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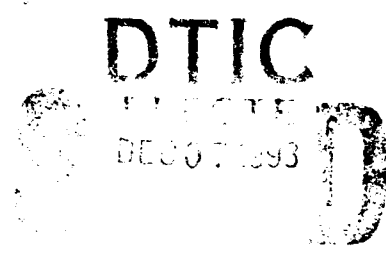
CENTER FOR ADVANCED ELECTRICAL

AND STRUCTURAL POLYMERS

AFOSR-90-0150

1 March 1990 - 28 February 1993

FINAL REPORT

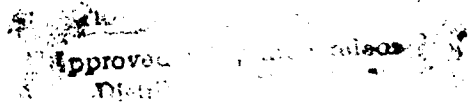


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# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 15 October 1993	3. REPORT TYPE AND DATES COVERED Final   Mar. 1990 - 28 Feb. 1993	
4. TITLE AND SUBTITLE  Center for Advanced Electrical and Structural Polymers		5. FUNDING NUMBERS  61103D 3484/CS	
6. AUTHOR(S)  Professor Frank E. Karasz		8. PERFORMING ORGANIZATION REPORT NUMBER  AEOSR-JR- 93 0046	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Dept. of Polymer Science and Engineering University of Massachusetts Amherst, MA 01003		10. SPONSORING / MONITORING AGENCY REPORT NUMBER  AFOSR-90-0150	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  AFOSR/NC 110 DUNCAN AVENUE SUITE B115 BOLLING AFB DC 20332-0001		11. SUPPLEMENTARY NOTES	
12a. DISTRIBUTION / AVAILABILITY STATEMENT  APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  Research in the U.R.I. has been organized into five thrust areas each comprising collateral and coordinated investigations in three departments at UMass and at Wright State University, Foster Miller Inc. and MIT. Electrical properties of $\pi$ -conjugated polymers are the focus of one thrust and are defined in terms of their structure-property relationships as well as long term applications. A prototypical polymer has been poly- <i>p</i> -phenylene vinylene. A second thrust has concentrated on non-linear optical effects in $\pi$ -conjugated and side chain liquid crystal polymers containing chromophoric mesogens which have been synthesized and characterized, as have low-molecular weight model compounds of systematically varying structure. The third thrust has focused on polymer blends and alloys including high temperature novel processible systems for application in extreme conditions. Miscibility studies in conventional model polymers has continued to yield insights into the fundamental principles underlying polymer-polymer interactions. A computer simulation project has complemented these studies. The thrust on novel macromolecular architecture and characterization has produced a range of new systems and techniques including measurements of polymer dynamics in constricted geometries, and detailed fine-structure investigations of block copolymers. A thrust on new processing technologies has largely centered on the FMI initiatives with respect to novel approaches for high temperature polymer blend melts.			
14. SUBJECT TERMS  electrical properties, non-linear optical effects, polymer blends and alloys, macromolecular architecture and characterization		15. NUMBER OF PAGES 76 16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UNCLASSIFIED

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### ACKNOWLEDGEMENT

The Principal Investigator would like to express his sincere thanks to Dr. Donald Ball, Director of Chemical Sciences, Air Force of Scientific Research, to the late Dr. Donald R. Ulrich, Senior Program Manager, Directorate of Chemical Sciences, to Dr. Charles Y-C Lee, Senior Program Manager, Directorate of Chemical Sciences and to Dr. B. Wilcox, Assistant Director, Material Science Division, Defense Advanced Research Projects Agency, for their unfailing cooperation, help and courtesy extended to him during the period of this grant.

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**I. TITLE:** Center for Advanced Electrical and Structural Polymers

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 AFOSR-90-0150 March 1, 1990 - February 28, 1993

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## VII. ABSTRACT OF ACCOMPLISHMENTS

This report presents in some detail the accomplishments of the last twelve months at the URI Center of Advanced Electrical and Structural Polymers at UMass. In addition this Final Report provides an overview of achievements during the three year period of the grant. In particular, the total output of publications over the period of the grant are listed.

Research has been organized into five thrust areas comprising collateral and coordinated investigations in three departments at UMass and at three extramural sub-contractors. Electrical properties of polymers are the focus of one thrust and these have covered a wide range of simple and increasingly complex  $\pi$ -conjugated systems defined in terms of their structure-property relationships as well as long term applications. A prototypical polymer has been poly-*p*-phenylene vinylene, extensively investigated with respect to its electrical, structural morphological and other relevant properties. These have been studied using a wide range of advanced instrumental techniques. A second thrust has concentrated on non-linear optical effects in  $\pi$ -conjugated systems and has involved extensive collaboration within and outside the URI. Side chain liquid crystal polymers containing chromophoric mesogens have also been synthesized and characterized, as has a wide range of relevant polymers and low-molecular weight model compounds (WSU) of systematically varying structure. The third thrust has focused on polymer blends and alloys. Strong collaboration with FMI and other industrial researchers in the area of high temperature systems had



produced a number of novel processible systems for application in extreme conditions. Miscibility studies in conventional model polymers has continued to yield valuable insights into the fundamental principles underlying polymer-polymer interactions and the effect of micro-structure on these properties. These studies have been complemented by an extensive simulation project which has shown, inter alia, the effect of the commonly employed mean-field approximation in this context. The thrust on novel macromolecular architecture and characterization has produced a range of new systems and new techniques of which the more recent measurements of polymer dynamics in constricted geometries is only one example. Another lies in the area of block copolymers for which detailed fine-structure features have become available in selected systems. Finally, the URI has incorporated a thrust on new processing technologies which has largely centered on the FMI initiatives with respect to novel approaches for high temperature polymer blend melts.

The contents of the five thrusts outlined above have been constantly modified and allowed to overlap as opportunities arose on the basis of new results. As always, it was necessary to make choices as funding levels changed and expansion or curtailment of particular investigations became appropriate. As an important academic by-product, the URI had considerable direct and indirect influence on graduate *education* and available *facilities* at UMass and at the sub-contractor sites. Over the course of the three year period some forty or fifty graduate students and post-doctoral fellows have received at least some direct

support from the URI; many more than this have benefitted indirectly through the ready availability of URI-funded facilities and infra-structure.

## VIII. DESCRIPTION OF RESEARCH UNDERTAKEN

### 1. INTRODUCTION

The URI program at UMass and sub-contractor sites has been organized as The Center for Advanced Electrical and Structural Polymers which operated with AFOSR/DARPA support for a total of 6 years. In the period covered by this report research was organized into five thrusts:

1. Electrical Properties of Polymers
2. Non-Linear Optical Properties of Polymers
3. Polymer Blends and Alloys
4. Novel Macromolecular Architectures and Characterization
- and 5. New Processing Technology.

Each of these thrusts involved collaborative interactions between the PI, Faculty associates, extra-mural subcontractors and government associates. The directions of the thrusts evolved and were modified as needed to take into account new research opportunities and, in later years, contractions necessitated by a decrease in available funding.

Details of the organizational changes have been given in earlier Annual Reports.

The URI has had major impact on polymer research at UMass and at the associated sites. Over the last three years it has been supported 26, fully or in part, post-doctoral fellows and 23 doctoral students. It has allowed the acquisition of several major state-of-the art instruments and facilities. In the period covered

by this Report *one hundred and ten* scientific publications have appeared or are in press, together with a number of patents as a result of URI support.

In the following sections some research highlights pertaining to each of the thrusts will be described. Chapter IX provides complete details of the scientific output in terms of publication citations.

## 2. ELECTRICAL PROPERTIES OF POLYMERS

In this thrust the synthesis, properties and applications of poly-*p*-phenylene vinylene and related macromolecules have been the main focus of attention. PPV is a prototypical  $\pi$ -conjugated chain, synthesized by novel precursor route, that has been a leading candidate for synthetic metal applications for a decade. We have studied this system comprehensively including (for example) the polymerization mechanism, the crystallographic structure, mechanical properties, electrical properties, copolymers, blends, processing,  $\chi^{(3)}$  behavior, electro-luminescence and other photophysical processes (see, for example, publications 5, 10, 14, 30, 37, 40, 54, 60, 64, 70, 71, 72, 73, 83, 87, 90, 94, 108, Chapter IX). Modified PPV's synthesized here constituted the first report of soluble macromolecular materials to exhibit blue (474 nm) electroluminescence and have been the subject of recent intense investigation.

## 3. NON-LINEAR OPTICALLY ACTIVE POLYMERS

This thrust has comprised three major efforts: a) An extensive synthetic program at WSU (See Appendix 2 for details.) which has systematically explored a variety of hetero-atom containing and other structures, including low molar mass

model components, and has thereby derived a comprehensive understanding of structure-property relationships (e.g. 6, 7, 8, 9, 45) b) A synthetic effort at UMass coupled with the electrical property thrust in which  $\pi$ -conjugated macromolecules based on PPV but involving derivatives, copolymers, hetero-atom analogs, alloys and novel sol-gel glass blends have been prepared and extensively studied. Some of these materials have large off-resonance  $\chi^{(3)}$ 's and this effort could yield materials of high practical applications, (22, 44, 87) c) A third effort has brought side-chain liquid crystalline materials into this thrust. In this program a number of mesogenic units and spacers have been attached to flexible chain backbones and have been investigated with regard to transitional properties, structure, alignments, etc.

All these sub-thrusts have involved extensive collaboration with WPAFB,(84, 88, 103, 104, 107) other URI laboratories and other academic and industrial organizations.

#### 4. POLYMER BLENDS AND ALLOYS

Much of this work has been described in previous reports. A fraction of this thrust has continued the directions of an earlier AF-DARPA program on high temperature blend systems and there has been a major synthetic effort in the area of polyimides of novel structure (63, 100) and blends of polyimides with sulfones, carbonates, etc. This work is closely coupled with the work of FMI (see Section 6 and Appendix 1) who have been able to scale-up some of the blend systems developed at UMass, (56).

In another facet of this program, the effect of copolymer sequence distribution on miscibility has been investigated in model systems. It is known for example that alternating and random copolymers and of course, block copolymers can differ markedly with respect to their interactions with other homo- or copolymers and thereby greatly affect miscibility behavior. This phenomena has been studied theoretically and in appropriate model systems and predictions of effects have been made. In a parallel effort, extensive use has been made of Monte Carlo lattice simulation technologies to investigate miscibility in a range of systems and under a variety of conditions. These studies have shed considerable light also on interfacial and surface properties of blends, (35, 44, 52, 79, 82).

#### 5. NOVEL MACROMOLECULAR ARCHITECTURE AND CHARACTERIZATION

Certain studies in this thrust have overlapped other thrust efforts and in some cases have therefore already been discussed. Highlights include the novel electron microscopic morphological investigations of Prof. Thomas (Appendix 3), (47, 48, 95, 96, 97) and the dynamic light scattering studies of solvated macromolecules in constricted geometries. In a series of investigations the translational diffusion of polymers in the channels of controlled pore glasses have been measured for the first time as function of macroscopic architecture and other parameters (11, 61, 77, 78, 85, 101). Also new solid state NMR techniques have been employed to investigate the microstructures of polymer blends, (34, 39, 60, 92).

This thrust has revolved around the developments in novel high temperature polymer blends carried out at FMI and is described extensively in Appendix 1.

APPENDIX 1

FOSTER MILLER INC.

PROCESSING AND PROPERTIES OF ULTRAHIGH  
PERFORMANCE POLYMER BLENDS

Submitted by:  
Kent G. Blizard  
Tom Fusco  
Mark A. Druy



## Processing and Properties of Ultrahigh Performance Polymer Blends

This report summarizes three years of effort devoted to processing of polymer blends under subcontract to the University of Massachusetts.

During the first year of the program, we investigated the processing, rheology, and thermal-mechanical behavior of polyimide (PI)/polyethersulfone (PES) blends. By blending the polyimide as the major component with PES under the proper conditions, the resulting blend was melt processible and optically translucent, while retaining outstanding thermal and mechanical properties. The polyimide (Ciba Geigy Matrimid 5218) by itself is not processible in the melt state, necessitating solution casting methods to obtain film. Because of the processing cost and environmental concerns, ultrahigh performance polymers such as Matrimid, to be of commercial interest, must be processible using standard melt processing equipment.

Specific accomplishments in processing and characterization studies of PI/PES melt blends include the following:

- Melt blending PES with PI with 50 to 80% PI in a Brabender torque rheometer resulted in a homogeneous, translucent blend similar to those obtained by coprecipitation from a mutual solvent
- Melt mixing studies on the Brabender were scaled up to the 25 mm Berstorff twin screw extruder
- The 67/33 PE/PES blend was melt processed with the twin screw extruder into rods and pellets. This scale up required an interactive optimization of the screw configuration and processing temperatures since the processing window is relatively narrow.
- Both the 67/33 and 80/20 blends were compression molded into films and sheets.
- Initial blend characterization studies indicated use temperatures of these blends in the range of 250°C to 300°C depending on composition.

While melt blending Matrimid with PES does not appear to give a molecularly miscible blend, this system retains the exceptional thermal and mechanical properties of the polyimide, along with optical translucency usually associated with molecularly miscible blends.

During the second year of this effort, we explored other polymer systems in a similar effort as in the first year. The second year's effort focused on the processing, rheology, and thermomechanical behavior of thermoplastic polyimide (TPI)/polyetherimide (PEI) blends. By blending the polyimide as a major component with this amorphous engineering resin, most of the outstanding thermo-mechanical properties of the polyimide were retained while substantially lowering the cost of the blend.

The thermoplastic polyimide (Aurum 450C of Mitsui Toatsu), while processable in the melt state, has the drawbacks of a semicrystalline material in composites manufacture and a price comparable to exotic materials such as Kapton. Films of TPI, PEI (Ultem 6000), and blends of these materials having 50 and 80 percent by weight of TPI were produced. These films were yellowish in color, but were transparent. Thermal analysis (DSC and DMTA) showed a single glass transition temperature ( $T_g$ ) which increased from  $227^{\circ}\text{C}$  to  $252^{\circ}\text{C}$  with increasing TPI content. The tensile properties of the films were similar to those reported by the vendors, with 0.32 Mpsi modulus, 12 kpsi tensile strength, and 30-60% elongation at break depending on composition. The alloys showed no unexpected trends either in solid or melt behavior. Significantly, unlike the TPI itself which showed 15% crystallinity on annealing, the blends alloys remained largely amorphous, with only 0.5% and 2.1% crystallinity, respectively, for the alloys containing 50 and 80% TPI. In addition, a 4-6 $^{\circ}\text{C}$  melt point depression was observed in the TPI crystalline phase when blended with PEI. The second year's effort resulted in the following conclusions:

- Blends of Aurum 450C with Ultem 6000 are miscible over the composition range studied (up to 50% Ultem).
- Crystallization is inhibited in the 80/20 TPI/PEI blend and virtually absent in the 50/50 blend. The semicrystalline TPI is largely incorporated into the amorphous alloy phase.
- DMTA corroborated the DSC evidence of a shift in  $T_g$  with composition, which monotonically increased with increasing TPI content.

- Melt flow behavior of the blends closely resembles that of both components, with an onset of shear thinning at about 10 s<sup>-1</sup>. Viscosities observed in the RMS were in relatively good agreement with those seen using the Brabender torque rheometer.
- Static tensile measurements were only slightly less than those reported by the vendors, and could be due to measurement differences. Lower transverse direction ultimate properties are likely due to film flaws since the TD modulus is not affected.

In the third and final year of the program the TPI/PEI blends were incorporated as matrices in carbon fiber composites and tested for mechanical behavior and physical attributes such as resin and void content. A summary of the test results on films and composites are shown in Table 1.

The superior electrical properties of the thermoplastic polyimide were retained in the blends. Increasing the TPI content did improve the high frequency and high temperature properties. Adhesion to copper foil, extremely poor in the TPI because of crystallization, was improved to the target value by alloying with 20% PEI, and to 13 pounds/linear inch (PLI) for the 50/50 blend.

Composite properties were good, but the composition of the matrix had little effect on the resulting composite. Void contents were quite low, 2% or less, but because of little resin bleedout, the fiber content was less than 50% rather than the target of 60%. The molding cycle was partially optimized, but factors such as resin film thickness and molding time still need to be further investigated.

