conference papers

Multifunctional macromolecular ultrastructures: Introductory Comments Speciality Polymers '86

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Every conference needs a theme. In reviewing the *Programme and Abstract Book for Speciality Polymers '86*, the theme which comes to mind is Multifunctional Polymer Structures (*Figure 1*). Within this theme I would categorize the topics of the conference into two main divisions: *structural scale ordering* and *electromagnetic processes*. The former comprises the molecular and supramolecular aspects of structure, oriented systems and liquid crystallinity. As a fourth I would add ordered, repetitive morphologies. The second category comprises electrical and optical effects, particularly non-linear optical processes, electrical conductivity, and ferroelectricity. I would emphasize in addition here that these processes be predictive, controlled and interactive, emphasizing stability. Taken together they would comprise the basis for the design of processible multifunctional electromagnetic polymer structures with mechanical, thermal and environmental integrity.

The theme of multifunctional structures summarizes the direction of the Air Force Office of Scientific Research (AFOSR) program in polymers since 1979. This began with two events in 1978 (*Table 1*). The first was the formation of the DoD Ultrasubmicron Electronics Research Committee (USER) composed of Horst Wittman from the Army Research Office, John Dimmock from the Office of Naval Research, Clarence Gardener and the author from AFOSR, and directed by George Gammota of the Office of the Secretary of Defense. The purpose of USER was to select directions of research to achieve the next generation of submicron structures beyond VHSIC (very high speed integrated circuits). The Air Force proposed a very radical approach, departing from the conventional wisdom of simply scaling down to finer dimensions current silicon circuits with new photoresists and photolithographic sources. AFOSR proposed utilizing the ordering and orientation of the submicron morphological features in liquid crystalline-derived molecular composites, polymer alloys and blends, and multi-block copolymer structures of electroactive polymers and passive dielectric phases as a new direction for designing submicron level devices (*Figure 2*). With expansion of the imagination this approach could also be visualized as the basis for polymeric integrated circuits, the problems of interconnections and heat dissipation being recognized as a major challenge. The design of electrically stable semiconductive electroactive polymer phases via liquid crystalline polymer routes was also proposed as part of this initiative.

The second event was the National Science Foundation Microstructures Workshop. Papers were presented on conducting polyacetylene polymers, which described the mechanims in terms of silicon semiconductor technology. AFOSR questioned presenting conducting polymers in terms of silicon semiconductor integrated circuit concepts. The structural

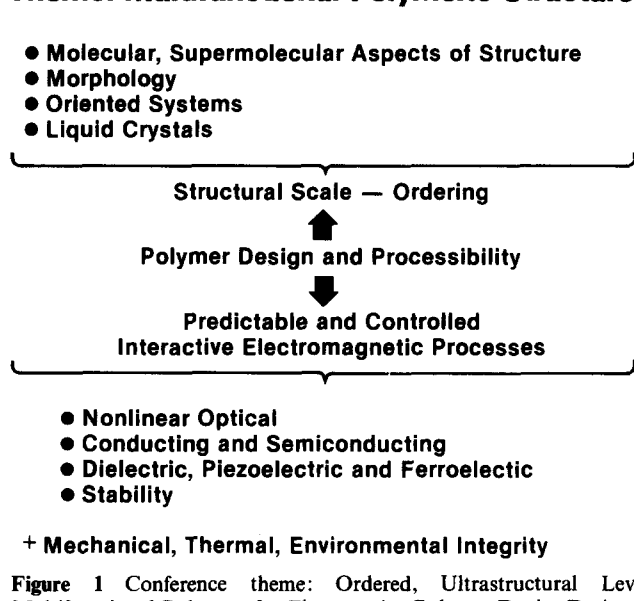

Figure 1 Conference theme: Ordered, Ultrastructural Level Multifunctional Polymers for Electroactive Polymer Device Design

Table 1 History of Air Force research in electromagnetic polymers

History

1978 — NSF Microstructures Workshop
1979 — OSD Ultrasubmicron Electronics Research (User) Committee

- AFOSR Questioned Polyacetylene Materials Science in Terms of
  - —Silicon Semiconductor Integrated Circuit Concepts
  - —Structural Concepts
- Silicon Requirements
  - —Highly *Ordered*, *Oriented*, Nonporous Substrate With *Specific* Crystal Orientation, Resistivity, and Carrier Type
  - —Specific Type Dopant in Parts Per Million (PPM) (N or P) Along Specific Crystal Direction in Specific Sites on a Repetitive Basis
  - —Theoretically Predictable

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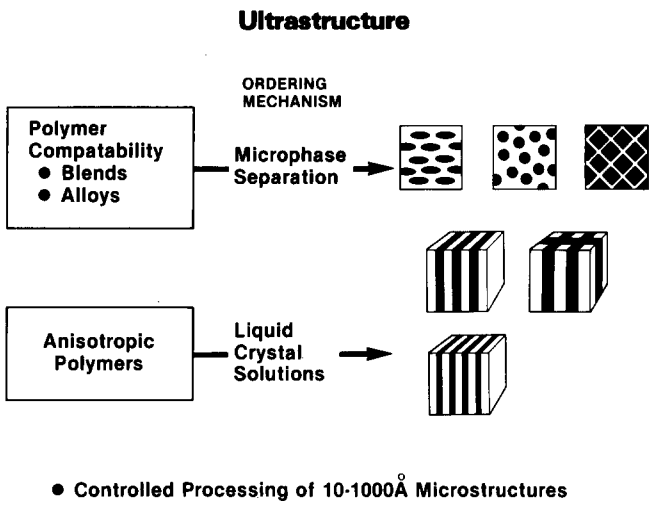


Figure 2 Concepts for ultrastructure ordering in polymers for submicron device design

concepts were also questioned (*Table 1*). First, semiconductor (not conductor as presented) silicon substrates are highly ordered, oriented and non-porous with specific crystal orientation, resistivity, and charge carrier type and number. They are electrically and environmentally stable. Electron micrographs presented showed polyacetylene to be a porous material composed of random fibrils. Second, the concept of doping was inappropriately used. In silicon doping refers precisely to specific dopants in parts per million (n- or p-type) distributed along specific crystal orientations in specific sites on a repetitive basis. The concept of dopants in polyacetylene was being applied to concentrations of additives up to 15 vol%, and which were randomly dispersed or aggregated in the porous, disordered polyacetylene substrates. Third, the results in silicon are theoretically predicted. Fourth, there was and has been no mention of stability testing, the 'acid' test in semiconductors being stress–voltage–temperature testing.

