes containing one terminal thiol group (PS-SH) were allowed to adsorb on evaporated gold films supported on glass. The resulting supported films were characterized by X-ray photoelectron spectroscopy, external reflectance infrared spectroscopy and scintillation counting of radioisotope-labelled polymers. The polymers adsorb rapidly and irreversibly and the polymer monolayers can be washed with fresh solvent without desorption. The effects of molecular weight and concentration on adsorbance were determined for PS-SH. Thus polystyrene containing a terminal thiol group $\text{PS}_x\text{-SH}$, ($M_n = 1000\text{-}200,000$) adsorbs to gold under conditions that polystyrene does not. At higher molecular weight ($M_n = 500,000$) adsorption does not occur. Film thickness varies with molecular weight and concentration in a fashion similar to the way polystyrene film thickness varies when unmodified polystyrene adsorbs from a poor solvent.

b. Monolayer Spectroscopy (Hsu)

We have adapted a most sensitive differential polarization technique to obtain infrared spectra of thin polymer films on external substrates. In addition, based upon the theoretical analysis developed last year we have been able to quantitatively interpret the vibrational spectra obtained. Our polarization modulation reflection technique modulates the two incident radiations to such high frequencies that their differences can be directly obtained by phase synchronization techniques, thereby improving the signal to noise ratio by several orders of magnitude.

We have given particular attention to chemi-adsorbed PS and their block copolymers bonded to gold substrate surfaces. These samples are definitively bound to the metallic surfaces and the coverage is uniform, since one or more sulfur functionalizations have been carried out by Professor McCarthy's students. The adsorptions have been carried out from good solvents so that all of the physi-adsorbed polymers have been washed off. From x-ray photoelectron spectroscopic experiments, we find that the thickness of the modified PS film is approximately 20 Å. The signal/noise ratio of our data is so high that even the combination bands near 1800 cm^{-1} are cleanly resolved. The generally weak conformationally sensitive bands in the mid-infrared region have also been detected. We have also found explicit evidence of the sulfide end caps. It is somewhat surprising that this functional group was observed since their concentration is not expected to be high. We may have observed a particular intensity enhancement due to the proximity of the functional group to a conductive medium, such as observations that have been found for surface enhanced Raman spectra. This is of significant interest from a purely spectroscopic viewpoint. It should also be emphasized that the relative intensities of the bands observed are different from transmission data. It has been speculated that the orientation of the aromatic ring can occur quite differently depending on chain conformation and orientation. These observations may be the most concrete evidence for such structural differences.

c. Diffusion in Constrained Media (Langley, Karasz)

Comparative measurements have been made of the diffusion of star and linear polymers in rigid media containing random, well-connected pores with

narrow pore size distributions, see Figure 8. For a given confinement λ_H , defined as the ratio of the hydrodynamic radius of the polymer to the pore radius, molecular architecture was found to affect the hindered diffusion. At a given λ_H , star polymers diffuse more slowly than linear polymers, with the 8-arm star polymer diffusing more slowly than the 4-arm star polymer. A scaling parameter κ has been calculated which relates the hydrodynamic radius to an equivalent hard sphere radius. For a given polymer-solvent system, the value of κ is independent of the parameters characterizing the porous glass and is thus found to depend only on the molecular architecture. The effective radius of a linear polymer is found to be smaller than the bulk solution value R_H . As the number of arms increases, the effective radius approaches the bulk solution value. There is also an indication that the polymer-solvent system affects the value of κ , as seen by the differences between the polyisoprene-TD and polystyrene-2FT systems.

In summary, the length scale characterizing the hydrodynamic effects of constraining walls on polymer diffusion is not the hydrodynamic radius derived from diffusion in dilute unbounded solution. The equivalent hard sphere radius depends on molecular architecture the stiffness of the polymer chain and polymer-solvent interaction.