Two important application areas for these blends have been identified: high performance electronics packaging, replacing such materials as Kapton, and a matrix resin for high temperature composites.

**Table 1. Summary of Polyimide Blend Results Achieved**

	<u>TPI/PEI Blend</u>	<u>Neat TPI</u>
<u>Films</u>		
Tensile Modulus, Mpsi	0.32	0.33
Tensile Strength, kpsi	12 .0	13.0
25°C Dielectric Constant (1 MHz)	3.2	3.2
250°C Dielectric Constant (1 MHz)	3.1	3.2
25°C Dissipation Factor (1 MHz)	0.01	0.01
250°C Dissipation Factor (1 MHz)	0.02	0.02
Adhesion to Copper, pounds/linear inch	13 .0	<4.0
<u>Composites</u>		
Fiber Content, %	48.0	47.0
Void Content, %	2.0	~0.0
In-plane Shear Modulus, Mpsi	1.1	1.3
In-plane Shear Strength, kpsi	30 .0	28.0

Publications:

Rheology and Mechanical Properties of Ultrahigh Performance Polyimide Melt Blends, K. G. Blizard, M. A. Druy, and F. E. Karasz ANTEC '92 p. 585, (1992)

FILMS AND COMPOSITES PRODUCED FROM  
POLYIMIDE MELT BLENDS

## SUMMARY

Two important application areas for these blends have been identified: high performance electronics packaging, replacing such materials as Kapton, and a matrix resin for high temperature composites.

By blending the thermoplastic polyimide as a major component with PEI under the proper conditions, most of the outstanding thermo-mechanical properties of the TPI were retained while substantially lowering the cost of the blend. The resulting blend films have been incorporated as matrices in carbon fiber composites and tested for mechanical behavior and physical attributes such as resin and void content. In addition, electrical properties of the films were measured and compared to the neat resins and lamination cycles to copper foil were established. A summary of the test results on films and composites is shown in Table 1.

The superior electrical properties of the thermoplastic polyimide were retained in the blends. Increasing the TPI content did improve the high frequency and high temperature properties. Adhesion to copper foil, extremely poor in the TPI because of crystallization, was improved to the target value by allowing with 20% PEI, and to 13 pounds/linear inch (PLI) for the 50/50 blend.

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25° C Dielectric Constant (1 MHz)	3.2	3.2
250° C Dielectric Constant (1 MHz)	3.1	3.2
25° C Dissipation Factor (1 MHz)	0.01	0.01
250° C Dissipation Factor (1 MHz)	0.02	0.02
Adhesion to Copper, pounds/linear inch	13	< 4
<u>Composites</u>		
Fiber Content, %	48	47
Void Content, %	2.0	≈ 0
In-plane Shear Modulus, Mpsi	1.1	1.3
In-plane Shear Strength, kpsi	30	28

---

Composite properties were good, but the composition of the matrix had little effect on the resulting composite. Void contents were quite low, 2% or less, but because of little resin bleedout, the fiber content was less than 50% rather than the target of 60%. The molding cycle was partially optimized, but factors such as resin film thickness and molding time still need to be further investigated.

## EXPERIMENTAL

### Film Production and Testing

This past year's effort has greatly advanced the melt processing technology for these blends. The thermoplastic polyimide (Aurum 450C of Mitsui Toatsu), while processable in the melt state, has the drawbacks of a semicrystalline material in composites manufacture and a price comparable to exotic materials such as Kapton. To overcome these limitations, blends of TPI with PEI having 50 and 80 percent by weight of TPI were produced. The details are presented as Appendix A. Thermal analysis (DSC and DMTA) showed a single glass transition temperature ( $T_g$ ) which increased from 227° C to 252° C with increasing TPI content. The tensile properties of the films were similar to those reported by the vendors, with 0.32 Mpsi modulus, 12 kpsi tensile strength, and 30-60% elongation at break, depending on composition. The alloys showed no unexpected trends either in solid or melt behavior. Significantly, unlike the TPI itself which showed 15% crystallinity on annealing, the blends alloys remained largely amorphous, with only 0.5% and 2.1% crystallinity, respectively, for the alloys containing 50 and 80% TPI.

Electrical testing was performed on extruded films. The dielectric constant of polymer films was measured by forming a capacitor from the material and measuring its performance effects on an AC electrical circuit. The parallel-plate capacitor was formed by sputtering a circular metal film (either gold or silver) of a known size (38 mm in diameter) onto both sides of the film. Gold lead wires were used to connect this capacitor to an HP 4284A LCR meter, which is capable of measuring all components of electrical impedance at any set of frequencies from 20 Hz to 1MHz.

Films of each composition were laminated to a JTCS 1 oz. copper foil. The cycle shown in Fig. 1 was used, although no optimization was performed.



## Composites Manufacture and Testing

The initial molding conditions for the trial composites were based on DSC curves, extrusion processing conditions and FMI composites manufacturing technology. The mold used for both the trial and test laminate fabrication was designed by Foster-Miller to allow hand layup of the composite along with a means to clamp and hold the fibers in place during the compression molding cycle. All compression molding was done using a programmable Tetrahedron press equipped with multi-stage temperature and pressure ramping capabilities.

A two stage molding procedure was adopted, both for the trial and for the subsequent test composites. A 6" x 6", four ply composite of [0,90,90,0] configuration was fabricated and processed as a trial sample. Each of the four plies consisted of 24 tows of fiber across, with a 2 mil thick film layer of 80/20 TPI/PEI blend between each ply. The fiber used in the manufacture of the composites was 12k T650/35 Thornel carbon fiber (Amoco). This layup was designed to yield a composite of 60% fiber by volume.

The initial molding conditions are shown in the mold cycle diagram in Fig. 2. All steps were done under vacuum. These molding cycle parameters were sufficient to "prepreg" the material to a point at which the composite was consolidated enough to handle, cut and remold during the optimization stage of the molding cycle. The original 6" x 6" composite was cut into nine 2" x 2" squares. Four sets of two each were taken and remolded at four different sets of conditions following the same type of cycle above. The four sets of conditions were as follows (no vacuum):

- 150 psi at 400° C
- 200 psi at 400° C
- 200 psi at 410° C
- 300 psi at 410° C

A 0.25" square sample was cut from each of the trial composites, along with a piece from the original prepregged material. Each sample was potted in clear epoxy. The epoxy was cured and the samples were ground down using different grades of fine sandpaper, 240 to 600 grit, and finally polished using a very fine diamond paste. A series of micrographs,

detailing the composites cross-section, were taken at 40X magnification. The micrographs (not shown) revealed that the samples molded at 200 and 300 psi at 410° C were of good quality. The dry fiber content was at a minimum while the consolidation was at a maximum. However, it was found that at 300 psi, there was excess resin bleedout and fiber washout that was not evident at 200 psi. Therefore, 200 psi at 410° C became the final molding conditions of choice.

The fabrication of the actual test composites followed the same two step procedure as for the trial composite. The prepregged material for each of the four film runs was two sets of [0,90,90,0] plies and was 12.5" square. Once each of the prepregs was fabricated at 400° C and 200 psi, a 6" x 6" piece was cut from the prepreg and remolded at the final conditions of 200 psi at 410° C. This composite served as the source of the test samples. A 24-ply composite of each material ("show" samples) was also made in the same fashion.

A number of 1/2" wide rectangular test samples were cut from each of the four eight-ply test laminates at a 45° angle with respect to the composite's fiber orientation for in-plane shear testing. These specimens were tabbed with 3/16" E-glass at each end. The tabbed area on each specimen, along with the back of the tab, was lightly abraded using 240 grit sandpaper. The abrasion allowed a mechanical lock when the adhesive was added. A thin film, epoxy adhesive was used to bond the tabs to the samples. All the tabbed specimens were tested in tension. The testing was performed on a United Tensile Tester equipped with a Sintech data acquisition system. The in-plane shear modulus and strength determinations were carried out separately. The modulus was measured with a MTS clip-on extensometer using a 2.0" gauge length. The sample was allowed to load to 40% of its expected breaking strength, at a speed of 0.05 in/min, to allow a best fit line to be drawn and a modulus value to be calculated. After the modulus testing was completed, the MTS extensometer was removed and the samples were tested to failure. Approximately three out of every four test specimens failed in the gage area. The few samples that failed in the tabbed area, had the failing point start at the tab and extend into the tabbed area. These samples were noted, but were included in the results since they were within one standard deviation of the excluded mean.

## RESULTS AND DISCUSSION

### Polyimide Blends for Electrical Packaging

In the electronics packaging field, polyimide films such as Kapton have found dominance in certain high performance niche applications. However, these materials are expensive, hygroscopic, and hazardous to process. There is a clear demand for a film having good thermal stability coupled with lower material and processing costs. Thermoplastic polyimide blends have all these potential advantages. By combining Aurum semicrystalline TPI with Ultem polyetherimide, a ductile amorphous copolymer, a miscible alloy is formed (see Appendix A). At a cost of several degrees in  $T_g$ , a film is produced with superior peel strengths to copper as well as excellent electrical properties. These findings are discussed in the following paragraphs.

The frequency dependence of the electrical properties of TPI/PEI blend films are shown in Figs. 3 and 4. The dielectric constant at room temperature (Fig. 3) is seen to be nearly identical to the TPI for blends containing 50 and 80% TPI. The dielectric constant was a slightly decreasing function of frequency from 1 kHz to 1 MHz. However, for the 50/50 blend and neat Ultem, the dielectric constant increases significantly at frequencies above about 400 kHz. The dissipation factor, shown in Fig. 4, remained below 0.01 for all blend compositions until the frequency approached 1 MHz. Both the blends and neat polyimides exhibited similar frequency response.

The temperature dependence of the electrical properties of TPI/PEI blend films are shown in Figs. 5 and 6. The dielectric constant decreases slightly from about 3.2 to 3.1 with increasing temperature from room temperature to 250° C for all polyimide films. Films containing Ultem PEI, however, show an increase in dielectric constant at 300° C that is proportional to the amount of PEI in the alloy, seen in Fig. 5. Dissipation factor is essentially the same for all blends, as shown in Fig. 6.

For use as dielectric layers, polymeric films should have at least 6 pounds/linear inch

(PLI) adhesion to copper foil. Ideally, this adhesion should be attainable thermally, i.e., without the use of adhesives which can detract from the performance of the board. This adhesion should also be achieved without sacrificing the ductility of the substrate (particularly for tape automated bonding and flex circuitry) as is often the case if the polymer crystallizes.

The use of Aurum by itself was limited by its crystallization behavior during lamination to copper foil. The result was an extremely brittle laminate that is prone to cracking. By alloying the TPI with Ultem, however, the crystallization was greatly reduced or eliminated, greatly improving the adhesion of the film to copper. These results are shown in Fig. 7 in which the peel strength is plotted as a function of the percent of Ultem in the blend. The target value was achieved with only 20% Ultem PEI, and with 50% PEI, peel strengths of 13 PLI, more than twice the target, were achieved. This performance advantage came while maintaining most of the TPI's thermal stability and superior high frequency dielectric properties.

#### **Polyimide Blends as Composite Matrices**

From the mechanical data obtained it was found that statistically there was little difference between the four composites with different resin formulations, as summarized in Table 2. Although the composite fabricated with neat Aurum 450C had the highest average in-plane shear strength and modulus, the standard deviation was high enough that these results overlapped with those from the other three composites. It was also apparent that the mechanical data for the composites were partially fiber-based, evidenced by in-plane shear strength and modulus values 2 to 3 times that of the film itself. Thus, it is possible that any or all of the mechanical results could be skewed depending on precisely what angle the test samples were cut. With the 3 or 4° tolerance in machining, it is very possible that two sets of specimens could be several degrees apart from each other relative to the fiber direction in each of the composites. The test results, beyond showing reasonable fiber-matrix adhesion, should be interpreted with caution.

**Table 2. Composite In-plane Shear Results**

Matrix Resin (TPI/PEI)	Strength kpsi	Modulus Mpsi
100/0	27.8 ± 1.2	1.28 ± 0.24
80/20	29.6 ± 1.6	1.01 ± 0.16
50/50	26.9 ± 1.2	1.05 ± 0.06
0/100	22.9 ± 2.0	1.09 ± 0.07

Samples of the composites made with neat Aurum 450C and the 50/50 blend were tested for fiber and void volume percentage by means of nitric acid digestion at 66°C according to ASTM D-3171. The results are summarized in Table 3. No difference was seen between the Aurum matrix resin and the 50/50 alloy.

**Table 3. Composite Composition by Acid Digestion and Optical Microscopy**

Matrix Resin TPI/PEI	Fiber Volume %		Resin Volume %		Void % Acid
	Acid	OM	Acid	OM	
100/0	47	39	53	61	≈ 0
80/20	-	49	-	51	-
50/50	48	45	52	55	2.0
0/100	-	40	-	60	-

A series of optical micrographs of a sample from each of the test laminates was taken. The samples were prepared as discussed earlier. The micrographs were taken not only to check the laminate quality, but also to visually confirm the fiber volume testing. The micrographs from each composite are shown in Fig. 8. In general the fiber wet out was very

good with minimum voids (black regions in the photos). However, visually the fiber volume looked somewhat low. This observation was confirmed by a fiber count of each composite specimen, the results of which are also shown in Table 3. In agreement with the acid digestion findings, the fiber content was only 39 to 49% rather than the 55 to 60% desired. The most likely cause of low fiber content was the use of 2 mil thick film plies. The relatively high viscosity of these alloys (see the appendix) resulted in only minimal resin bleedout. By utilizing  $\approx$  1.5 mil film for the layup, an amount of resin closer to the theoretical requirements for a 60 vol% fiber content composite should result in less pronounced resin rich regions.

## ACKNOWLEDGMENTS

Work at Foster-Miller was performed under a subcontract to the University of Massachusetts through . . . Force grant AFOSR-90-0150. We would like to acknowledge the able assistance of John Larouco and Barry Treadway in characterizing the blends.