As a result in 1979 (*Table 2*), a program was undertaken to establish the polymer requirements for designing semiconductor polymers. Based on the silicon requirements delineated in *Table 1*, the polymer requirements were established. The substrate had to be highly ordered at the molecular and morphological levels. The best candidate at the time was determined to be poly(*p*-phenylene-2,6-benzobisthiazole) (PBT), developed by Jim Wolfe at SRI International and Fred Arnold of the Air Force Materials Laboratory in the AFWAL/AFOSR (now AFWAL/ML, the Air Force Wright Aeronautical Laboratory/Materials Laboratory) Ordered Polymer Program. It was a conjugated, rigid chain, anisotropic liquid crystalline polymer. It was processible, environmentally stable at higher temperatures, of high strength and modulus and showed increased thermal conductivity.

A non-topological approach based on *ultrastructure* concepts was followed, rather than simply attempting to build on the planar technology of silicon by placing polymer films on silicon integrated circuits. Ultrastructure is a recognizable solid state structure with characteristic dimensions of a few hundred angstroms. This was demonstrated first in ceramics and then extended to polymers in the form of ordered block copolymer electroactive systems.

The results of the latter approach were first reported by Frank Karasz and H. H. Winter in 1983 at the *First International Conference on the Ultrastructure Processing of Ceramics, Glasses, and Composites* (Wiley, 1984, edited by Larry L. Hench and Donald R. Ulrich). Advantage was taken of combining the formation of domains in an ordered three dimensional array with the systematic formation of ordered layers and structures by elongational shear fields produced by stagnation flow die geometries. This concept was first successfully demonstrated when applied to commercially available styrene-butadiene-styrene triblocks and holds promise as a very selective technique for controlled macromolecular ultrastructure development (*Figure 3*).

The comprehensive theme of multifunctional polymers in terms of ultrastructured materials is schematically shown in *Figure 4*. This is based on ordered liquid crystalline polymers, ordered inorganic polymers, and organometallics in a hierarchical structure of molecular composites, sol–gel nanocomposites, and polymer blends and alloys. This paper discusses the macromolecular ultrastructure approach based on the ordered liquid crystalline polymers in molecular composites and blends and alloys.

A team effort was put in place in 1979–1981 to establish the principles for the design, synthesis and processing of ultrastructured, electroactive polymers. This was composed of Larry Dalton of the University of Southern California, Jim Mark of the University of Cincinnati, Ed Barker of the University of Virginia, the late Paul Flory of Stanford, Frank Karasz of the University of Massachusetts, Jim Wolfe of SRI International, and Ivan Goldfarb of AFWAL/ML, several of whom are speakers at this conference.

It was determined that the two primary efforts should be to establish the electron dynamics required for conductivity in the ordered polymers and to theoretically predict dopant level effects in these materials. In 1982–

Table 2 Polymer requirements for designing semiconductor structures derived from silicon requirements

1979
Polymer Requirements For Designing Semiconducting Structures

- **Highly Ordered at Molecular and Morphological Levels** — PBT
  - —Rigid Chain
  - —Liquid Crystalline
  - —Conjugated
  - —Anisotropic
- **Processible**
- **Environmentally Stable**
- **High Strength**
- **Increased Thermal Conductivity (?)**
- **Non-Topological Approach**
  - —Ultrastructure: Recognizable Multiphase Solid State Structure With Characteristic Dimensions of a Few Hundred Angstroms
    - --First Considered In Ceramics, Then Polymers
    - --Ordered Block Copolymer Electroactive Systems
- **Research Priorities**
  - —Establish Electron Dynamics
  - —Theoretically Predict Dopant Level Effect.