In the case of strongly confined linear chains, up to the highest molecular weight and confinement probed by these data, no clear power law dependence of D_{∞} on molecular weight was found. This agrees with the predictions of computer simulations, though the porous medium used here is uniform as compared to the truly random porous structure developed in the simulations. Our data also indi-

cate that the presence of an additional length scale in the porous network plays an important role in the diffusion of strongly confined chains.

d. Ultrastructural Morphology (Thomas)

Our work over the past two years has concentrated on studies of the packing and organization of macromolecules at the molecular and supramolecular levels. Research utilizes high resolution electron microscopy (HREM) for the study of crystalline polymers such as poly(p-phenylene vinylene) and poly (p-xylylene) and conventional TEM and small angle x-ray scattering techniques for the investigation of amorphous/amorphous diblock copolymers such as polystyrene/polyisoprene. the polymers studies are both model systems and technically interesting materials in their own right. In additon to fundamental research on polymeric materials we have also made signifacnt contributions in the theory and practice of digital image analysis.

e. Structure of Crystalline Polymers (Thomas)

Poly (p-phenylene vinylene) (PPV), is a conjugated polymer which becomes highly electrically conducting when treated with certain dopants. We have investigated the crystalline structure and packing defects in oriented PPV film using x-ray and electron diffraction. Our more rectn work concerns the crystal-crystal phase transofmation induced by dopants such as AsF₅, SbF₅ and H₂SO₄. The crystalline phase of the doped materials are all similar in struture, displaying orthorhombic unit cells. The detailed structure involves an alternating layer arrangement of PPV chains separated by chemical dopant species. We also used dark field microscopy to establish the size, shape and orientation of the new conducting phase. Of special interest was the nucleation of the con-

ducting phase at the grain boundaries of the PPV phase.

Small, less than one micron diameter, thin (10 nm) chain folded crystals of poly (p-xylylene) (PPX) can be grown from dilute solution in alpha methyl naphthalene. We have investigated (110) and (130) twin boundaries in monoclinic PPX crystals using HREM and electron diffraction. Since the chains are inclined to the lamellar surface normal, a three-dimensional "roof-like" structure of the two twin components arises. Multiple twins and coalesced monoclinic/hexagonal polymorph bycrystals are also described by the basic twin model. The work clearly demonstrates the quite general principle of chain axis invariant twinning.

f. Image Processing (Thomas)

Our efforts in digital image analysis have been motivated by our success in obtaining very high resolution images of crystalline polymers (~ 0.2 nm). But because polymers suffer radiation damage, the signal to noise ratio of our HREM images is less than can be achieved than in the case of metallic and ceramic samples, thus we have spent considerable time developing appropriate image processing algorithms so as to best utilize signal averaging in a bias-free manner to improve the available high resolution detail from our micrographs. In two papers we have written on signal processing of aperiodic images (e.g. images of crystalline regions containing defects such as dislocations, twin boundaries etc.) are now in press and while our applications are specific to polymer science, the approach is quite general and should prove useful in other areas of physical and biological science where one needs to rescue nonperiodic signals from noise.

g. Structural Investigations of Block Copolymers and Block Copolymer/Homopolymer Blends (Thomas)

The main goals in this area were to establish if the ordered bicontinuous double diamond (OBDD) morphology occurred in both the polyisoprene-rich region of the A/B diblock temperature-composition diagram and to explore the temperature dependence of the OBDD morphology in the weak segregation limit (i.e. near the microphase separation transition. Our previous work showed the OBDD morphology occurred for a composition window of 62-66 volume % polystyrene (PS) in linear PS/PI diblock copolymers. A series of PS/PI diblocks were prepared from 20-40% PS with typical molecular weights (M_n) in the range of 20,000 - 80,000. The OBDD morphology was indeed found over the window of 28-33 volume % PS for samples in the strong segregation limit (high M_n). Thus the morphology diagram has 7 regimes dependent on the composition. The slight asymmetry about the 50/50 composition is likely due to the difference in density and Kuhn statistical step length for PS and PI. In addition to the composition dependence, a new transition between ordered microdomain types was observed at constant composition. A transition from the cylindrical phase to the OBDD took place at 64.5% PS when the M_n was increased from 23,000 to 39,000. This demonstrates that the morphology diagram depends on temperature and M_n in the weak segregation limit and should provide stimulus for improved theories of the order-disorder phase transition.