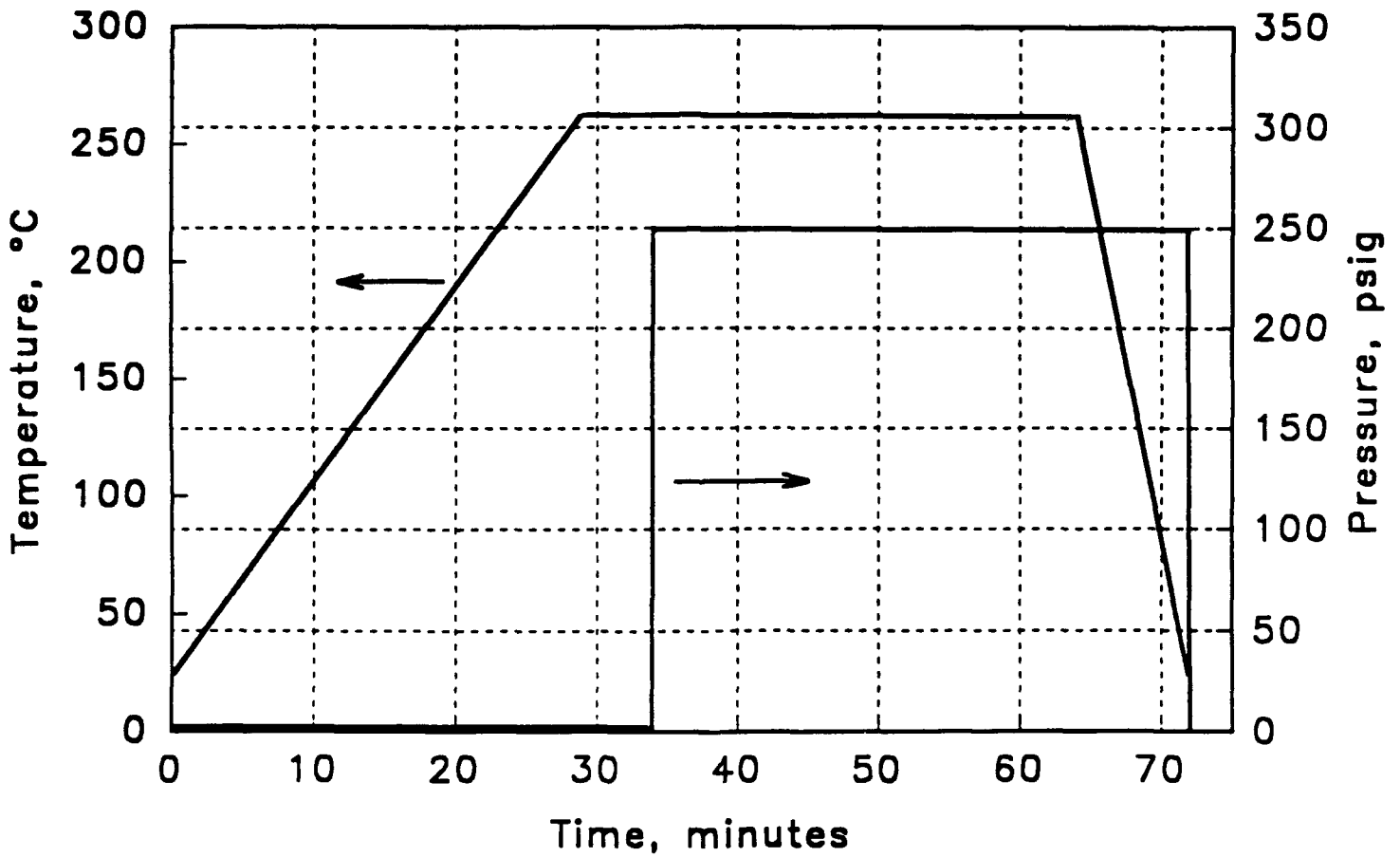


Figure 1. Lamination Cycle for Copper / Polyimide / Copper



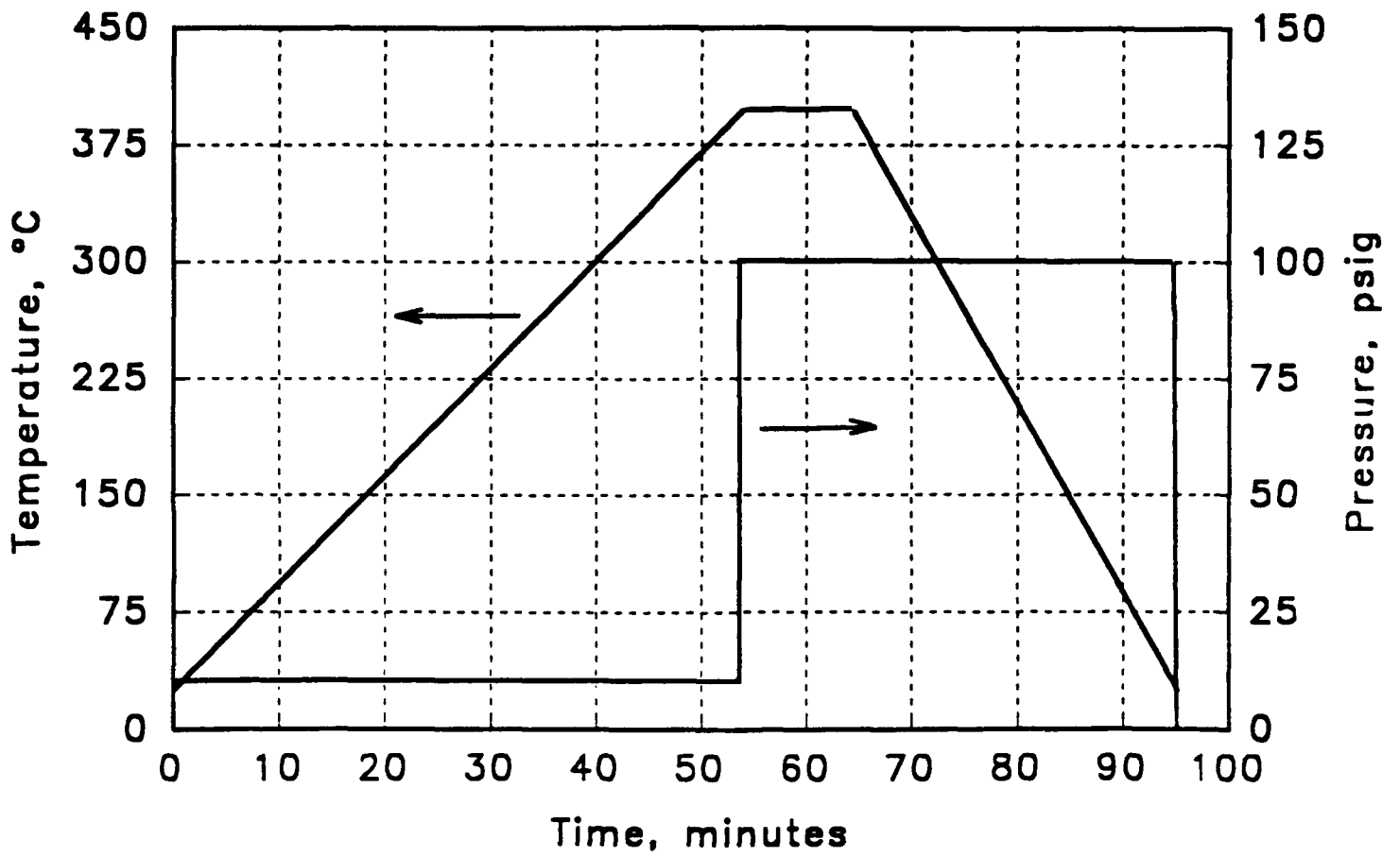


Figure 2. Initial Molding Cycle for Polyimide / Carbon Fiber Composites

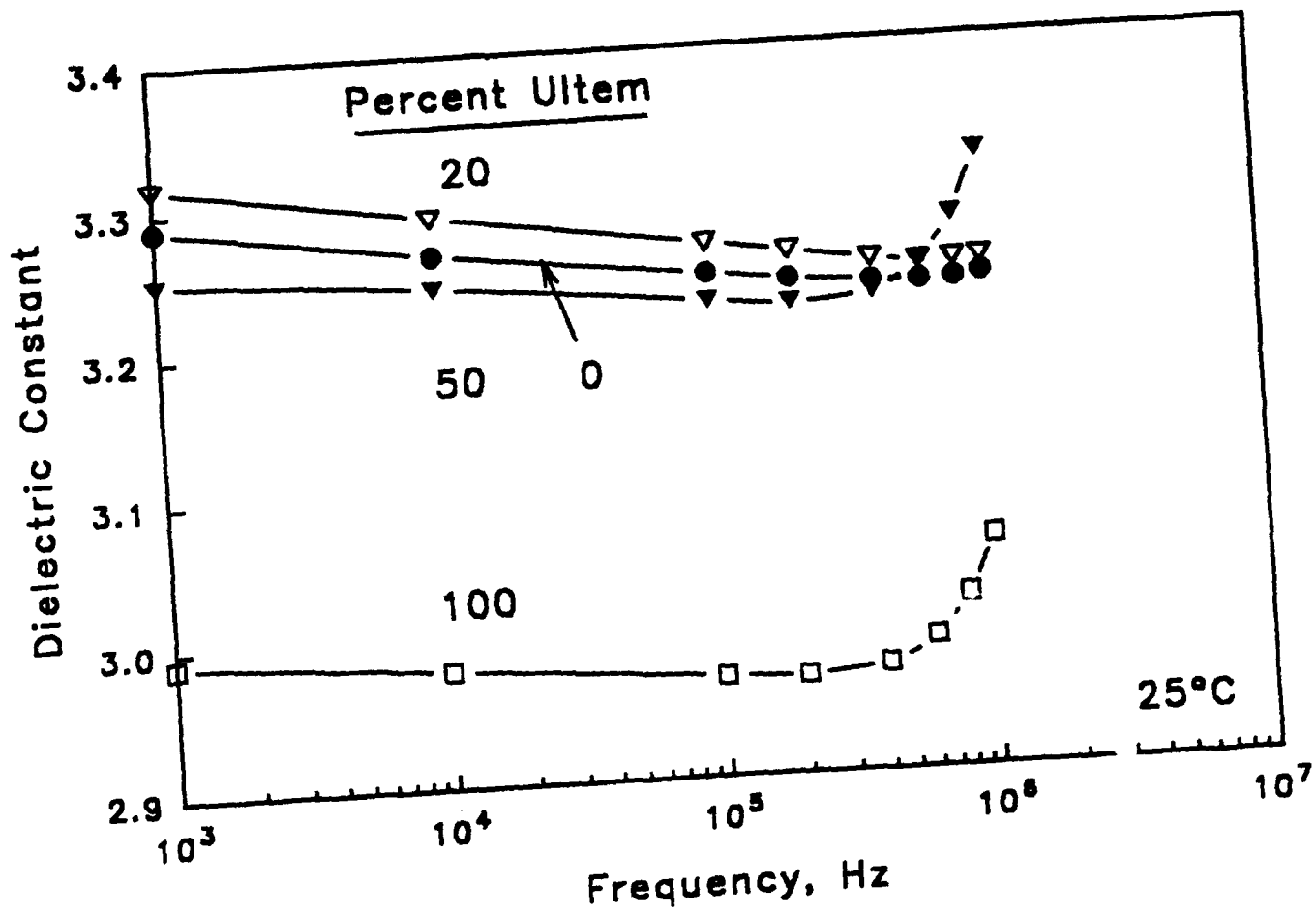


Figure 3. Frequency Dependence of Dielectric Constant

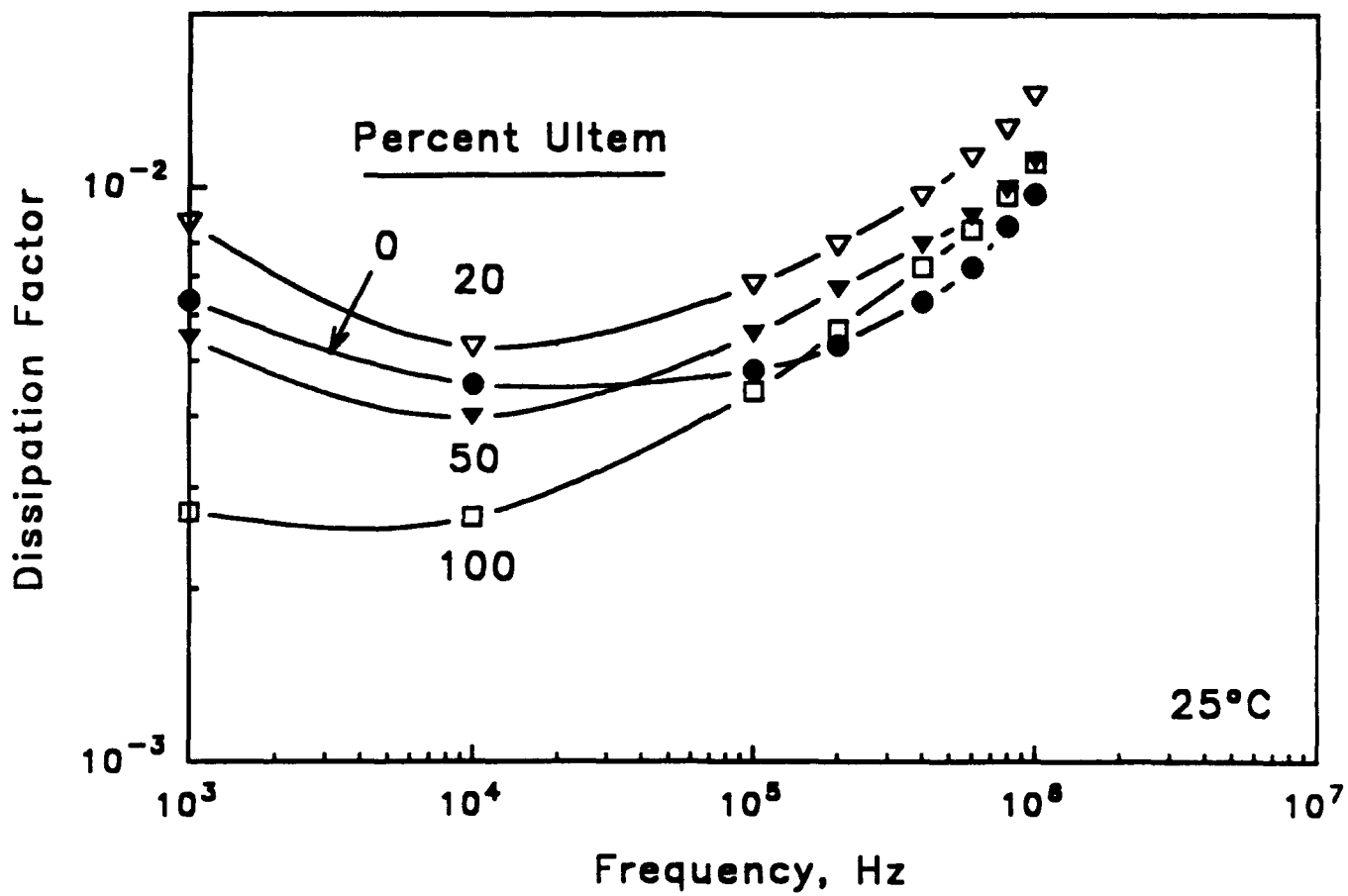


Figure 4. Frequency Dependence of Dissipation Factor

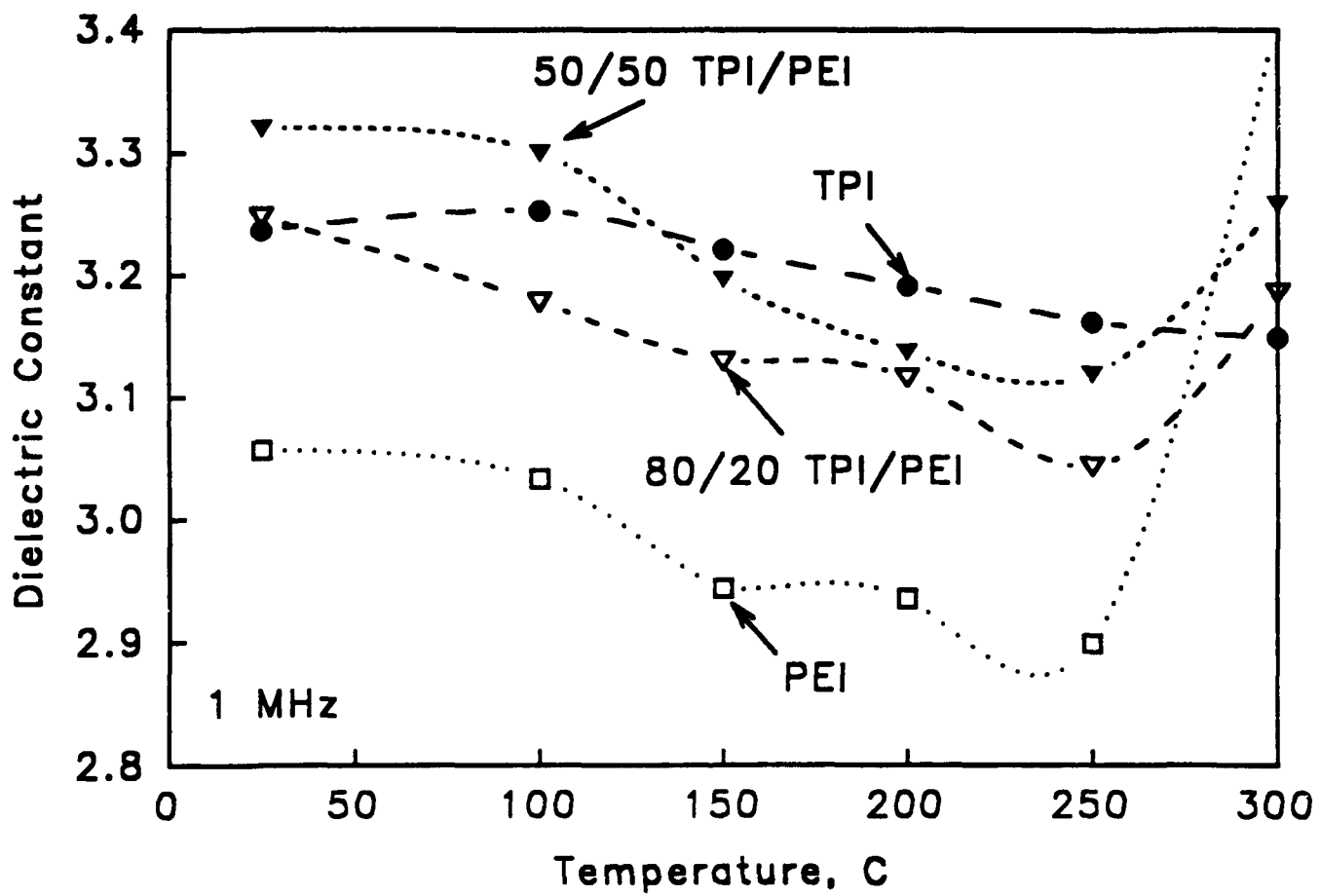


Figure 5. Temperature Dependence of Dielectric Constant