Stagnation Flow Structuring of Polymers

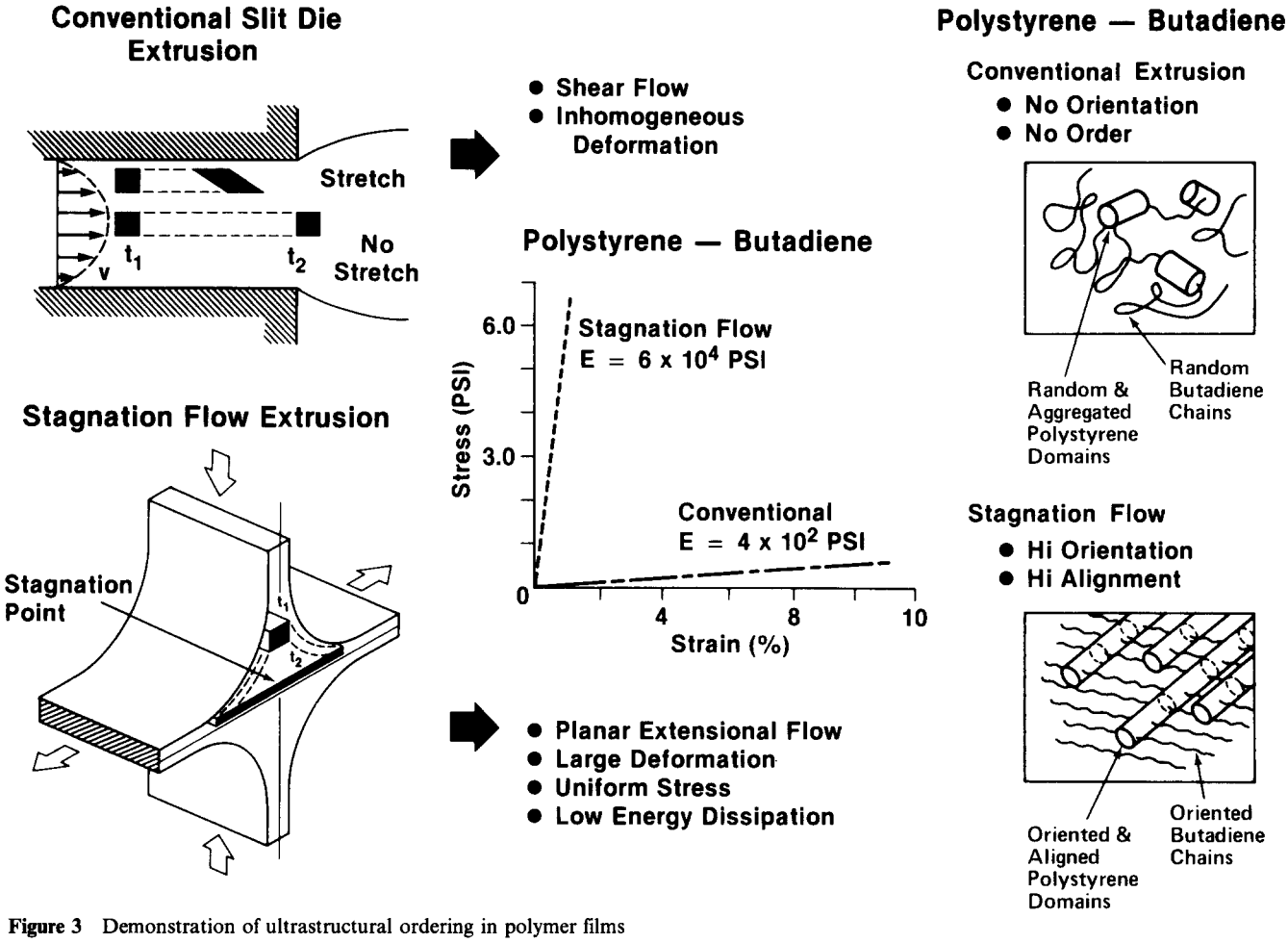


Figure 3 Demonstration of ultrastructural ordering in polymer films

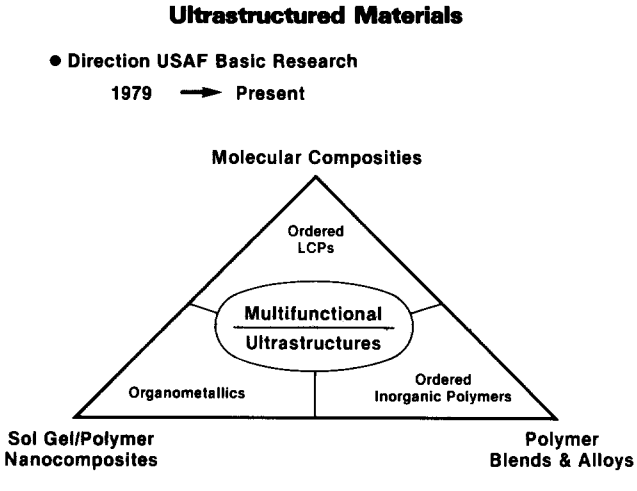


Figure 4 Approaches to ultrastructured multiplastic polymers

1983 this approach was expanded to include non-linear optical polymers, both semi-conducting NLO polymers and liquid crystalline. Among others the team for this expanded approach included Tony Garito of the University of Pennsylvania, Paras Prasad of SUNY, Buffalo, Alan Buckley and Jim Stamatoff of Celanese Research Corporation, Tobin Marks and Steve Carr of Northwestern, Howard Reiss of UCLA, Rick Lytel of Lockheed Research Laboratory-Palo Alto, and Andy Griffin of the University of Southern Mississippi.

Ten years ago the AFWAL/ML and AFOSR identified an area of research called the Air Force Ordered Polymers Program aimed at the synthesis and processing of particularly rigid polymers for use in aerospace vehicles where the properties of high strength, high modulus, and environmental stability were key goals. The structure–property relationships that led to the molecular design of poly(*p*-phenylene-2,6-benzobisthiazole), or PBT, and (*p*-phenylene-2,6-benzobisoxazole), or PBO, were: (1) the rigid rod structure to impact liquid crystalline orderability; and (2) a wholly aromatic structure to impact high modulus as well as thermal and thermooxidative stability.

In contrast to the majority of polymers, which are coiled and analogous to cooked spaghetti, the unique chain structure of the ordered polymers as illustrated by PBT and PBO is shown in *Figure 5*. These can be described by the simple model of uncooked spaghetti.

The high modulus and strength are shown in the comparative properties chart of *Figure 6*. Values of modulus and tenacity, respectively of 55 Msi and 600 Ksi with an elongation of 1.1% in dry-jet wet spinning have been produced. Efforts are continuing under Air Force support to optimize and scale up the fibre spinning process at Du Pont and Celanese. Uniaxially oriented

ribbons have been processed at Celanese with modulus and tenacity values to 40 Msi and 500 Ksi, respectively.

The work of Barker at the University of Virginia and Arnold at AFWAL/ML presents promising evidence for unique electrical conducting properties for these excellent structural polymers as exemplified by PBT and BBL (benzimidazoisquinoline) (*Figure 7*). The work of Dalton, Mark, Barker and others have shown that PBT, PBO, and BBL are characterized by extensively delocalized π-electrons and that this π-electron delocalization profoundly influences electrical conductivity. Electron nuclear double resonance (ENDOR) and relaxation measurements suggest that electron–electron interactions are important for long range electron delocalization and thus for electrical conductivity. An extensively delocalized π-electron defect of metallic character is observed. Preliminary results indicate that intra-

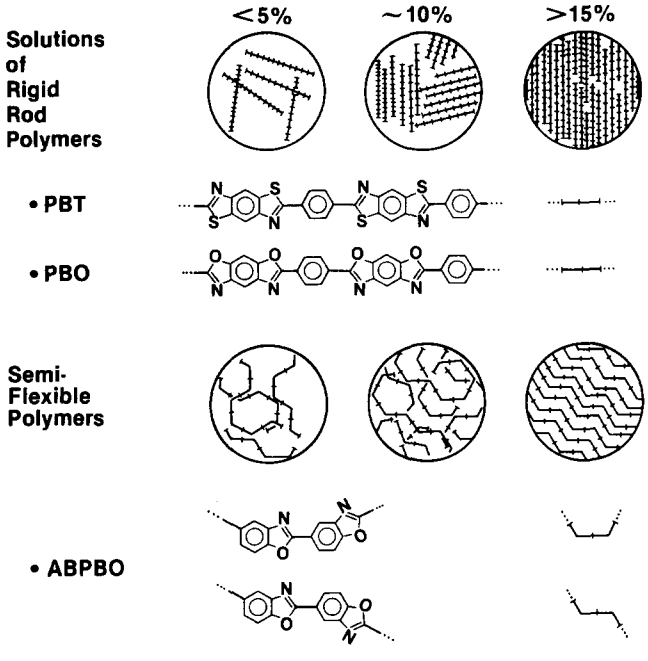


Figure 5 USAF rigid chain and semiflexible chain ordered polymer assembly and alignment in solution