Other work still in progress addresses the effects of molecular architecture on spherical micelle formation in diblock copolymer/homopolymer blends. The

dependence of critical micelle concentration, micelle core and corona size on molecular weight, arm number, composition and concentration of diblock are being investigated with particular attention to whether the inner or outer arm block is aggregating species.

h. New Polymer Research at W.S.U. (Feld)

Substituted PBT/NLO Synthesis

The concept of reinforcement on the molecular level using intrinsically rigid-rod polymers represents one of the most exciting, emerging technologies in the field of structural materials. Considerable research effort in recent years has been directed toward the development of new structural materials having low density, high strength, high modulus, and long-term retention of these properties at elevated temperatures.

Poly(benzothiazole) (PBT) and its derivatives have been found to be a type of polymeric materials that exhibits a high degree of molecular order, thermal stability, and can be fabricated into items of high strength and modulus.¹ In addition, PBT has been spun into highly oriented fibers that have tensile moduli greater than 2000 g/denier and tenacities greater than 20 g/denier.²

The realization of ultrahigh mechanical properties from an organic polymer depends on the cooperation of numerous factors such as chemical structure, molecular weight, method of synthesis, and the characteristic of processing and solubility. The object of this research, therefore, was the preparation of a new type of aromatic, heterocyclic, rigid-rod molecule, a poly(benzothiazole) with pendants perpendicular to the parent polymer chain.

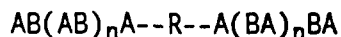
In addition, PBT has been shown to exhibit a significant nonlinear optical (NLO) response. The generation of substituted (fixed orientation and identity) PBT derivatives and their precursors was also an object of this research.

The goals of one part of the synthesis effort have been (1) to synthesize a series of 2-phenylbenzothiazole-4,7-dicarboxylic acids, by way of the corresponding methyl substituted compounds, with various substituents on the 2-phenyl substituent and (2) to correlate structure with NLO response, and (3) to investigate the polymerization of the diacids with 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT).

PBT Compressive Strength Synthesis: Block Copolymer

Poly(benzothiazole) (PBT) and related polybenzazole systems exhibit exceptionally high strength and high modulus but low compressive strength. One approach to this problem is to sacrifice some modulus to gain compressive strength. It was proposed that an ABA triblock polymer with rigid A blocks and flexible B block could provide a balance between modulus and compressive strength. All components must have high thermal stability, resistance to acid (PPA), and be amenable to subsequent reaction. The identity and length of the A and B blocks has been and is currently under investigation.

The use of star or multichain polymers offers a synthetic pathway for the synthesis of the flexible B section of the ABA (Rigid-Flexible-Rigid) triblock polymer. Star polymers are synthesized by the use of an RA_f or RB_f (multifunctional) monomer and an AB



monomer. Star polymers exhibit narrower molecular weight ranges when compared to systems involving AA and BB monomers in condensation polymerizations. The higher the functionality, f , of the multifunctional center, the narrower the molecular weight range of the polymer produced. Because only AA or BB ($f=2$) monomers are being considered for the multifunctional center, the narrowing effect will be minimal. The termination of the resultant multichain polymer, the flexible B section, dictates the identity of the AA or BB monomer chosen. Because this investigation is centered on polymers composed only of benzoxazole or benzothiazole units, carboxyl terminations are indicted. It seems unlikely, but not entirely impossible, that the o-aminothiol or o-aminophenol function would survive the rigors of PPA polymerization. The AA (multifunctional) monomer will therefore be a diacid.

The goals of this part of the synthetic effort were (1) the synthesis of an AB rigid-rod monomer, and (2) the polymerization of the AB monomer alone and with preformed non-rigid-rod ABPBO or ABPBT.

i. Substituted Polyimidazoles at W.S.U. (Kane)

The interest in N,N'-di-substituted polybenzodiimidazoles is to a large extent based on the expectation that the substituents would improve solubility properties of the rigid-rod systems. This has been realized to the extent that the polymers are soluble in formic acid. Plans have included placing different substituents (including flexible and even aliphatic groups) on each nitrogen in the polymer repeat unit with the intention of reducing the symmetry and therefore improving solubility. The ground work for synthesis of the requisite

tetraamines has already been established with the synthesis and characterization of intermediates. Reaction of these with another primary amine would provide the precursor for the desired unsymmetrically substituted tetraamine monomers.