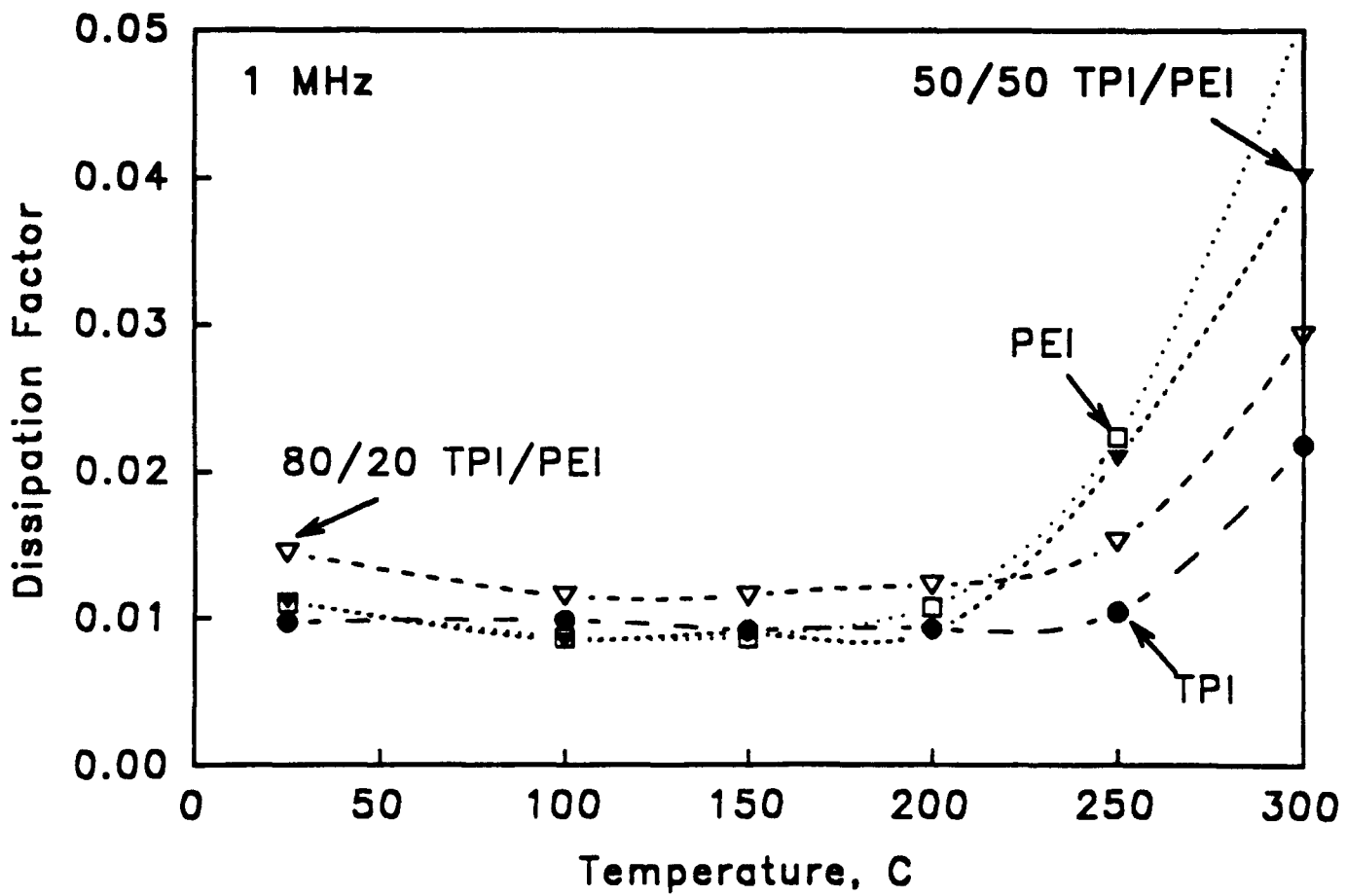


Figure 6. Temperature Dependence of Dissipation Factor

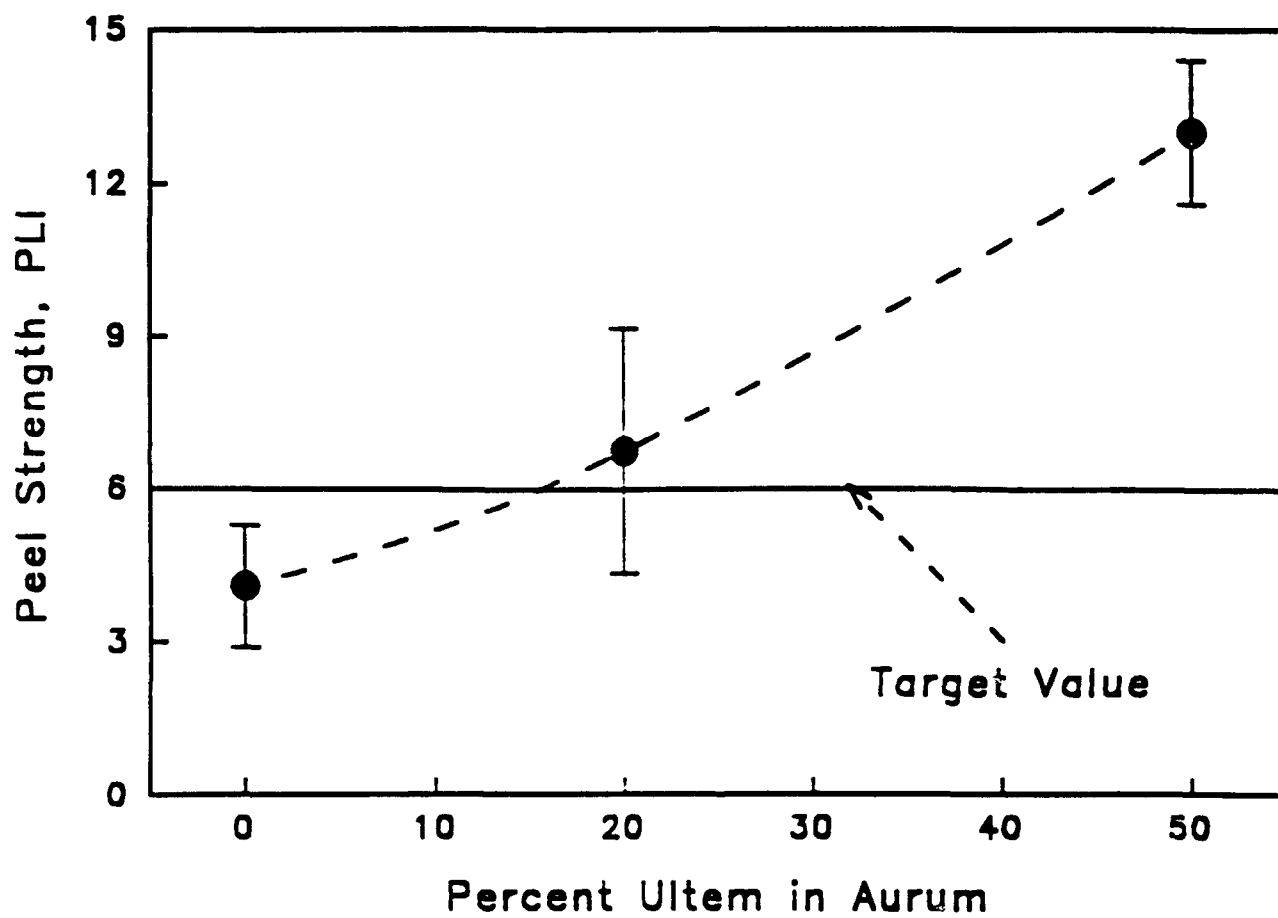


Figure 7. Peel Strength of Polyimide Melt Blends

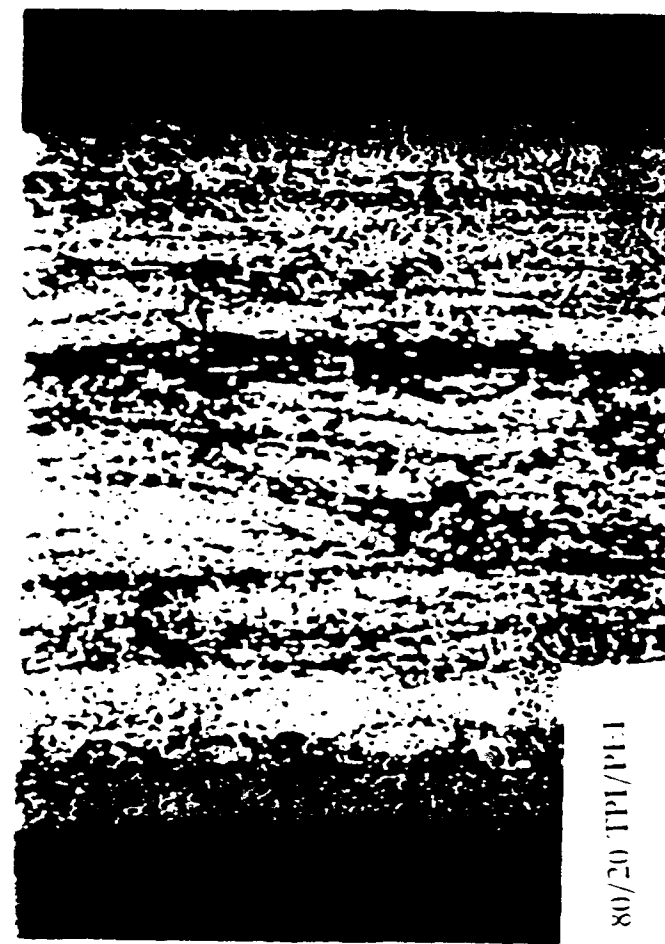
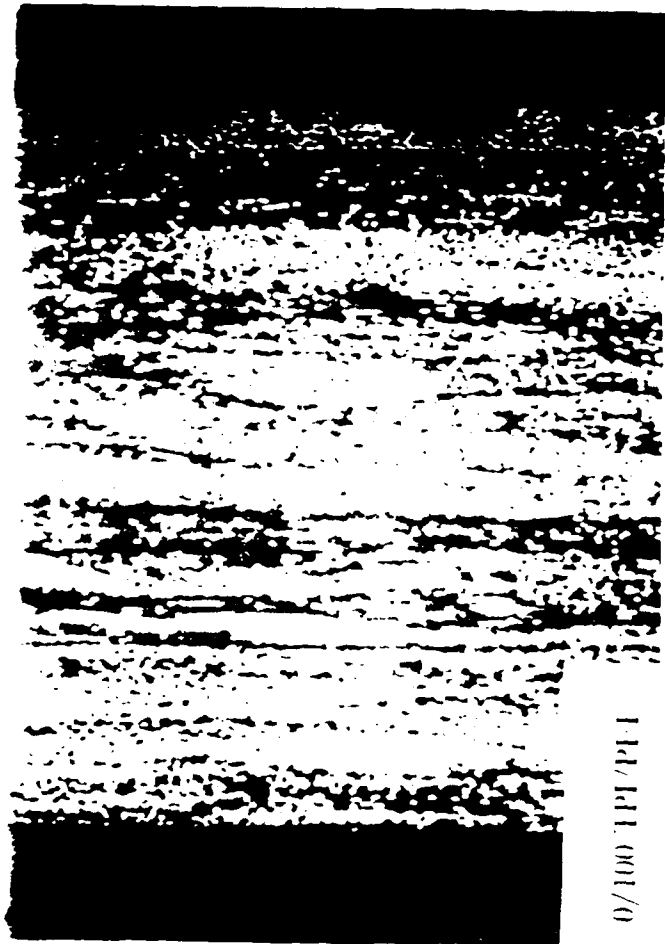
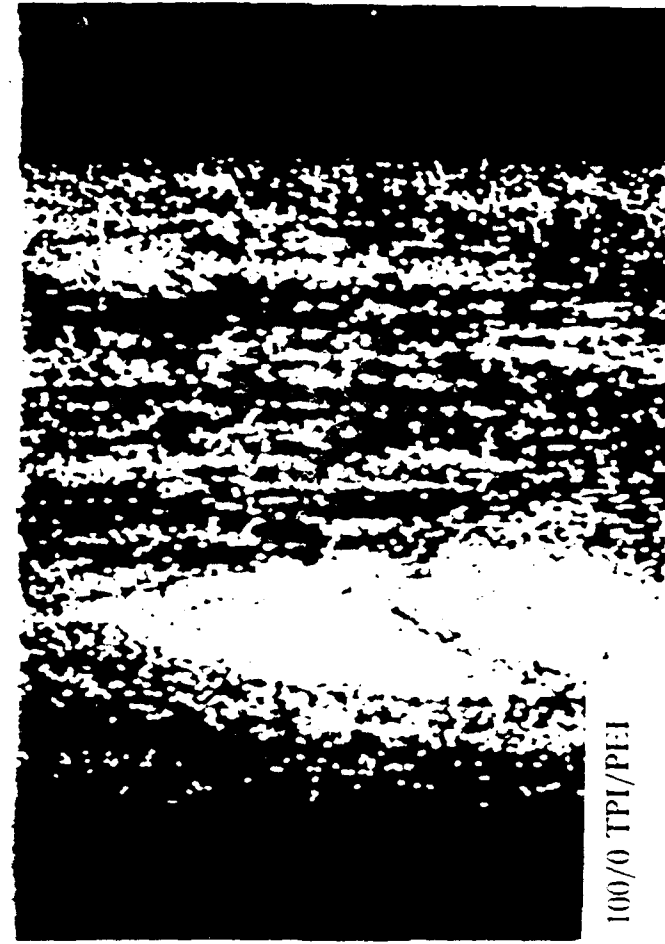
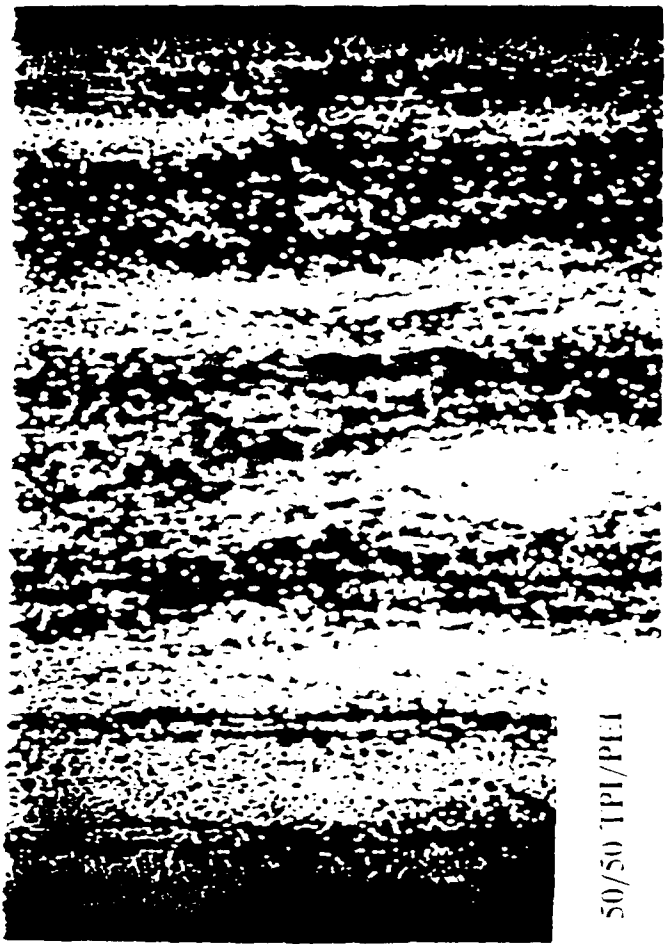


Figure 8. Optical Micrographs of Polyimide / Carbon Fiber Composites

APPENDIX 2

WRIGHT STATE UNIVERSITY

Submitted by W.A. Feld, P.I.