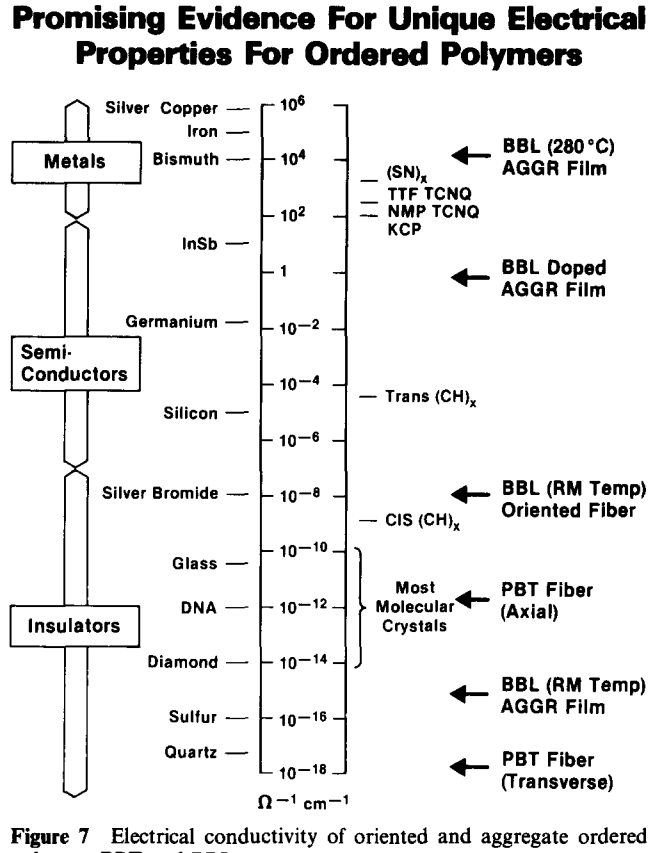


Figure 7 Electrical conductivity of oriented and aggregate ordered polymers PBT and BBL