The two stage synthesis suggested by Korshak's work was examined in order to take advantage of the well known efficiency of polyaramid forming low temperature condensation polymerizations between di-acid chlorides and di functional primary amines. The precursor polyamide would then establish the chain length for the polybenzodiimidazole systems. However, the data clearly shows that the molecular weights of the polyamides are disappointingly low. Even polymers which because of their Kevlar like structure would be expected to have considerably higher inherent viscosities than observed in the current project.

In the process of attempting to derivatize the tetraamines prepared in this project, it was observed that they all degrade rapidly in the presence of HCl. This observation suggests that the HCl by-product of the polycondensation reaction upsets the stoichiometry of the reaction by promoting degradation of the tetraamine monomers. Thus, it appears rather self-defeating to pursue this two-stage synthetic route to the desired polybenzodiimidazoles. Thus we have explored alternative routes, for example, condensation of the tetraamines with bis-aldehydes to form the intermediate poly-amis. All of the model compounds have been submitted to the Polymer Branch for evaluation of their non-linear optical properties.

6. NEW PROCESSING TECHNOLOGY

a. Computer Vision A. I. Techniques of Polymer Processing (Riseman, Malone, Karasz)

This project (now terminated) has demonstrated the feasibility of using computer vision techniques and optical microscopy to follow the kinetics and microstructure during spinodal decomposition of a polymer blend. Among other features, the mean of the population of the local maxima of the gradients in each image has been computed; this global feature was shown to co-develop with the phase separation of the blend. An algorithm was developed which employs the gradient magnitude technique to analyze optical images of spinodally decomposing polymer blends. This algorithm has been used to extract the Cahn-Hilliard spinodal growth rates for a binary blend of polystyrene with poly(vinyl methyl ether). We have shown that the spinodal temperature can be found from the temperature dependence of this growth rate, and how additional shape features such as compactness might be used to study the same binary blend.

We have described an algorithm to study specifically the interface region in a spinodally decomposing blend. A particular population of concentration gradients is suggested that (a) co-develops with the process in its early stages, (b) can be used to characterize and follow its kinematics, and (c) might be potentially useful in process control and automated polymer processing, since microcircuits can be fabricated to perform much of the analysis. The concentration gradient magnitude is obtained by methods known as "low-level vision", developed in the field of computer vision and image understanding. The

algorithm was tested by analyzing simulated images of spinodal decomposition in a binary blend of polystyrene and poly(vinyl methyl ether). We have experimentally obtained microscopy video images of a PS/PVME blend above its lower critical solution temperature (LCST). The resulting Cahn-Hilliard spinodal growth rates were compared with the literature values.

More recent results have focused on designing and testing algorithms with increased flexibility and robustness. This was necessary because microscope images of the blends in the early stages of phase separation have poor contrast, and the early stages of the phase separation cannot be interpreted adequately with more conventional techniques. Our new algorithms identify the boundaries of phase regions in images of phase-separating blends, by identifying image points where the first derivative of the intensity attains a local maximum, taking into account contextual information from neighboring boundary segments and exploiting estimates of the background noise in the image. This has a number of advantages over the previous approach, principally an improved rejection of false edges. We have successfully tested the algorithm on a new series of images for our model PS/PVME blend, as well as on past image sequences of other blends. Using the new algorithms, we have also verified that a previously used measure - the average value of the gradient of the image intensity at the identified edge points - remains a good numerical characterization of the phase separation process for the new image sequence, and is a good candidate for a control variable.

b. Advanced Processing Techniques for High Performance Multicomponent Polymeric Systems (FMI)

Under subcontract to UMass, Foster-Miller has developed equipment and procedures to uniaxially orient extended conjugated polymers such as polyphenylene vinylene. Foster-Miller also has processed high performance polyimides and their blends, and multicomponent sol-gel microstructures. Foster-Miller has undertaken mechanical testing, characterization, bonding and fabricating test samples of these high performance polymer films.