J. J. Kane, Co. P.I.

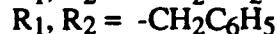
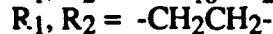
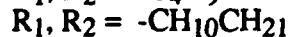
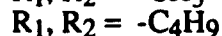
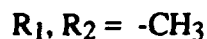
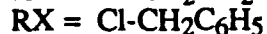
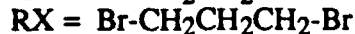
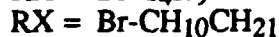
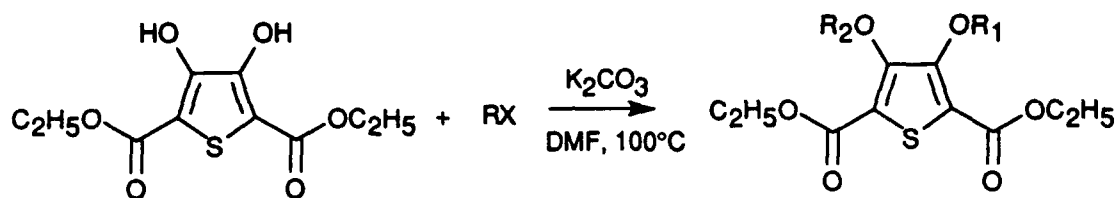


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## I. A Facile Synthesis of 3,4-Dialkoxythiophenes.

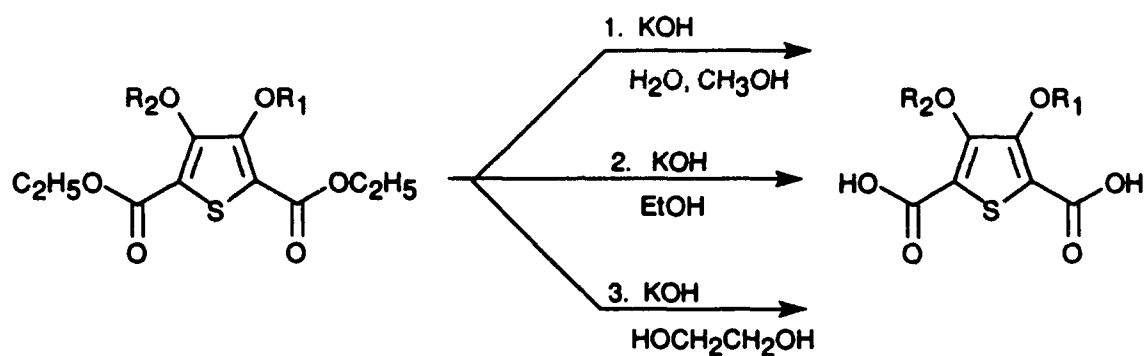
Alkylation of diethyl 3,4-dihydroxy-2,5-thiophenedicarboxylate with dimethyl sulfate, 1-bromobutane, 1-bromodecane, 1,2-dibromoethane, 1,3-dibromopropane, or benzyl chloride with potassium carbonate in DMF yielded diethyl 3,4-dimethoxy-2,5-thiophenedicarboxylate, diethyl 3,4-dibutoxy-2,5-thiophenedicarboxylate, diethyl 3,4-didecyloxy-2,5-thiophenedicarboxylate, diethyl 3,4-ethylenedioxy-2,5-thiophenedicarboxylate, diethyl 3,4-propylenedioxy-2,5-thiophenedicarboxylate and diethyl 3,4-dibenzyloxy-2,5-thiophenedicarboxylate, respectively.



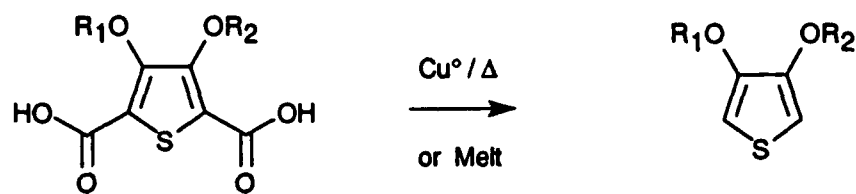
Hydrolysis of these dialkoxy compounds yielded 3,4-dimethoxy-2,5-thiophenedicarboxylic acid, 3,4-dibutoxy-2,5-thiophenedicarboxylic acid, 3,4-didecyloxy-2,5-thiophenedicarboxylic acid, 3,4-ethylenedioxy-2,5-thiophenedicarboxylic acid, 3,4-propylenedioxy-2,5-thiophenedicarboxylic acid and 3,4-dibenzyloxy-2,5-thiophenedicarboxylic acid, respectively.

Decarboxylation of the diacids yielded 3,4-dimethoxythiophene, 3,4-dibutoxythiophene, 3,4-didecyloxythiophene, 3,4-ethylenedioxythiophene, 3,4-propylenedioxythiophene, and 3,4-dibenzyloxythiophene, respectively. The yields for these reactions were good and the products were distilled or recrystallized. Some of the dialkoxythiophenes were unstable and decomposed upon standing. In addition, reaction of 3,4-didecyloxy-2,5-thiophenedicarboxylic acid with mercuric acetate and iodine and with thionyl chloride yielded 3,4-didecyloxy-2,5-diiodothiophene and 3,4-didecyloxy-2,5-thiophenedicarbonyl chloride, respectively. Reaction of

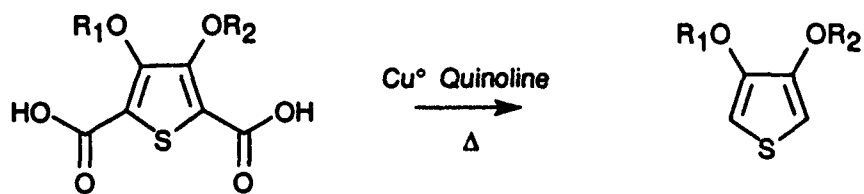
3,4-didecyloxy-2,5-thiophenedicarbonyl chloride with ammonium hydroxyde yielded 3,4-didecyloxy-2,5-thiophenedicarboxamide.



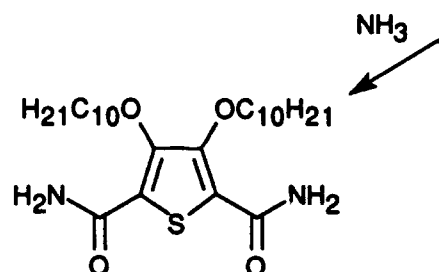
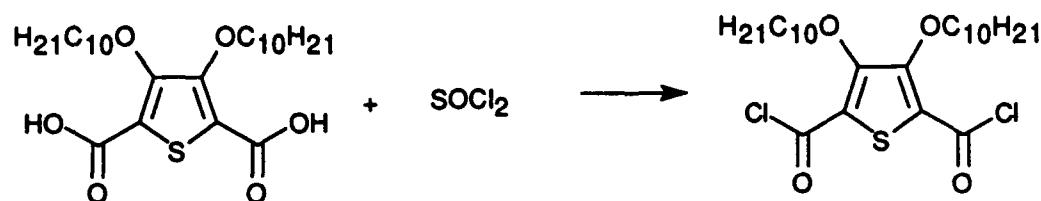
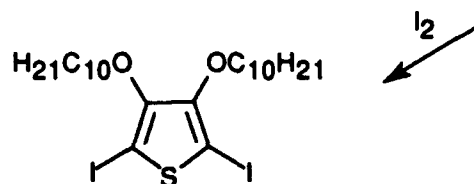
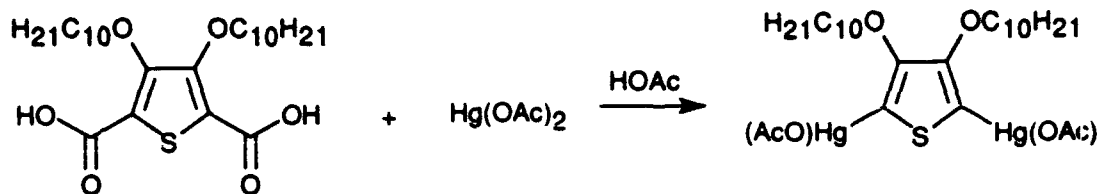
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 R<sub>1</sub>, R<sub>2</sub> = -CH<sub>10</sub>CH<sub>21</sub>  
 R<sub>1</sub>, R<sub>2</sub> = -CH<sub>2</sub>CH<sub>2</sub>-  
 R<sub>1</sub>, R<sub>2</sub> = -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-  
 R<sub>1</sub>, R<sub>2</sub> = -CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>



R<sub>1</sub>, R<sub>2</sub> = -C<sub>4</sub>H<sub>9</sub>  
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R<sub>1</sub>, R<sub>2</sub> = -CH<sub>3</sub>  
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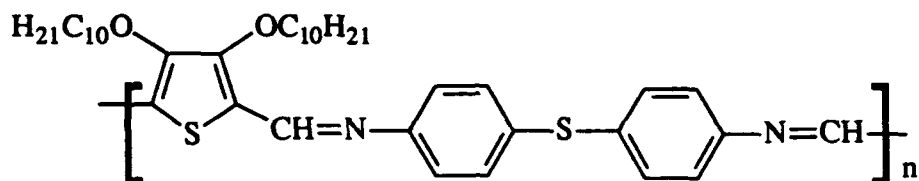


## II. Synthesis of a Series of Thiophene Containing Schiff Base Polymers and Model Compounds

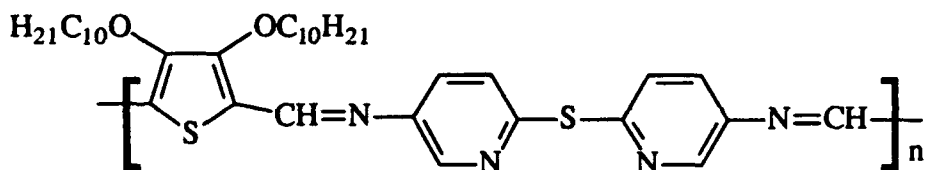
Four new poly(Schiff bases), poly[[3,4-bis(decyloxy)-2,5-thiophenediyl]methylidynenitrilo-4,1-phenylenethio-1,4-phenylenenitrilomethylidyne], poly[5,2-pyridinediyl-thio-2,5-pyridinediylnitrilomethylidyne[3,4-bis(decyloxy)-2,5-thiophenediyl]methylidynenitrilo], poly[[3,4-bis(decyloxy)-2,5-thiophenediyl]methylidynenitrilo-1,3-phenylenenitrilomethylidyne] and poly[[3,4-bis(decyloxy)-2,5-thiophenediyl]methylidynenitrilo-1,4-phenylenenitrilomethylidyne] were synthesized by the condensation of 3,4-didecyloxythiophene-2,5-dicarboxaldehyde with 4,4'-diaminodiphenyl sulfide, 5,5'-diamino-2,2'-dipyridyl sulfide,

*m*-phenylenediamine, and *p*-phenylenediamine, respectively. With the exception of poly[[3,4-bis(decyloxy)-2,5-thiophenediyl]methylidynenitrilo-1,3-phenylenenitrilomethylidyne], the polymers were soluble in methylene chloride, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and tetrahydrofuran. Poly[[3,4-bis(decyloxy)-2,5-thiophenediyl]methylidynenitrilo-1,3-phenylenenitrilomethylidyne] was soluble in methanesulfonic acid.

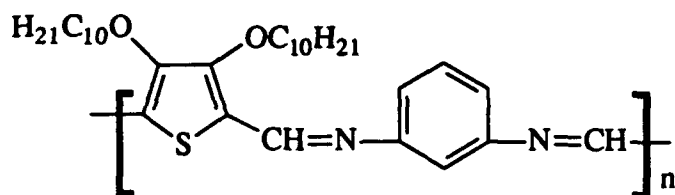
- 1) Poly[[3,4-bis(decyloxy)-2,5-thiophenediyl]methylidynenitrilo-4,1-phenylene-thio-1,4-phenylenenitrilomethylidyne]



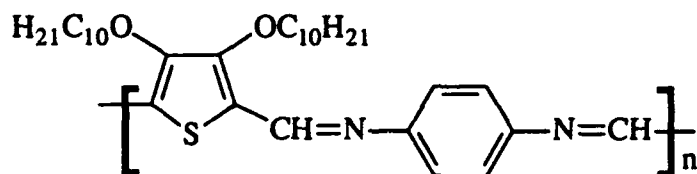
- 2) Poly[5,2-pyridinediylthio-2,5-pyridinediylnitrilomethylidyne[3,4-bis(decyloxy)-2,5-thiophenediyl]methylidynenitrilo]



- 3) Poly[[3,4-bis(decyloxy)-2,5-thiophenediyl]methylidynenitrilo-1,3-phenylene-nitrilomethylidyne]

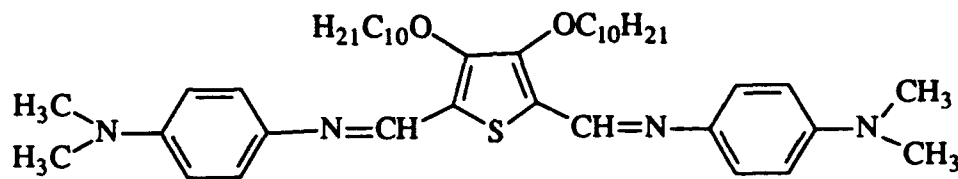


- 4) Poly[[3,4-bis(decyloxy)-2,5thiophenediyl]methylidynenitrilo-1,4-phenylene-nitrilomethylidyne]

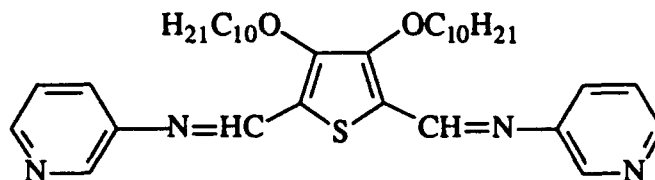


Two new model compounds, N-[[3,4-bis(decyloxy)-2,5-thienyl]methylene]-N',N'-dimethyl-1,4-benzenediamine and N-[[3,4-bis(decyloxy)-2,5-thienyl]methylene]-3-aminopyridine, were also synthesized by the condensation of 3,4-didecyloxythiophene-2,5-dicarboxaldehyde with N,N-dimethyl-1,4-phenylenediamine and 3-aminopyridine respectively.