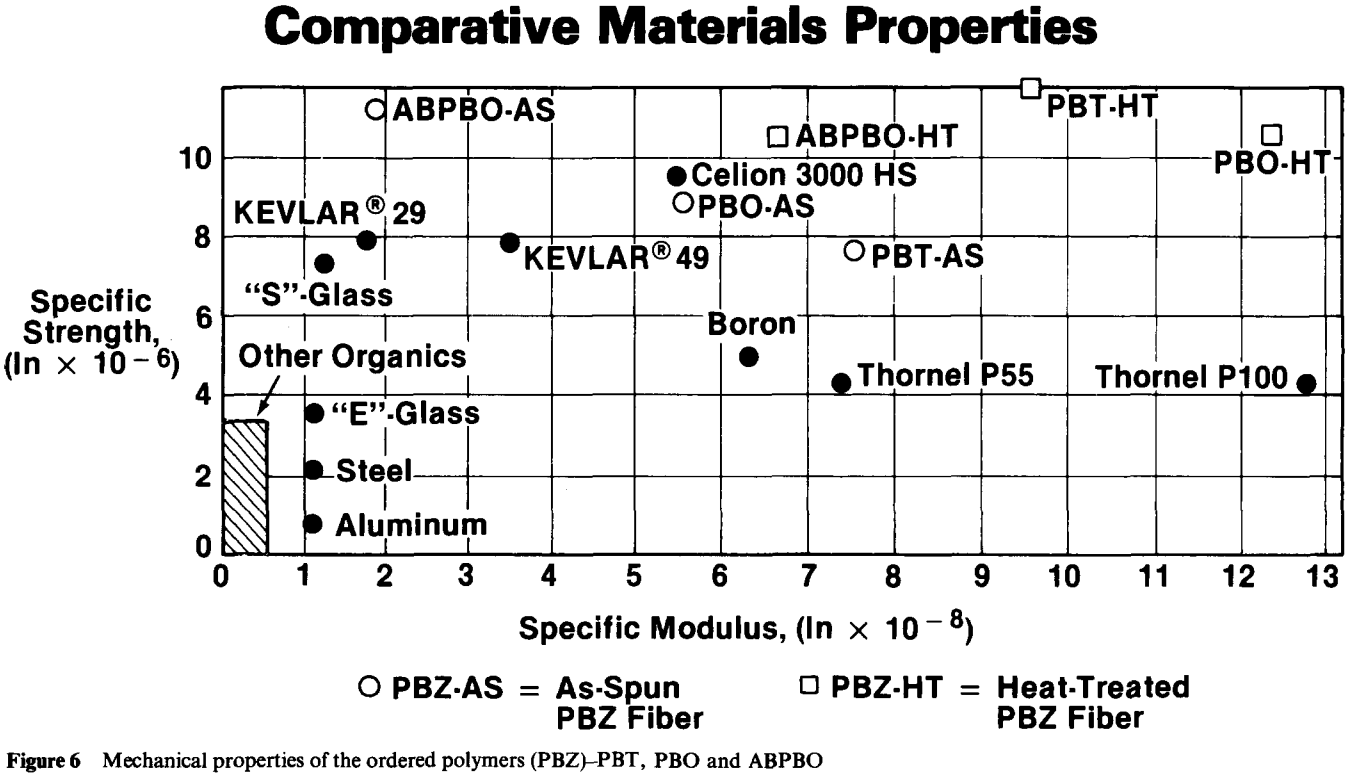


Figure 6 Mechanical properties of the ordered polymers (PBZ)–PBT, PBO and ABPBO

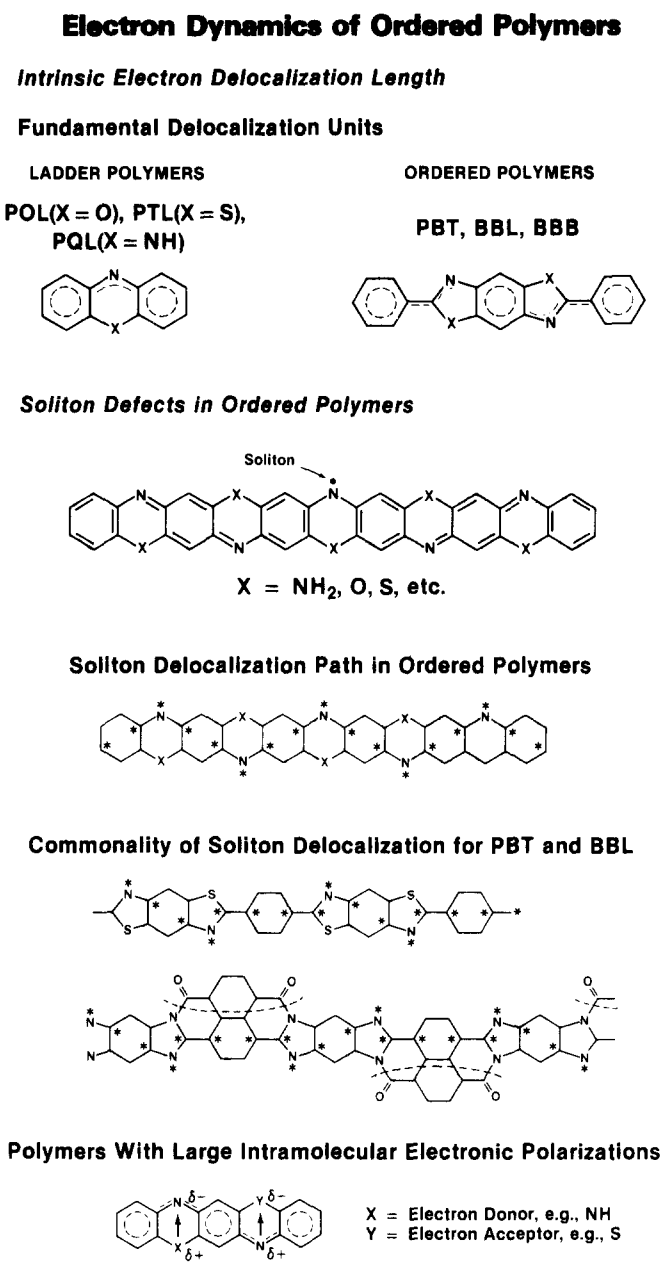


Figure 8 Electron dynamics defining the design of controlled semiconductivity and conductivity in ordered and ladder polymers

molecular charge transfer plays an important role in defining intrinsic electrical properties. ENDOR and electron spin echo envelope modulation (ESEEM) studies have established the existence and permitted the characterization of stable, reversible charge transfer complexes formed between polymers and dopants; such complexes are shown to change π-delocalization and alter polymer solubility. Spectroscopic measurements of delocalization and of both intra and intermolecular charge transfer have been correlated with electrical conductivity. Significant increases in electrical conductivity with exposure to electron donor or acceptor dopants is observed for the ordered polymers. Of exception and high interest is that that the lack of such increase in conductivity for PBT with doping is likely due to a closely packed lattice which prevents dopant intercalation.

Since ENDOR data is observed to be independent of polymer morphology, the intrinsic electron delocalization and intramolecular charge transfer is determined by intramolecular interactions. The intrinsic electron delocalization lengths have been defined for PBT, BBL and BBB. The intrinsic electron delocalization is consistent with the structures shown in *Figure 8*. Conductivity changes on the order of several orders of magnitude can be controlled by variation of X in ladder polymers and by control of the metal redox state in copolymers of ladder polymers with metallomacrocycles.

The commonality of the defect delocalization path for PBT and BBL is shown in *Figure 8*. Their defect delocalization path is greater than 200 Å in the polymer backbone because of high perfection in polymer symmetry. On the other hand it has been shown that polyacetylene often has a delocalization path of less than 100 Å because of symmetry breaking lattice perturbants such as *cis*-polyacetylene segments.

Experimental substantiation of theory is demonstrated by the CNDO/2 MO calculations on geometric positions of acceptor ion dopants (I_3^- and Br_3). These are located symmetrically above bisbenzothiazole units which are aligned along axes of the polymers.

In summary, this long-time, painstakingly careful work intiated in 1979, has started to verify the polymer requirements as set out in *Table 2* for the design of semiconducting and conducting polymers of high order and symmetry. The results of some of this work were presented at the 1985 Air Force Conference on Ultrastructure of Organic and Inorganic Polymers at the University of Massachusetts. For example, PBT has better electron delocalization; the tightly packed fibres demands a non-diffusion doping process via precursor polymers such as that demonstrated by Frank Karasz and Robert Lenz in AFOSR supported research with PPV (poly(*p*-phenylene vinylene)). On the other hand, BBL with a planar structure is favourable for doping by a diffusion process. Electron donors and acceptors enhance conductivity in the same way. In addition, an interpentrating network of PBT and phthalocyanine has been developed by Steve Carr and Tobin Marks at Northwestern University which preserves the electrical conductuvity, mechanical properties, and anisotropy in charge transport.

Third harmonic generation measurements by Garito and degenerate four wave mixing experiments by Prasad have shown that the lyotropic liquid crystalline PBT, PBO and PBI (poly-2,2′(m-phenylene)-5,5′bibenzimidazole) also possess large, non-resonant third order optical susceptibilities whose origin resides in ultrafast, lossless excitations of highly charged correlated π-electron states (*Figures 9–11*, *Tables 3* and *4*). These results have now been predicted theoretically. Thus, we now have for the first time polymers with outstanding structural, thermal and environmental properties which can be designed into self supporting films or sheets, monolayer structures or conformable shapes having ultrafast (10^{-13} to 10^{-15} s) non-resonant optical switching times for optical computing or signal processing. Other examples of Air Force—DARPA liquid crystalline polymers are the divinyldiacetylenes (DVDA) and diphenyldiacetylenes (DPDA).

Figure 9 and *Table 4* show the current state of these polymers relative to semi-conducting electronics and hybrid-lithium niobate devices. The focus of current research is to reduce the switching element power

Air Force Electrooptic Polymers
Nonlinear Optical Switching Materials

- Exceptionally Large $\chi^{(3)}$
- Purely Electronic $\chi^{(3)}$
- Ultrafast Switching 10^{-14}–15^{-15} Seconds
- Low Energy Switching $\leq 1 \times 10^{-12}$ Joule at 10^{12} Hz
- Lossless Virtual Optical Excitation
  - Nonabsorbing/ Nonresonant
- High Optical Damage Thresholds

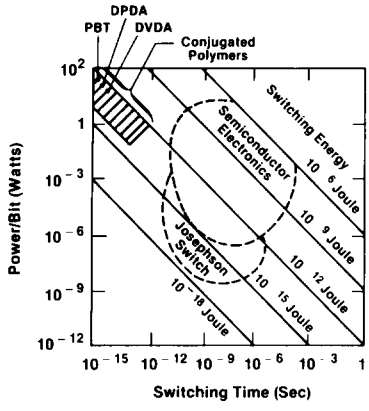
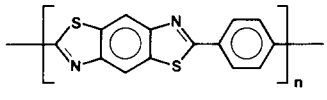


Figure 9 Current status of NLO polymers — research emphasis is to reduce power/bit



$\chi^{(3)} \simeq 10^{-11}$ ESU

Poly (p-phenylenebenzobisthiazole) (PBT)