IX PUBLICATIONS, AFOSR/DARPA Supported (December 1986 - October 1988)

1. Macromolecules 20, 2023-2026 (1987) (with Paul M. Lahti and Jan Obrzut) "Use of the Pariser-Parr-Pople Approximation To Obtain Practically Useful Predictions for Electronic Spectral Properties of Conducting Polymers".
2. European Polymer Journal 23, 745-751 (1987) (with C. Silvestre, W.J. MacKnight and E. Martuscelli) "Morphology of Poly(ethylene oxide)/Poly(vinyl acetate) Blends".
3. Journ. Chem. Physics 87, 2349-2358 (1987) (with J. Obrzut) "Ultraviolet and Visible Spectroscopy of Poly(paraphenylene vinylene)".
4. Synthetic Metals 20, 85-95 (1987) (with David R. Gagnon, Edwin L. Thomas and Robert W. Lenz) "Molecular Orientation and Conductivity in Highly Drawn Poly(p-phenylene vinylene)".
5. Polymer 28, 1190-1199 (1987) (with C. Silvestre, S. Cimmino, E. Martuscelli and W.J. MacKnight) "Poly(ethylene oxide)/Poly(methyl methacrylate) Blends: Influence of Tacticity of Poly(methyl methacrylate) on Blend Structure and Miscibility".
6. Poly. Comm. 28, 236-240 (1987) (with Saburo Akiyama, W.J. MacKnight and Junji Nambu) "Miscibility in Polycarbonate/Poly(styrene-co-methacrylic acid) Blends and the Ternary System Involving Styrene-Butyl Acrylate Block Copolymer".
7. Poly. Comm. 28, 261-262 (1987) (with C.C. Han and R.W. Lenz) "Highly Conducting, Iodine-Doped Copoly(phenylene vinylene)s".
8. J. Polymer Sci. 25, 2531-2540 (1987) (with C. Silvestre, S. Cimmino, and W.J. MacKnight) "Crystallization, Thermal Behavior, and Compatibility in Isotactic Polystyrene/Poly (o-chlorostyrene-co-p-chlorostyrene) Blends".
9. J. Chem. Phys. 87, 6178-6184 (1987) (with J. Obrzut) "Defects in the Electronic structure of poly(p-phenylene vinylene): Electronic Spectra, Electrochemical behavior, and Molecular Orbital calculations".
10. Eur. Polym. J. 24, 123-127 (1988) (with R. Vukovic, G. Bogdanic, V. Kuresevic, and W.J. MacKnight) "Miscibility and Phase Behavior in Poly (2,6-Dimethyl-1,4-phenylene Oxide) and Poly(fluorostyrene-co-bromostyrene) Blends".
11. Macromolecules, 21, 231-234 (1988) (with Gaetano Guerra, Soonja Choe, David J. Williams, and William J. MacKnight) "Fourier Transform Infrared Spectroscopy of Some Miscible Polybenzimidazole/Polyimide Blends".
12. Poly. Comm., 29, 14-16 (1988) (with Slavka Stankovic, Gaetano Guerra, David J. Williams, and William J. MacKnight) "Miscible Blends of Polybenzimidazole and a Diisocyanate-based polyimide".