1) N-[[3,4-bis(decyloxy)-2,5-thienyl]methylene]-N',N'-dimethyl-1,4-benzenediamine

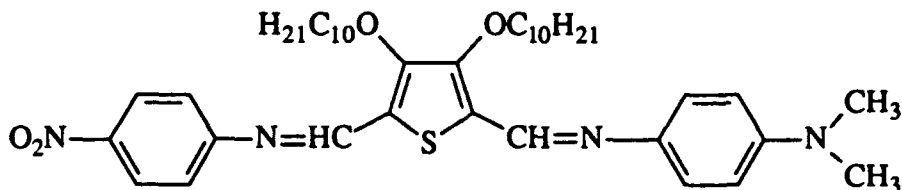


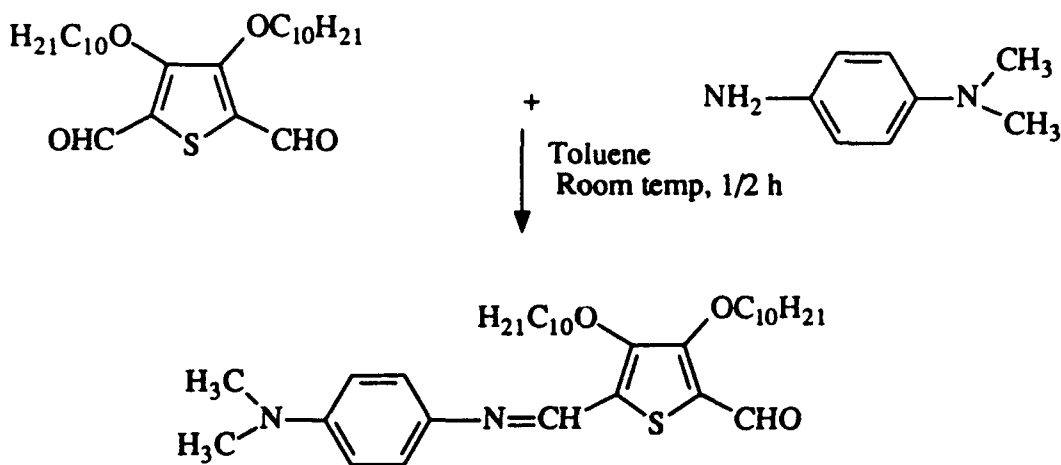
2) N-[[3,4-bis(decyloxy)-2,5-thienyl]methylene]-3-aminopyridine



N-[[3,4-bis(decyloxy)-5-carboxaldehyde-2-thienyl]methylene]-N',N'-dimethyl-1,4-benzenediamine was also prepared as a precursor for the future synthesis of donor-acceptor model compound.

N-[[3,4-bis(decyloxy)-5-[[4-nitrophenyl]imino]methyl]-2-thienyl]methylene]-N',N'-dimethyl-1,4-benzenediamine

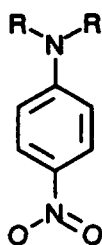




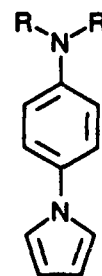
### III. Evaluation of Second Order Polarizability ( $\beta$ ) Using Solvatochromism.

The second order polarizabilities ( $\beta$ ) of five organic compounds were evaluated using solvatochromism. Solvatochromism uses a two level approximation in the determination of  $\beta$ . According to the two level approximation,  $\beta$  depends only on ground state and first excited state dipole moment. Solvatochromism can measure the change in dipole moment resulting from the transition.

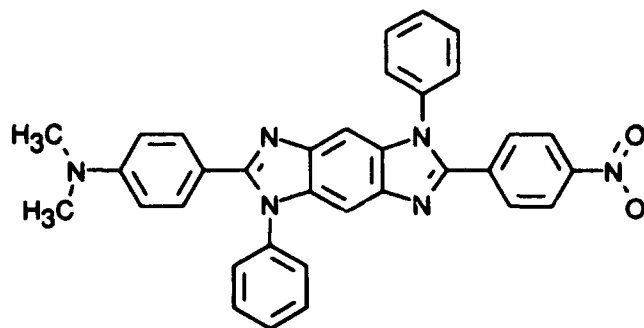
Five compounds were analyzed for their NLO activity, p-nitroaniline (I), N, N dimethyl-p-nitroaniline (II), 1,6-diphenyl-2- [4(N, N-dimethylamino) phenyl ] -5- (4-nitrophenyl) benzo (1,2-d;4,5-d') diimidazole (III), 1,4-diphenyl-2- [4(N, N-dimethylamino)phenyl] -5- (4-nitrophenyl) benzo (1,2-d;4,5-d') diimidazole (IV), and N, N dimethyl-p-anilinopyrrole (V).



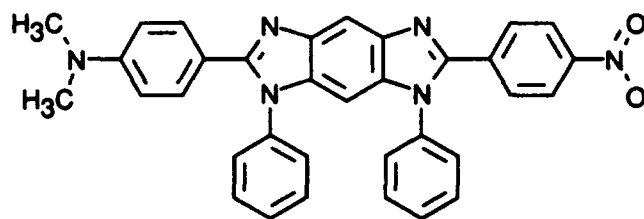
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V



III



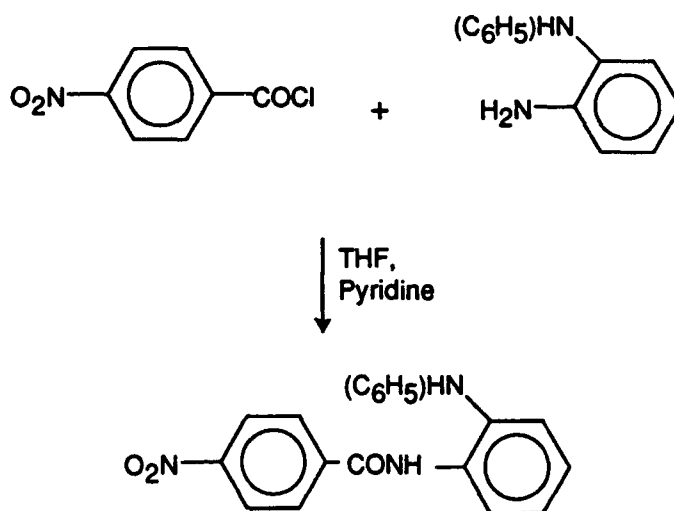
IV

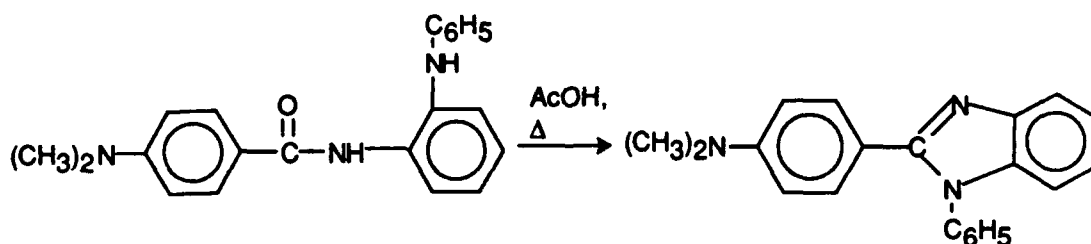
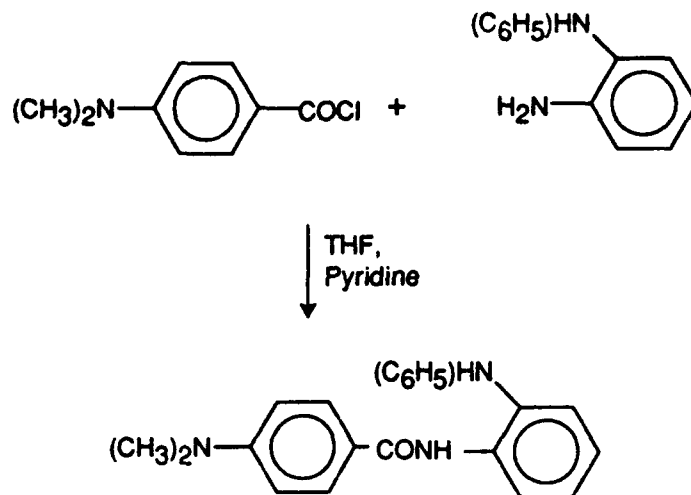
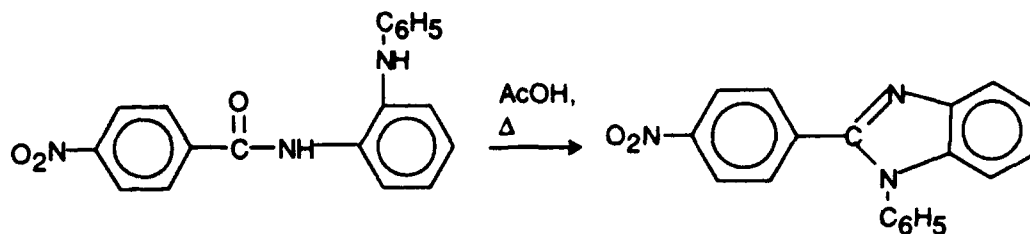
The two level model has been shown to be an easy way to evaluate  $\beta$ . There are however some limitations to this model. As it was shown by compounds III and IV, the two level model could give suspect values. The two level model will only work for compounds that have exactly one low-lying charge transfer excited state. If more than one excited state appears than the two level model will be unusable. The evaluation of the parameter  $\mu_g$  is also troublesome. Some of these types of compounds are hardly soluble in the standard solvent used which is usually non-polar. If this is the case then the  $\mu_g$  will have a large uncertainty. For this work the solvent availability was limited. It would be better for solvatochromic shift measurements to have more solvents. The effect of temperature can also be reduced if the environment of the experiment can be controlled. There is no doubt that temperature fluctuation reduces the accuracy of the results obtained.



#### IV. Synthesis and Evaluation of Second Order Polarizabilities of Novel Benzimidazoles using Solvatochromism.

The reaction of 2-aminodiphenylamine with 4-nitrobenzoyl chloride and 4-(dimethylamino)benzoyl chloride provided N-(2-anilinophenyl)-4-nitrobenzamide and N-(2-anilinophenyl)-4-(dimethylamino)benzamide, respectively. The benzamides were thermally dehydrated to 1-phenyl-2-(4-nitrophenyl)benzimidazole and 1-phenyl-2-[4-(dimethylaminophenyl)]benzimidazole. The benzamides and benzimidazoles were characterized employing  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, and elemental analysis. The second order polarizabilities ( $\beta$ ) were determined by a two-level model approximation using solvatochromism. The parameters  $\mu_{eg}$  (transition dipole moment),  $\omega_{eg}$  (frequency of transition in the solvent),  $\mu_g$  (ground state dipole moment),  $\mu_e - \mu_g$  (difference in the excited and ground state dipole moment), and  $\mu_e$  (excited state dipole moment) used in the evaluation of  $\beta$ , were determined experimentally. For 1-phenyl-2-(4-nitrophenyl)benzimidazole,  $\omega_{eg} = 2.95 (10^6) \text{ m}^{-1}$ ,  $\mu_{eg}$  was 3.73 D,  $\mu_g = 4.03 \text{ D}$ ,  $\mu_e - \mu_g = 2.39 \text{ D}$ ,  $\mu_e = 6.14 \text{ D}$ , and  $\beta = 47.09 (10^{-30}) \text{ esu}$  at 1064 nm. For 1-phenyl-2-[4-(dimethylaminophenyl)]benzimidazole,  $\omega_{eg} = 3.06 (10^6) \text{ m}^{-1}$ ,  $\mu_{eg} = 3.73 \text{ D}$ ,  $\mu_g = 4.96 \text{ D}$ ,  $\mu_e - \mu_g = 1.39 \text{ D}$ ,  $\mu_e = 6.95 \text{ D}$ , and  $\beta = 34.11 (10^{-30}) \text{ esu}$  at 1064 nm.

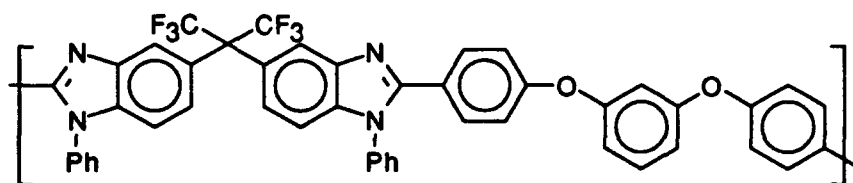




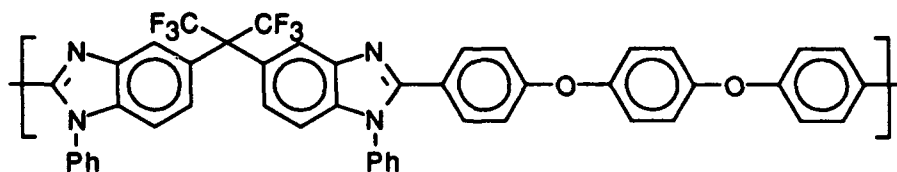
### V. Synthesis of Poly(aryl ether N-substituted benzimidazoles) by Nucleophilic Aromatic Substitution.

Five new poly(aryl ether N-substituted benzimidazoles) were synthesized by nucleophilic aromatic substitution in which the generation of an aryl ether linkage is the polymer forming reaction. The new difluoro bisbenzimidazole monomer, 2,2-bis[1-phenyl-2-(4-fluorophenyl)benzimidazole-5-yl]hexafluoropropane, was prepared and polymerized with bisphenols in N-methyl-2-pyrrolidone in the presence of  $\text{K}_2\text{CO}_3$  to afford the new PBIs, poly[1-phenyl-2,5-

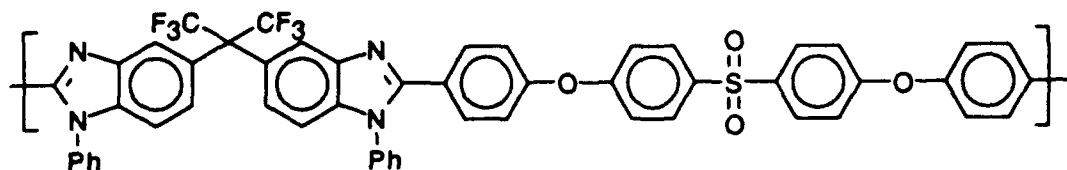
benzimidazolediyl)[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene](1-phenyl-5,2-benzimidazolediyl)-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylene], poly[1-phenyl-2,5-benzimidazolediyl)[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene](1-phenyl-5,2-benzimidazolediyl)-1,4-phenyleneoxy-1,3-phenyleneoxy-1,4-phenylene], poly[1-phenyl-2,5-benzimidazolediyl)[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene](1-phenyl-5,2-benzimidazolediyl)-1,4-phenyleneoxy-1,4-phenylene[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4-phenyleneoxy-1,4-phenylene], poly[1-phenyl-2,5-benzimidazolediyl)[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene](1-phenyl-5,2-benzimidazolediyl)-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylene], poly[1-phenyl-2,5-benzimidazolediyl)[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene](1-phenyl-5,2-benzimidazolediyl)-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene]. The polymers exhibited excellent thermal stability up to 500° C, and showed good solubility in common organic solvents. This synthetic method is found to be a convenient and effective synthetic approach to poly(aryl ether N-substituted benzimidazoles).