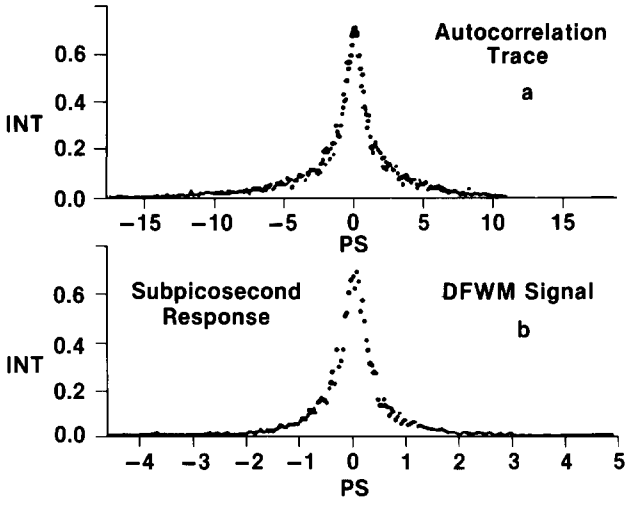


Figure 10 Subpicosecond response of nonlinear optical processes in biaxial PBT films by degenerate four wave mixing

requirement. The importance of the non-absorbing, non-resonant lossless virtual optical excitation of the ordered polymers is shown. The non-resonant macroscopic third order susceptibility $\chi^{(3)}$ is independent of wavelength and absorption processes, thus having a high value of $\chi^{(3)}$ over a wide range of optical frequencies. In GaAs and $LiNbO_3$ an absorptive response is required with material transformation resulting in a slower response time.

Under an Air Force program, Foster–Miller has been able to process biaxial films of PBT where both high strength and large $\chi^{(3)}$ is a function of film orientation. Prasad has shown (*Figure 10*) the subpicosecond response of non-linear optical processes in these films where the $\chi^{(3)}$ response time is considerably shorter than the autocorrelation pulse. This demonstrates the subpicosecond response of the non-linear optical process. The value of $\chi^{(3)}$ depends on the orientation of the film which can be explained by its tensor property in a biaxial symmetry. *Figure 11* shows a polar plot of the relative values of $\chi^{(3)}$ as a function of the angle of rotation of the film. Squares represent the data points obtained for the vertical polarization of all the beams for degenerate four wave mixing and circles correspond to the data points obtained when the pump beams are vertically polarized but the probe beam and the signal are horizontally polarized. The solid curves represent the theoretical fits.

Polar Plot:
$\chi^{(3)}$ As A Function of Film Rotation Angle

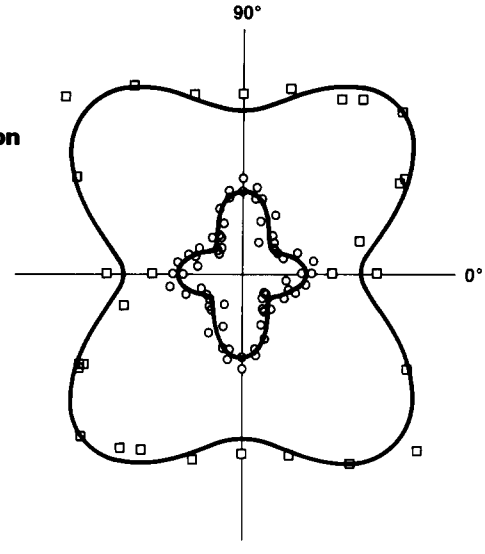


Figure 11 Polar plot of non-resonant microscopic third order susceptibility $\chi^{(3)}$ in biaxial PBT as a function of orientation

Table 3 Non-linear optical structural polymers

Air Force Electrooptical Polymers
Nonlinear Optical Switching Materials

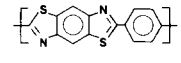
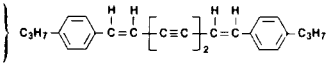
- Liquid Crystalline Polymers
  - Polybenzothiazole (PBT) 
  - Divinyldiacetylenes (DVDA)
  - Diphenyldiacetylenes (DPDA) 
- Fastest Switching Observed in Nonlinear Optical Materials
- Excellent Mechanical Properties
- Outstanding Thermal and Environmental Stability
- Thin Films or Conformable Shapes

Table 4 NLO response of ordered polymers — origin and characteristics

Exceptional Nonlinear Optical Response of Liquid Crystalline Polymers

- Origin in Lossless Excitation of π-Electron Charge Correlated States and Natural Cooperative Alignment of Liquid Crystalline Ordered Polymers
- In GaAs and $LiNbO_3$, an Absorptive Response is Required with Material Transformation — Slower Response Time

MATERIAL	$\chi^{(3)}$
PBT and PBI	100×10^{-12} ESU
DVDA	50
Liquid Crystals	.3—4
$LiNbO_3$	~0
GaAs	~0

- Biaxial PBT Films — Speed is Orientation Dependent
  - 3 Times Faster in One Direction
  - New NLO Devices Possible