13. J.Poly.Sci., Physics Ed., 26, 301-313 (1988) (with Gaetano Guerra, David J. Williams, and William J. MacKnight) "Miscible Polybenzimidazole Blends with a Benzophenone-based Polyimide"
14. J.Applied Polymer Science, 35, 679-693 (1988) (with Gyorgy Banhrugui and Peter Hedvig) "Analysis of Temperature-Dependent AC Dielectric Loss Data"
15. Macromolecules, 21, 446-451 (1988) (with Peter Cifra and William J. MacKnight) "Distribution of Interactions in Binary Polymer Mixtures: A Monte Carlo Simulation Study"
16. Cell Biophysics, 11, 91-104 (1987) (with Anna Balazs and William J. MacKnight) "The Aggregation of Reverse Micelles: A Computer Simulation"
17. Brit.Polym.Jrnl., 20, 149-155 (1988) (with C.K. Sham, C.H. Lau, D.J. Williams, and W.J. MacKnight) "Upper Critical Solution Temperature Behavior in Poly(ether ether sulphone)/Poly(ether ether ketone-co-ether ether sulphone) Blends"
18. Nonlinear Optical and Electroactive Polymers, ed. P.N. Prasad and D.R. Ulrich, Plenum Publ. Corp. (1988), 273-280. (with Jan Obrzut) "Optical Properties of Poly(p-Phenylene Vinylene)"
19. Macromolecules 21, 1193-1194 (1988) (with E.J. Beckman, R.S. Porter, W.J. MacKnight, J. Van Hunsel, and R. Koningsveld) "Estimation of Interfacial Fraction in Partially Miscible Polymer Blends from Differential Scanning Calorimetry Measurements"
20. Polymer, 29, 1016-1020 (1988) (with C.K. Sham, G. Guerra and W.J. MacKnight) "Blends of two poly(aryl ether ketones)"
21. J. Appl. Poly. Sci., 36, 243-248 (1988) (with A. Nelson, G. Guerra, D.J. Williams and W.J. MacKnight) "Catalytic Activity of Benzimidazole in the Imidization of Polyamic Acids"
22. J. Polym. Sci., Chem. Ed., 26, 1809-1817 (1988) (with S. Antoun and R.W. Lenz) "Synthesis and Electrical Conductivity of Poly(arylene Vinylene). I. Poly(2,5-Dimethoxyphenylene Vinylene) and Poly(2,5-Dimethylphenylene Vinylene)"
23. SPIE, 878, 123-127 (1988) (with G. Williams and G.S. Attard) "Functional Polymers and Guest-host Polymer Blends for Optical and Electronic Applications"
24. Polymer, 29, 1412-1417 (1988) (with J.M. Machado and R.W. Lenz) "Electrically Conducting Polymer Blends"
25. J. Polym. Sci: Part B: Polymer Physics, 26, 2379-2383 (1988) (with P.Cifra, and W. J. MacKnight) "Computer Simulation of a Binary Polymer Mixture in Three Dimensions"
26. J. Polym. Sci. Part B: Polymer Physics, 26, 2247-2256 (1988) (with J.B.Schlenoff, J.M. Machado, P.J. Glatkowski) "Chemical and Electrochemical Doping in Poly(Paraphenylene Vinylene) Blends"

27. J. Amer. Chem. Soc. 110, No. 21, 728-729 (1988) (with P.M. Lahti, D.A. Modarelli, F.R. Denton, III, R.W. Lenz) "Polymerization of α, α' -Bis(dialkylsulfonio)-p-xylene Dihalides via p-Xylylene Intermediates: Evidence for a Nonradical Mechanism"
28. J. Polym. Sci :Part A :Polymer Chemistry 26, 3241-3249 (1988) (with Robert W. Lenz, Chien-Chung Han, John Stenger-Smith) "Preparation of Poly(phenylene Vinylene) from Cycloalkylene Sulfonium Salt Monomers and Polymers"
29. Coll. & Polym. Sci. 266, No. 8, 701-715 (1988) (with G. Bánhegyi, P. Hedvig) "DC Dielectric Study of Polyethylene/CaCO₃ Composites"
30. Polymer, 29, 1940-1942 (1988) (with B.P. Singh and P.N. Prasad) "Third-Order Non-Linear Optical Properties of Oriented Films of Poly(p-Phenylene Vinylene) Investigated by Femtosecond Degenerate Four Wave Mixing"
31. Kem. Ind, 37, 347-349 (1988) "Polymer Blends"
32. Macromolecules, 21, 3438-3442 (1988) (with M. Masse and H. Ueda) "Miscibility in Chlorinated Polybutadiene/Chlorinated Polyethylene Blends: Effect of Chain Microstructure"
33. J. Polym. Sci: Part B Polym. Physics, 27, 199-203 (1989) (with J. Machado, J. Schlenoff, and F.R. Denton) "Analytical Methods for Molecular Weight Determination of Poly(p-Xylylidene Dialkyl Sulfonium Halide): Degree of Polymerisation of Poly(p-Phenylene Vinylene) Precursors"
34. Comprehensive Polymer Science, Volume 7 (S.L. Aggarwal ed.) Pergamon Press, Oxford p.111-130 (1989) , "Polymer Blends" (with W. MacKnight)
35. Macromolecules, 22, 458-464 (1989) (with M.R. Obrzut) "X-ray Photoelectron Spectroscopy of Neutral and Electrochemically Doped Poly(p-phenylene vinylene)"
36. J. Polym. Sci: Part B Polym. Physics, 27, 469-487 (1989) (with T. Granier, E. L. Thomas and F. Karasz) "Paracrystalline Structure of Poly(paraphenylene vinylene)"
37. Macromolecules, 22, 1220-1231 (1989) (with M. Bishop and K. Langley) "Dynamic Light-Scattering Studies of Polymer Diffusion in Porous Materials: Linear Polystyrene in Porous Glass"
38. Macromolecules, 22, 1964-1973 (1989) (with J. Machado and J. Schlenoff) "Morphology, Doping, and Electrical Properties of Poly(p-phenylene vinylene)/Poly(ethylene oxide) Blends"
39. Synthetic Metals, 29, E109-E114 (1989) (with J. Obrzut and M.J. Obrzut) "Photoelectron Spectroscopy of Poly(p-Phenylene Vinylene)"
40. Synthetic Metals, 29, E103-E108 (1989) (with J. Obrzut and M.J. Obrzut) "Photoconductivity of Poly(p-Phenylene Vinylene)"