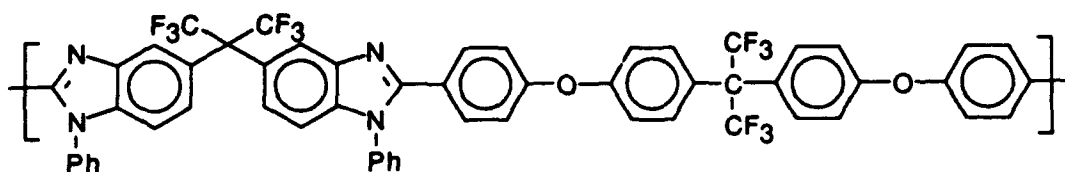
Poly[(1-phenyl-2,5-benzimidazolediyl)[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene](1-phenyl-5,2-benzimidazolediyl)-1,4-phenyleneoxy-1,3-phenyleneoxy-1,4-phenylene]



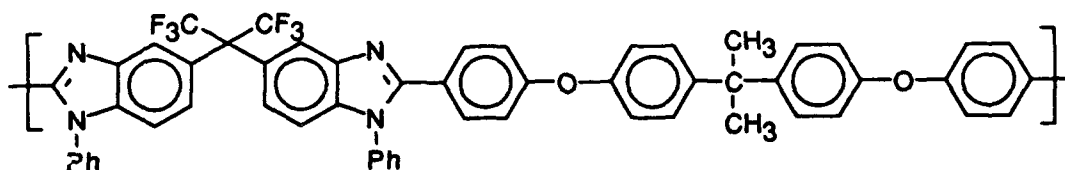
Poly[(1-phenyl-2,5-benzimidazolediyl)[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene](1-phenyl-5,2-benzimidazolediyl)-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylene]



Poly[(1-phenyl-2,5-benzimidazolediyl)[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene](1-phenyl-5,2-benzimidazolediyl)-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene]

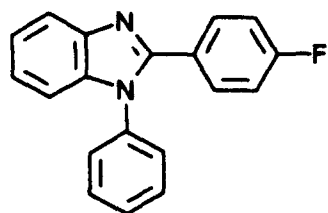


Poly[(1-phenyl-2,5-benzimidazolediyl)[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene](1-phenyl-5,2-benzimidazolediyl)-1,4-phenyleneoxy-1,4-phenylene[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4-phenyleneoxy-1,4-phenylene]

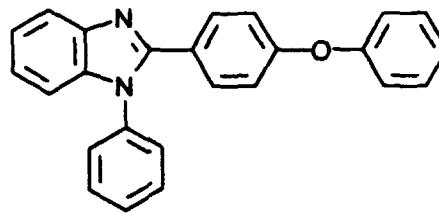


Poly[(1-phenyl-2,5-benzimidazolediyl)[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene](1-phenyl-5,2-benzimidazolediyl)-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylene]

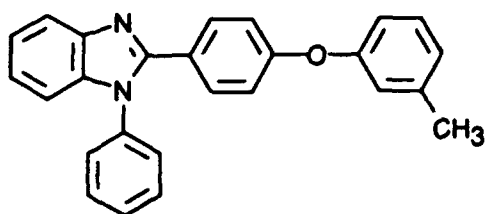
The new model compounds, 1-phenyl-2-(4-fluorophenyl)benzimidazole, 1-phenyl-2-(4-phenoxyphenyl)benzimidazole, 1-phenyl-2-[4-(3-methylphenoxy)phenyl]benzimidazole, 1,4-bis[4-(1-phenylbenzimidazole-2-yl)phenoxy]benzene, 2,2-bis[1-phenyl-2-(4-(3-methylphenoxy)phenyl)benzimidazole-5-yl]hexafluoropropane, were also prepared. FTIR,  $^1\text{H}$  nmr and  $^{13}\text{C}$  nmr spectra of the model compounds and polymers are presented and discussed. Thermal properties and viscosity data of the five new polymers were also determined



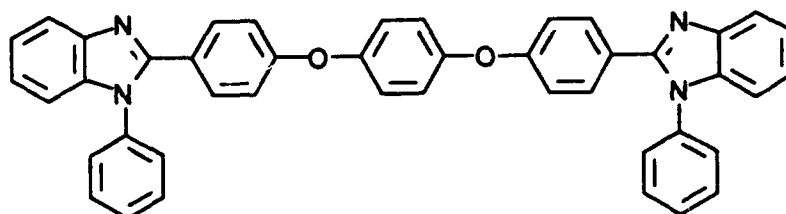
1-phenyl-2-(4-fluorophenyl)benzimidazole



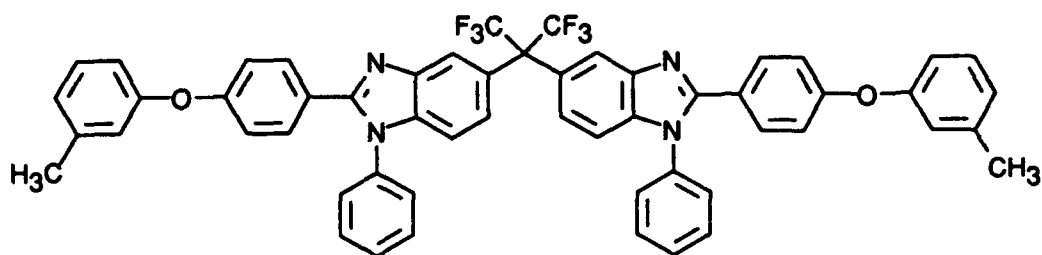
1-phenyl-2-(4-phenoxyphenyl)benzimidazole



1-phenyl-2-[4-(3-methylphenoxy)phenyl]benzimidazole



1,4-bis[4-(1-phenylbenzimidazole-2-yl)phenoxy]benzene



2,2-bis[1-phenyl-2-(4-(3-methylphenoxy)phenyl)benzimidazole-5-yl]hexafluoropropane

## VI. Synthesis of a Series of Conjugated Enyne Polythiophenes

Our laboratories have been directing certain research efforts toward development of new materials possessing optimal third-order nonlinear optical (NLO) properties. This property is primarily concerned with the response of a dielectric material to an intense beam of light. Thus we are compiling a NLO model compound database in order to uncover third-order molecular structure-NLO property relationships. These data will serve to further refine guidelines for design of organic polymeric materials predicted to exhibit optimal properties in this regard. Previous reports<sup>1</sup> have established that extended pi conjugation and heterocyclic groups such as thiophenes are among the structural features which enhance third-order NLO responses.

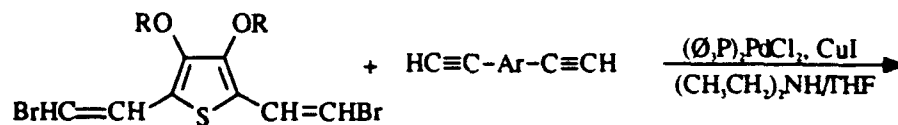
The paper presents the synthesis of new series of conjugated polymers (and a representative model compound) intended for evaluation of third-order NLO properties. The polymeric systems have enyne and thiophene units in the polymer backbone. Also included as a structural feature are decyloxy appendages at the 3,4 positions in the thiophene rings in an effort to overcome the well known solubility limitations of conjugated polymers.

### Synthesis of Model Compound and Polymers

A series of four (VI-IX) conjugated enyne polythiophenes were synthesized by palladium (II) catalyzed coupling<sup>2,3</sup> of 3,4-didecyloxy-2,5-bis( $\beta$ -bromoethenyl)thiophene with an aromatic diethynyl compound as shown in Scheme 1. The resulting polymers were all dark red and were cast into thin films from THF. Once dried, none of the polymers would redissolve.

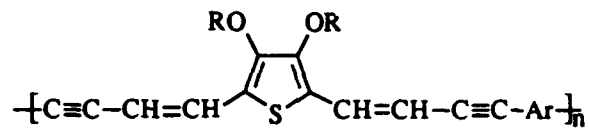
DSC scans of VI - IX are similar showing a single large exotherm with onset ranging from 300 to 380° C. (Table 1) TGA scans indicated two-stage degradation with extrapolated onset ranging from 281 to 325° C followed by a second shoulder ranging from 496 to 548° C (Table 1).

Solution viscosities were measured in THF at 30° C and extrapolated to zero concentration. Values ranged from 0.27 to 0.90 dL/g (Table 1).



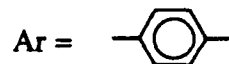
IVa: trans, trans

IVb: cis,trans

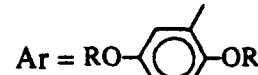


VI, VII, VIII, IX

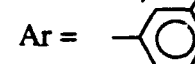
Polymer VI    trans, trans



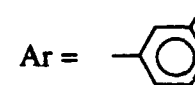
Polymer VII    trans, trans



Polymer VIII    trans, trans



Polymer IX    mixture of trans, trans  
and cis, trans



R = OCH<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub>

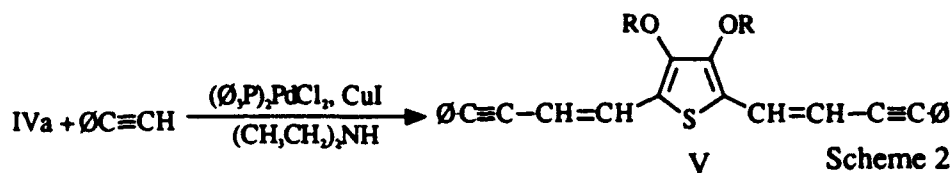
Scheme 1

Table 1

Thermal and Viscosity Data for Polymers VI - IX

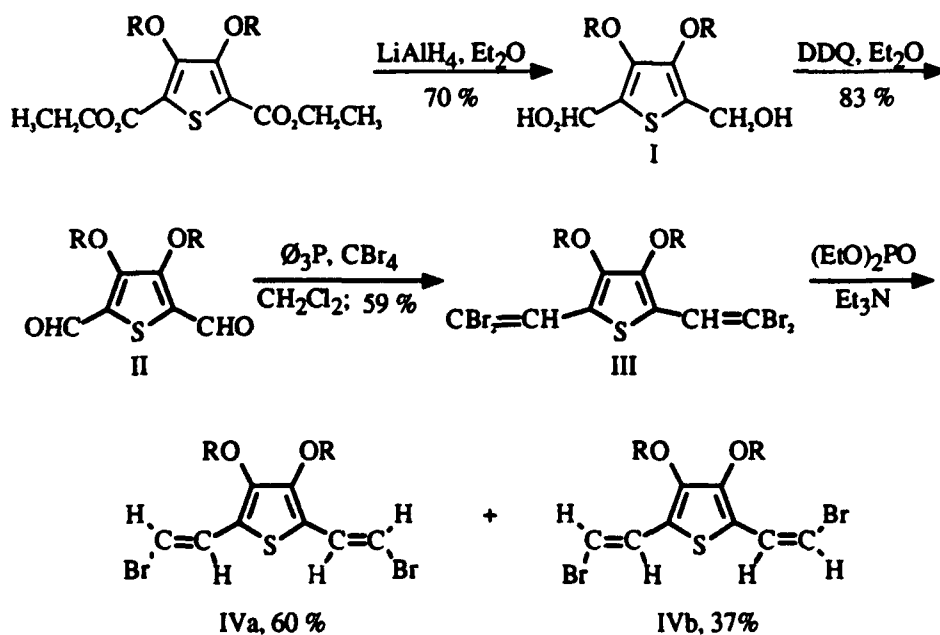
Polymer	DSC/onset ° C	TGA/onset ° C	TGA/2nd ° C	[η] dL/g
VI	300	281	496	0.32
VII	350	325	548	0.90
VIII	380	327	532	0.27
IX	350	328	534	0.74

The model compound *trans, trans*-3,4-didecyloxy-2,5-bis(4-phenylbut-1-en-3-yn-1-yl)-thiophene, V, was prepared by coupling IVa and ethynyl benzene as shown in Scheme 2. This compound decomposed on standing at room temperature.



### Synthesis of Monomers

Monomer IV was prepared by a five-step sequence (Scheme 3) starting with diethyl-3,4-didecyloxythiophene-2,5-dicarboxylate which was reduced to the diol, I, with  $\text{LiAlH}_4$ . Oxidation of I with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) gave dialdehyde, II. A Wittig<sup>4</sup> type reaction with tetrabromomethane converted II to bis-vinylidene bromide, III. Finally, III was converted to 3,4-didecyloxy-2,5-bis( $\beta$ -bromoethenyl)thiophene, IV, by reduction with diethyl phosphite<sup>5</sup> to give a 60 percent yield of the *trans, trans* isomer, IVa and a 37 percent yield of the *cis, trans* isomer.



Scheme 3.



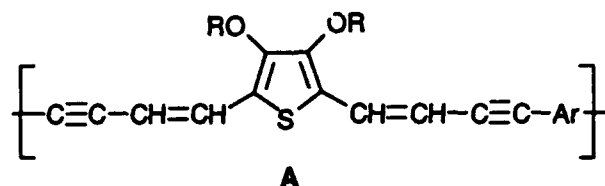
The diethynyl monomers 1,3- and 1,4-diethynylbenzene were made by modifications of published<sup>6,7</sup> methods. The synthesis of 1,4-diethynyl-2,5-didecyloxybenzene will be described in a later publication.

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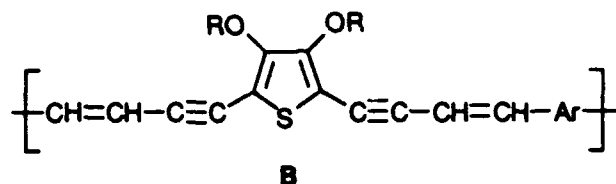
## VII. Synthesis of a Series of Conjugated Enyne Polythiophenes, II.

Recently we reported<sup>1</sup> the synthesis of a series of enyne polythiophenes based on structure A. This effort is part of our ongoing program to develop new materials possessing optimal third-



order non-linear optical (NLO) properties. This property is primarily concerned with the response of a dielectric material to an intense beam of light. Thus, we are compiling an NLO model compound database in order to uncover molecular structure-NLO property relationships. These data will serve to further refine guidelines for design of organic polymeric materials predicted to exhibit optimal NLO properties. Previous reports<sup>2</sup> have established that extended pi conjugation and heterocyclic groups such as thiophenes are among the structural features which enhance third-order NLO responses.

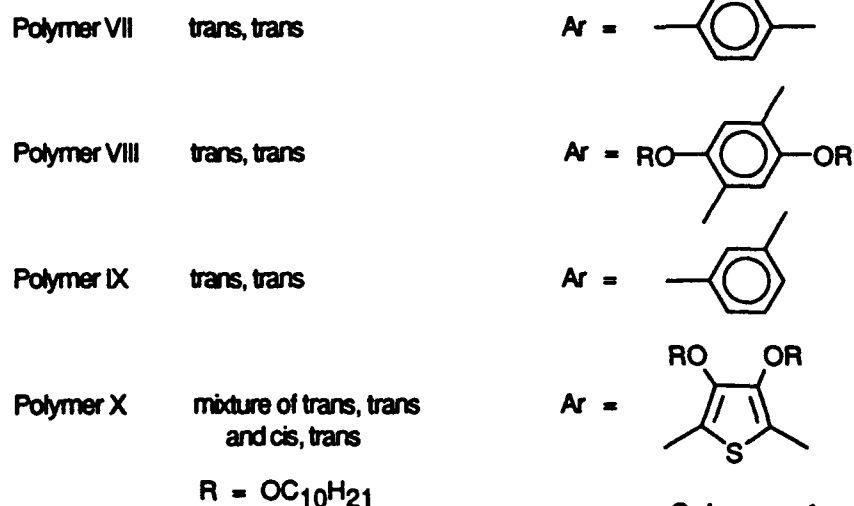
This paper presents the synthesis of a model compound and a series of four new enyne polymers, three (VII, VIII, and IX) of which are isomers (see structure B) of series A and



incorporate the enyne and the thiophene and benzenoid rings in the polymer backbone. The fourth polymer (X) incorporates the enyne and thiophene rings in the polymer backbone. The effects of these structural variations in series A and B on NLO properties will be the subject of a later publication.

### Synthesis of Model Compound and Polymers

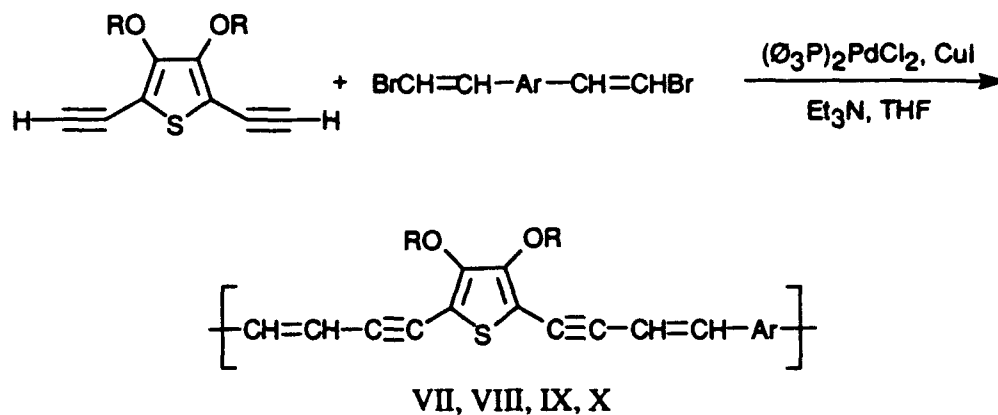
A series of four (VII-X) conjugated enyne polythiophenes were synthesized by palladium (II) catalyzed coupling<sup>3,4</sup> of 3,4-didecyloxy-2,5-diethynylthiophene, I, with aromatic ois( $\beta$ -bromovinyl) monomers as shown in Scheme 1. The resulting polymers were obtained in quantitative yields. They were orange in color and were cast into thin self-supporting films from THF. Once dried, the polymers did not redissolve.