Molecular Composites Concept

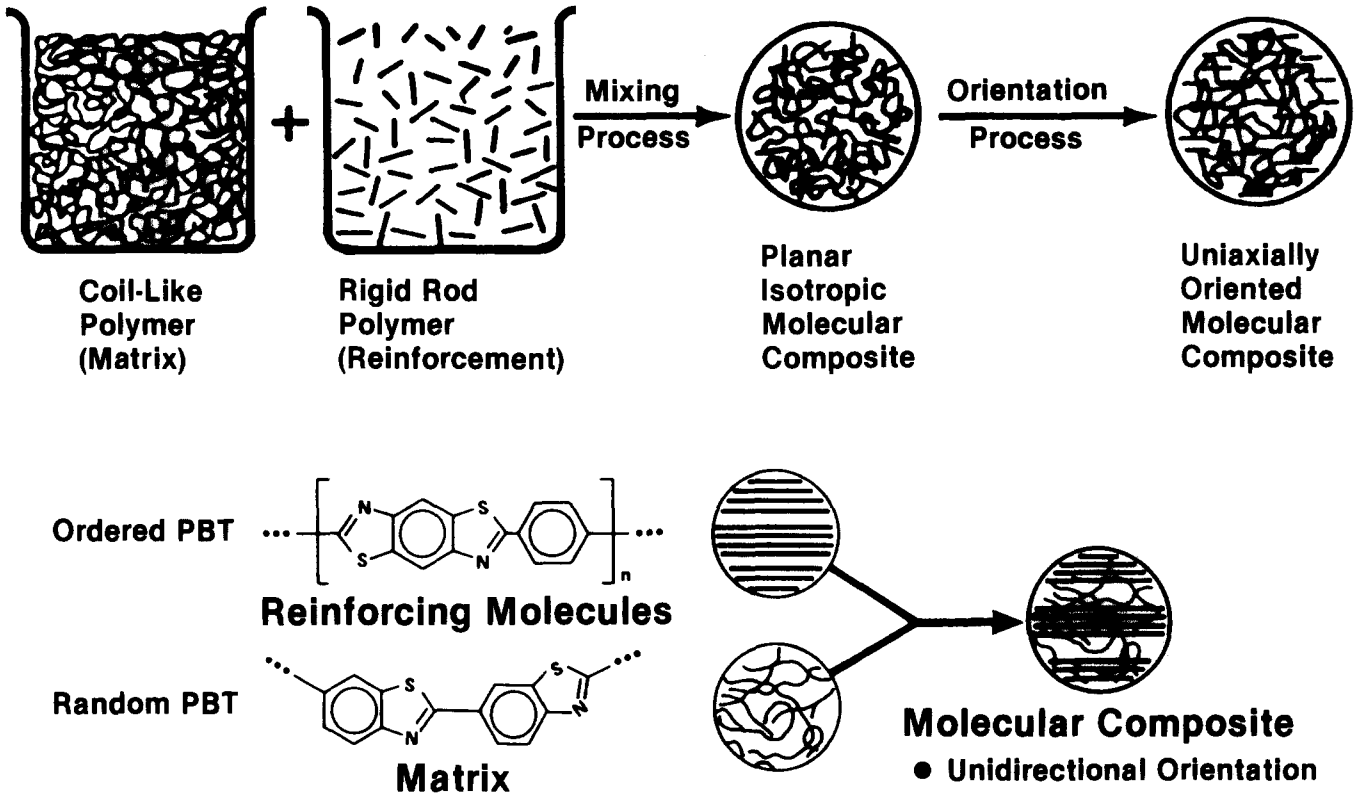


Figure 12 Molecular composite concepts for ordered polymers

The significance of these results is that they demonstrate the feasibility of performing optical and electronic functions in anisotropic polymers without compromising structural performance or ease of processing. They demonstrate the concept for multifunctional polymer structures.

A natural extension of these advances is to develop multifunctionality in molecular composites of the ordered polymers (*Figure 12*). A patented advance by Jim Wolfe and P. D. Sybert, under joint AFOSR-AFWAL/ML support, called the adjustable polyphosphoric polymerization process, allowed the discovery that semi-rigid polymers, such as poly(2,6-benzothiazole) (ABPBT) and poly(2,5-benzoxazole) (ABPBO), could be polymerized in the nematic phase with high molecular weight. Based on the theoretical and synthetic work of Paul Flory with Fred Arnold, Ted Helminak and Bob Evers at AFWAL/ML, molecular composites were developed where rigid chains of PBT reinforced a matrix of ABPBT in one homogeneous material on a molecular level. These have been shown to be the molecular analog of chopped fibre macroscopic composites. This has now been demonstrated with PBO/ABPBO. These principles for molecular engineering design in polymers offer pay off for multifunctional polymer composites and structures in the near future.

These materials have provided the basis for the major Air Force Forecast II project in Ultrastructured Materials where AFOSR and AFWAL/ML are the officers of primary responsibility (OPRs). Several Air Force laboratories including AFWAL/ML, the AFWAL Avionics Laboratory, the Air Force Weapons Laboratory, and Rome Air Development Center are participating with AFOSR in this pioneering effort, building on what Air Force basic research has developed. The Polymer Branch of AFWAL/ML will reorient its research program from a 100% structural polymer effort to at least 50% NLO polymer by Fiscal Year 1988.

In very recent work, Larry Dalton has shown that the molecular design itself is of fundamental importance to NLO applications with ENDOR and ESEEM measurements of intrinsic or short time-scale (less than 10^{-11} s) π-electron highest occupied molecular orbital (HOMO) delocalization. The experimentally observed delocalization is 28–30 atoms for the ladder polymers (POL (X=O), PTL (X=S), and PQL (X=NH) which implies that the fundamental delocalization unit is as shown in *Figure 8*. The experimentally observed delocalization for rigid rod (PBT) and ladder polymers (BBL and BBB (benzimidazo-benzophenananthroline)) is found to be 42–46 atoms also consistent with the fundamental unit shown in *Figure 8*. Since NLO activity is a short time phenomenon, the above units are almost certainly the relevant lengths (if the highest occupied molecular orbital plays a role in NLO effects).

The second important factor which can elucidated in Dalton's ENDOR and ESEEM studies is the role of X in intramolecular charge transfer and hence electronic polarization. He has observed the ordering of intramolecular charge transfer to be NH>S>O. Even

Molecular Organization of LC Polymers

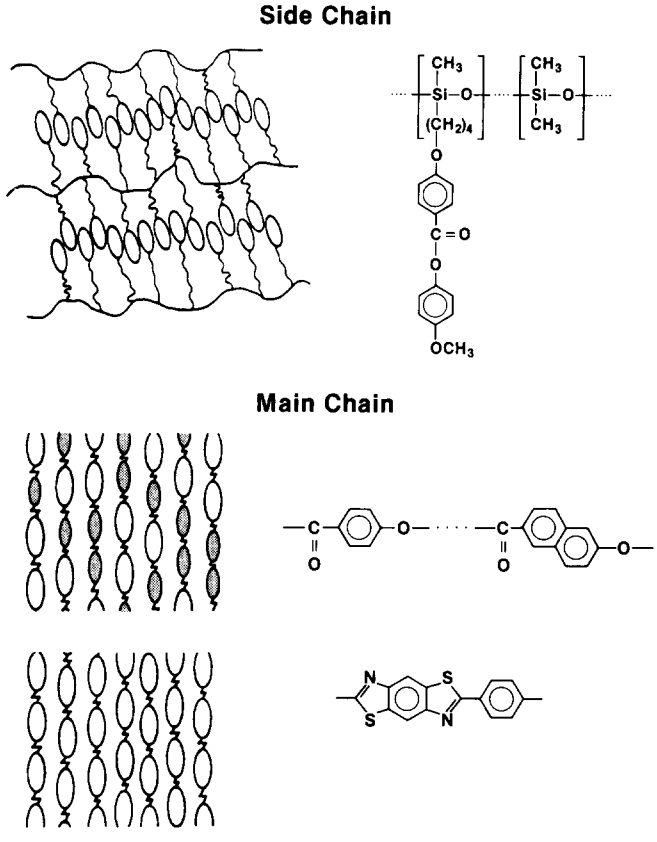


Figure 13 Molecular organization for liquid crystalline NLO polymers

more importantly he has shown how such substituents can be used to control electrical and non-linear properties via sequential synthesis. It may be possible to produce polymers with large intramolecular electronic polarizations (*Figure 8*).