41. Synthetic Metals, 29, E97-E102 (1989) (with J. Grobelny and J. Obrzut)
"Solid-State ¹³C NMR Study of Neutral Insulating and Electrochemically Doped Conducting Poly(p-Phenylene Vinylene)"
42. Netsu Sokutei, 16, (2), 65-75 (1989) (with Y. Maeda and W. MacKnight)
"Effect of Pressure on the Miscibility of Polymer Blends by High Pressure Differential Thermal Analysis"
43. Philosophical Magazine A, submitted July, 1988 (E.L. Thomas and P. Pradere) "Three Dimensional Model for Twinning in Polymer Single Crystals with Inclined Chains"
44. Maaterials Research Soc. Proceedings 138 (1989) (E.L. Thomas and P. Pradere) "Generation of Three Dimensional Structures by Crystal-Crystal Coalescence of Poly p xylylene in Solution" (in press)
45. Ultramicroscopy, submitted (E.L. Thomas and P. Pradere) "Image Processing of Partially Periodic Lattice Images of Polymers: The Study of Crystal Defects"
46. Acta Cryst. (E.L. Thomas, D.M. Anderson and D.C. Martin) "Maximum Entropy Data Restoration Using Both Real and Fourier Space Analysis" (in press)
47. Macromolecules (in press) (P. Pradere, E.L. Thomas) "Antiphase Bonding and Ordering Defects in S-Polystyrene Crystals"
48. "Morphology of Diblock Copolymers in the Weak Segregation Regime" (E.L. Thomas, Z. Xu, D. Gobran and L. Fetters) (in press)
49. "Morphological Studies of Micelle Formation in Star Diblock Copolymer/Homopolymer Blends" (E.L. Thomas and Z. Xu) (in press)
50. Macromolecules, 21, 1204, (1988) (J.M. Stouffer and T.J. McCarthy) "Polymer Monolayers Prepared by the Spontaneous Adsorption of Sulfur-Functionalized Polystyrene on Gold Surfaces"
51. Langmuir American Chemical Society (1989) (S.L. Hsu, D.A. Waldman, B. Kolb and T.J. McCarthy) "A Spectroscopic Analysis of Functionalized Polystyrene Adsorbed on a Metallic Surface" I. Experimental Studies (in press)
52. MRS National Meeting 1988 (in press) (N. Akmal, M. Sinsky, C. Jariwala and J. J. Kane) "Synthesis of New Nitrogen Substituted Polybenzimidazoles"
53. Journal of Applied Physics, "Oscillator Model of Piezoelectricity in Hydrated Polymers" (in press)
54. Proceedings of the Electrochemical Society, 1987, "Improved Mass Transport in Rechargeable Electrodes Employing Conducting Polymer Blends" (in press)
55. New Polymeric Materials, "A Continuous Process for Preparing Highly Conducting, Uniaxially Oriented Poly(Phenylene Vinylene) Film" (in press)