**Scheme 1**

DSC scans of VII - X, like their isomers in Series A, showed a single large exotherm which is attributable to decomposition when compared to the TGA scans. TGA data (Table I) showed

the characteristic two stage degradation with onset ranging from 255 to 328°C followed by a second shoulder ranging from 386 to 520°C (in air).



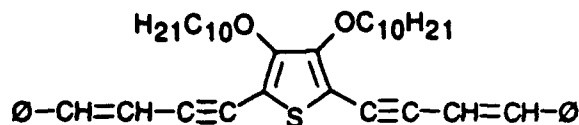
Solution viscosities were measured in THF at 30°C and extrapolated to zero concentration. The intrinsic viscosities ranged from 0.53 to 0.87 dL/g (Table I).

**Table I**

**Thermal and Viscosity Data for Polymers VII - X**

Polymer	TGA/onset ° C, (air)	TGA/2nd ° C, (air)	[η] dL/g
VII	273	386	0.88
VIII	255	417	0.53
IX	280	483	0.72
X	328	520	0.60

The model compound 3,4-didecyloxy-2,5-bis(4-phenyl-3-buten-1-ynyl)thiophene, II, was prepared by coupling reaction of monomer I with β-bromostyrene. The low melting yellow solid, unlike its isomer, 3,4-didecyloxy-2,5-bis(4-phenyl-1-buten-3-ynyl)thiophene, is stable at room temperature.



II

### Monomer Synthesis

3,4-Didecyloxy-2,5-diethynylthiophene, I, was made by treatment<sup>5</sup> of 3,4-didecyloxy-2,5-bis( $\beta$ ,  $\beta$ -dibromoethenyl)thiophene<sup>1</sup> with *n*-butyl lithium. This monomer was quite unstable and had to be refrigerated and re-purified immediately before use. The *trans*, *trans*-1,4-bis( $\beta$ -bromovinyl)benzene was made from 1,4-phenylenediacrylic acid by the method of Mitchell and co-workers<sup>6</sup>. The monomers *trans*, *trans*-2,5-didecyloxy-1,4-bis( $\beta$ -bromovinyl)benzene, IV, and *trans*, *trans*-1,3-bis( $\beta$ -bromovinyl)benzene, VI, were made by conversion of the corresponding dialdehydes to their respective bis( $\beta$ , $\beta$ -dibromovinyl)benzene derivatives with carbon tetrabromide and triphenyl phosphine followed by reduction with diethyl phosphite<sup>1</sup>. The synthesis of 2,5-didecyloxy-1,4-benzodialdehyde (starting material for monomer IV) will be described in a later publication.

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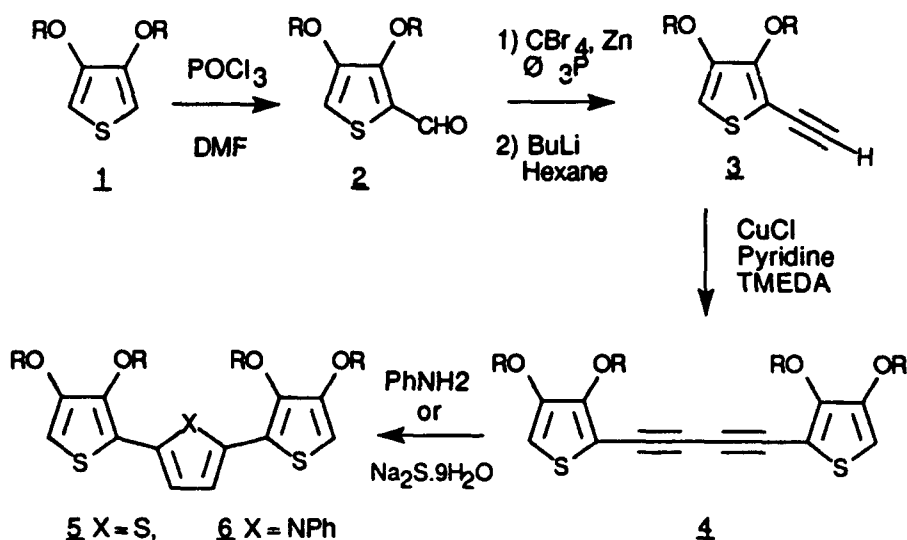
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2. M. Zhao, M. Samoc, P. N. Prasad, B. A. Reinhardt, M. R. Unroe, M. Prazak, R. C. Evers, J. J. Kane, C. Jariwala and M. Sinsky, *Chem. Mater.*, **2**, 670 (1990).
3. K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Letters*, **50**, 4467 (1975).
4. B. A. Reinhardt and F. E. Arnold, U. S. Pat. No. 4,417,039 (Nov., 1983).
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### VIII. The Synthesis of Alternating Poly(heterocycles): Poly(3,4-Didecyloxythiophene-alt-thiophene and Poly(3,4-Didecyloxythiophene-alt-(N-phenylpyrrole))

We have recently reported a versatile and improved route to 3,4-dialkoxythiophenes [1]. As part of a project directed toward the synthesis of thiophene containing 2nd and 3rd order NLO materials, we now report the use of 3,4-dialkoxythiophenes and related thiophene derivatives in the preparation of alternating poly(heterocycles). These thiophene polymers are potential conducting materials when doped and are also potential NLO materials.

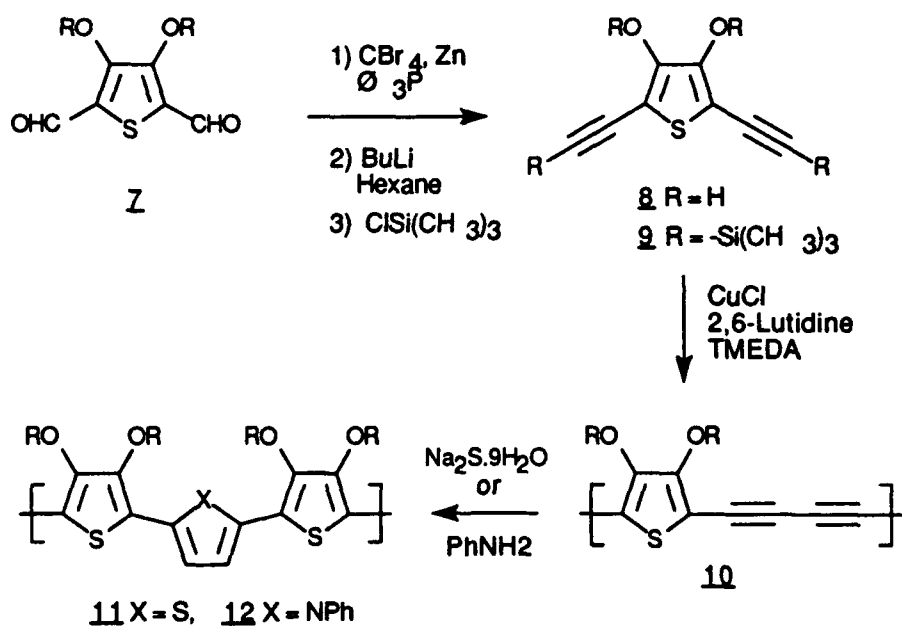
#### Model Compound Synthesis

The aldehyde, 3,4-didecyloxy-2-thiophenecarboxaldehyde **2** can be prepared in excellent yield from the corresponding 3,4-didecyloxythiophene **1**. Bisformylation did not occur even under pressing conditions and excess reagents. The application of the Corey-Fuchs procedure [2] to **2** yields 2-ethynyl-3,4-didecyloxythiophene **3**, a relatively unstable material that was used directly in a copper (I) catalyzed coupling reaction [3] to provide 1,4-bis(3,4-didecyloxy-2-thienyl)butadiyne **4**. Reaction of **4** with sodium sulfide nonahydrate [4] or aniline [3] provided 3,4,3',4'-tetradecyloxy-2,2':5',2"-terthiophene **5** and 2,5-bis(3,4 didecyloxy-2-thienyl)-N-phenylpyrrole **6**. All new compounds were fully characterized as listed in the Experimental part.



## Monomer and Polymer Synthesis

The synthesis of appropriate monomeric material involved the improvement of previously reported synthetic step for the preparation of 3,4-didecyloxy-2,5-thiophenedicarboxaldehyde **7**. The modified procedures, which are given in the Experimental section, consist of an improved workup of a reported reduction and an  $\text{MnO}_2$  oxidation of a diol to the dialdehyde **7**. The reaction of **7** under standard Corey-Fuchs conditions [3], yielded 3,4-didecyloxy-2,5-diethynylthiophene **8** which could be transformed into 3,4-didecyloxy-2,5-bis(2-trimethylsilylethynyl)thiophene **9**, a more stable material than **8**. A coupling reaction related (2,6-lutidine was used as the solvent) to that used in the preparation of the butadiyne **4** was employed as a polymerization reaction provide poly(3,4-didecyloxythiophene-2,5-diyl-1,4-butadiynediyl) **10**. The conversion of **9** to the alternating poly(heterocycle) poly(3,4-didecyloxythiophene-2,5-diyl-2,5-thiophenediyl) **11** was accomplished with sodium sulfide nonahydrate [4]. The polymer **11** had limited solubility as compared with poly(3,4-didecyloxythiophene-2,5-diyl) [5]. The reaction of **10** with aniline [3] provided poly[3,4-didecyloxythiophene-2,5-diyl-2,5-(N-phenylpyrrole)diyl] **12**. All new compounds in this series were fully characterized as reported in the Experimental section.



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APPENDIX 3

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Submitted by E.L. Thomas



**Final Technical Report**

**AFOSR 90-0150**

**"Investigations of Nanoscale Composites and High Performance Polymers."**

**March 1, 1990 - February 28, 1993**

**E. L. Thomas**

**1.0 Abstract**

During the past three years our research efforts have focussed upon the investigation of novel nanoscale composites based on the self assembly of A/B block copolymer systems. In addition, we examined several high performance polymers having outstanding electrical or mechanical properties. Our aim has been to establish processing/structure/property relationships by careful study of sample morphology using a variety of structural characterization tools and correlating the sample microstructure with processing conditions and observed properties.

In order to optimize properties, we are learning how to process the samples to achieve controlled size, shape and connectivity of the microstructural elements. One approach for achieving highly ordered arrangements at the nanoscale level is to utilize thermodynamic self-assembly of diblock copolymers or diblock copolymer/homopolymer blends wherein the mutual repulsion of the A and B segments for typical molecular weights of  $10^5$  leads to periodic nanoscale structures.

Another approach is to have the block copolymer undergo self-assembly in a biased field. We have developed such a processing approach utilizing a roll casting technique that enables large film (12 cm x 2 cm 1 mm) specimens of single crystal geometry to be fabricated and affords the opportunity for samples to exhibit highly anisotropic properties.

High performance rigid-rod polymers have been developed by the Air Force which exhibit the highest known values for tensile modulus and strength of any organic material. However, these outstanding tensile properties are not matched in compression. Rigid-rod fibers fail in compression by kink band formation. We have investigated the micromechanisms of kink band

formation and their relationship to compression strength and fiber microstructure in order to learn how sample microstructure may be altered to improve compressive strength.

We have utilized the soluble precursor of poly-*p*-phenylene vinylene (PPV) which affords good processability of film and fiber in order to relate sample microstructure to electrical properties. Toward that goal, we have characterized crystal defects, such as grain boundary regions, in PPV as well as in high modulus, high strength rigid-rod polymers through extensive use of high resolution electron microscopy.

## 2.0 Detailed Progress of Researchers Funded by this Grant

A dominant factor in the determination of the domain morphology in A/B diblock copolymers is area-minimization of the spatially periodic intermaterial surface, subject to fixed volume fractions. The 3D geometry of such surfaces strongly influences material physical properties. Nanocomposites based on block copolymers and block copolymer/homopolymer blends can exhibit properties which are sensitive to the component(s) which have high phase connectivity. For example, the double diamond microdomain morphology, associated with a newly discovered family of triply periodic constant mean curvature surfaces, exhibits a tensile modulus which is higher than either a lamellar cylindrical or spherical microdomain geometry at a fixed composition due to the 3rd dimensional connectivity of the double diamond phase network. A doubly periodic boundary, corresponding to a classically known minimal surface (Scherk's First Surface), was found to be a good model for the grain boundary region between lamellar microdomains. This low energy grain boundary structure helps explain gas transport measurements in polygranule lamellar samples which exhibit connectivities higher than 2.

An improved technique for casting highly oriented films of block copolymers from solutions subjected to flow was developed. Polymer solutions were rolled between two counter-rotating adjacent cylinders while at the same time the solvent was allowed to evaporate. As the solvent evaporated, the block copolymers microphase separated into *globally oriented* structures. We

termed this new process "roll casting." The process has been applied to polystyrene-polybutadiene-polystyrene (PS/PB/PS) triblock copolymer cast with and without additional high molecular weight homopolymers. TEM and SAXS demonstrated that the pure copolymers films consist of polystyrene cylinders assembled on a hexagonal lattice in a polybutadiene matrix in a near single crystal structure. Blends of copolymers with high molecular weight polystyrene and/or polybutadiene, phase separated into ellipsoidal regions of homopolymer embedded in an oriented block copolymer matrix. Annealing the films resulted in conversion of the homopolymer regions to spheres accompanied by some misalignment of the copolymer microdomains. We examined how processing parameters influence the resultant sample microstructure. Preliminary measurements of mechanical properties (stress-strain behavior) were done on roll-cast samples as a function of applied strain with respect to the single crystal microdomain geometry. The tensile modulus is quite sensitive to overall sample orientation and correlates well with the orientational order parameter measured by 2D SAXS.

The crystal morphology of oriented films of poly (p-phenylene vinylene) (PPV) was investigated using electron microscopy and X-ray diffraction. An X-ray diffraction rotation series confirmed the existence of fibre symmetry in bulk oriented films. Dark-field imaging by transmission electron microscopy revealed small diffracting regions of the order of 7 nm in size with an aspect ratio near 1. These diffracting regions were shown by high resolution transmission electron microscopy to be composed of small crystallites with an average size of 5 nm. Imaging of the lateral packing by HREM allowed the evaluation of local variations in crystallite orientation. This HREM method of orientation function determination compares well to bulk methods (e.g. wide-angle X-ray scattering, infrared dichroism) for PPV of similar draw ratio. A micellar model was developed to describe the crystalline morphology of oriented PPV. The model depicts PPV as a highly connected network of small crystallites. The well-formed crystalline regions are thought to compose approximately 50% of the sample volume with the remainder of the volume being grain boundaries. Doping by AsF<sub>5</sub> led to the formation of an electron-dense overlayer, thought to be arsenic oxide, which prohibited dark-field imaging of the crystallites.

After doping with  $H_2SO_4$ , crystallites of the electrically conductive phase were observed. The general morphological character is preserved in the conversion from insulating to conducting foams. For the conditions employed, the doped diffracting regions were 4 nm in size and retained the orientation initially present in the pristine film.

Single crystals of poly(p-xylylene) were grown in dilute  $\alpha$ -methylnaphthalene solution and studied by bright-field and high-resolution electron microscopy (HREM). The crystallization process was discussed in terms of the dependence of crystal form on crystallization conditions. A 0.15 nm resolution was achieved from high-resolution images of a frozen liquid crystalline phase. High-temperature electron diffraction patterns confirmed the existence of the liquid-crystalline phase in agreement with the previous work of Lieser. The HREM images show the molecular packing in the smectic B phase.

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