56. Colloid and Polymer Science, "Comment on the 'Dielectric Properties of LDPE/Ny6 Blends' by Mantia et al" (in press)
57. Macromolecules, "Computer Simulation of Copolymer-Copolymer and Copolymer-Homopolymer Mixtures with a Single Interaction Energy" (in press)
58. J. Polym. Sci., "Crystalline Phases of Electrically Conductive Poly(p-Phenylene Vinylene)" (in press)
59. Phys. Rev. B, "Temperature Dependence of the Electrical Conductivity of AsF₅ Doped Poly(p-Phenylene Vinylene)" (in press)
60. Makromolekulare Chemie, "Structural Characterization of Vinylidene Fluoride-Vinyl Fluoride Copolymers" (in press)
61. Polym. Eng. and Sci., "Computer Vision Methods for the Study of Spinodal Decomposition in Polymer Blends" (in press)
62. Polymer, "Anisotropic Mechanical Properties of Uniaxially Oriented Electrically Conducting Poly(p-phenylene vinylene)" (in press)
63. J. Appl. Polym. Sci. "Dielectric Relaxation Properties of Polypropylene-Polyurethane Composites" (in press)
64. Polymer Composites, "Thermal and Electrical Properties of Some Epoxy Based urethane Composites" (in press)
65. Macromolecules, "Short Range Fluctuations in Spinodal Decomposition of Binary Polymer Mixture" (in press)
66. Brit. Polym. J. "Processing and Characterization of a Biaxially Oriented Conducting Polymer" (in press)
67. Biennial Polymer Symposium, "Thermal and Phase Behavior in Miscible Polybenzimidazole/Polyetherimide Blends" (in press)
68. Makromolekulare Chemie, "Miscibility Behavior in Blends of Poly(2,6-Dimethylphenylene oxide) and Random or Block Styrene-Methylmethacrylate Copolymers" (in press)
69. Materials Research Society Proceedings, "Lattice Simulation of Mixtures of Flexible and Semi-Flexible Chains" (in press)
70. J. Polymer Science, "Phototransport in Poly(p-Phenylene Vinylene)" (in press)
71. J. of Matls. Sci. "Crystal Morphology in Pristine Doped Films of Poly(p-Phenylene Vinylene)" (in press)
72. Macromolecules, "Diffusion of Weakly Confined Star and Linear Polymers and Strongly Confined Linear Polymers in a Porous Material" (in press)
73. Makromolekulare Chemie "Miscibility in Blends of Modified Polyolefins" (in press)

74. Third International Conference on Polyimides, "Thermal and Spectroscopic Behavior in Miscible Polybenzimidazole/ Polyimide Blends" (in press)
75. Polymer, "Large Optical Birefringence in Poly-P-Phenylene Vinylene Films Measured by Optical Wave Guide Techniques" (in press)
76. Macromolecules, "Hydrogen Bonding in Polybenzimidazole/Polyetherimide Blends: A Spectroscopic Study" (in press)
77. European Polymer Journal, "Electrical Conductivity of Iodine Doped Poly(butadiene-co-2-vinyl pyridine) Diblock Copolymers" (in press)
78. Polymer, "The Effects of Concentration on Partitioning of Flexible Chains into Pores" (in press)
79. Macromolecules, "Hindered Diffusion of Polystyrene in Controlled Pore Glasses" (in press)
80. Macromolecules, "Dopant Concentration Profiles in Conducting Poly(p-phenylene vinylene) by Rutherford Backscattering Spectrometry" (in press)

Publications 53-80 are with P.I. as author or coauthor.

PATENTS: Applications, U.S. and Foreign

F.E. Karasz, et. al: "High Performance Blends of Aromatic Polyimides with Aromatic Polyethersulfones"