He also points out the importance of polymer order for practical NLO materials. Obviously, phase conjugation cannot be accomplished in disordered materials such as Shirakawa polyacetylene. Also, it is to be noted that practical NLO utility depends more upon the ratio of non-linear susceptibility to absorption coefficient than on just the former.

In a recent trip to Europe I visited NLO polymer researchers in industry, universities, and macromolecular research institutes. There are major material efforts and European Economic Community (EEC) programs underway. The work of Garito, Dalton and of Prasad forms the basis for a major direction of research by these investigators. Of fundamental importance is that the ordered polymer molecules, exemplified by PBT, are the model for this approach, which is to design for mechanical and thermal stability first, followed by the tailoring of the NLO second or third order polarizabilities for second and third harmonic response. This applies to thick and thin films as well as Langmuir–Blodgett monolayer studies.

In addition, our research has shown that side-chain molecular organization (*Figure 13*) is important along with main chain organization in designing of liquid crystalline (LC) NLO polymers. Side chain mesogens can contribute to NLO enhancement and particularly to the alignment of structures by the application of electrical fields or poling. We have demonstrated that the proper side chain mesogen concurrent with poling technique results in a LCP being either opaque or completely transparent. Poling is a topic of several papers at this conference and is an important consideration in the design of multifunctional structural polymers.

The Langmuir–Blodgett technique has been used by Garito, Buckley and Stamatoff to predict, synthesize and demonstrate an NLO polymer structure with second harmonic generation (SHG) at 800 nanometers, the wavelength required for GaAs solid state lasers. Based on a centrosymmetric quinoid polymer with large second order polarizability β (200×10^{-30} esu), macroscopic structures with large SHG efficiency have been designed by mimicking the required non-centro-symmetric polymer structure through asymmetric and symmetric multi-layer construction (*Figures 14* and *15*).

Another multifunctional approach is being designed around polymer alloys and blends. It is well known that high molar mass homopolymer pairs are generally not miscible.

Now the thermodynamic factors which control the blending of immiscible polymer pairs into high

Quinoid Containing Langmuir Blodgett Multi-Layers

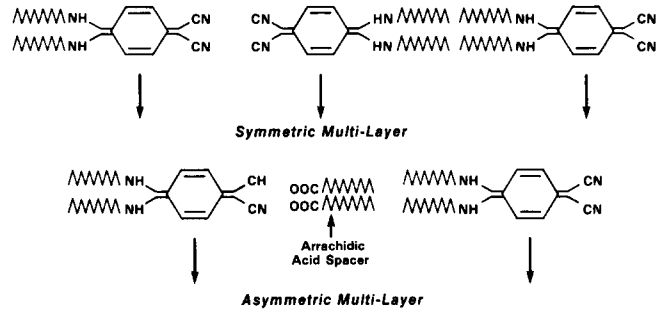


Figure 14 Multilayer NLO polymer structure with large SHG efficiency — precursor for organic superlattices

NLO Polymer With SHG At 800 NM

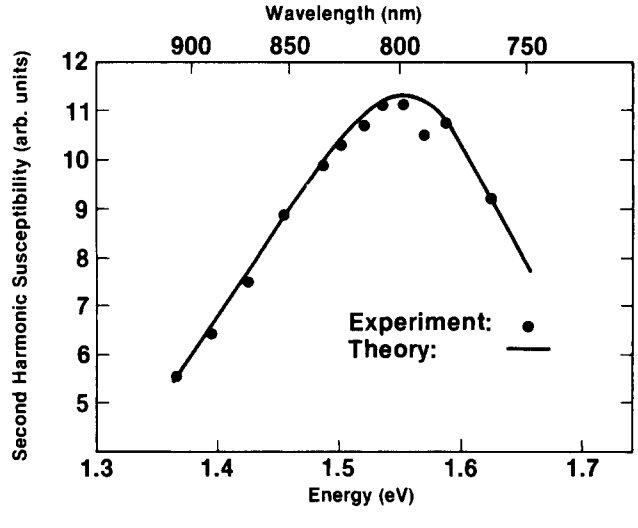


Figure 15 NLO polymer structure of *Figure 14* showing high SHG efficiency at 800 nm, the GaAs solid state laser wavelength

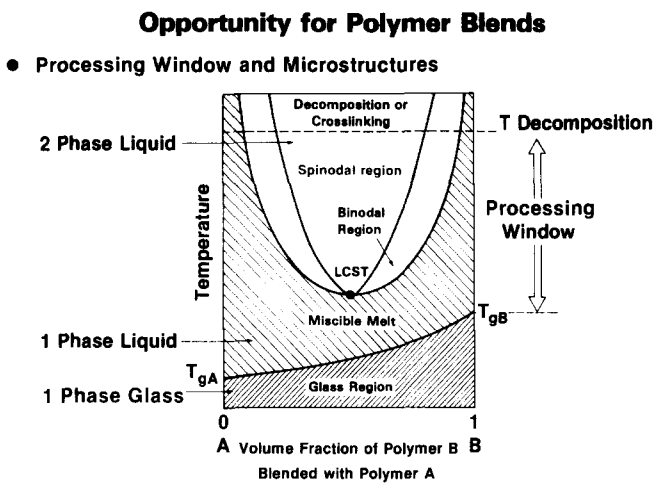


Figure 16 Three basic morphologies for compatible polymers via blending

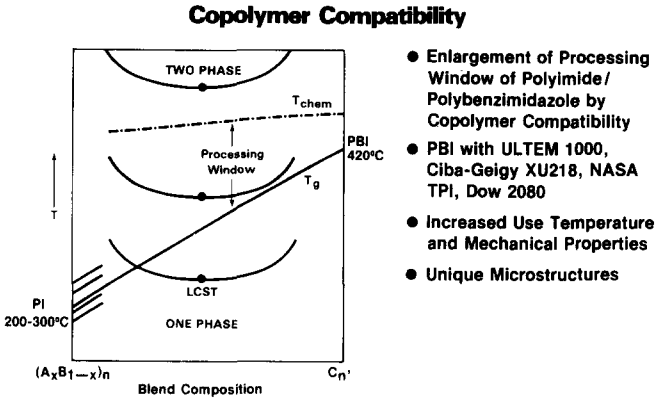


Figure 17 Control of morphology by shifting of the lower critical solution temperature (*LCST*) for copolymer blends

performance polymer blends have been established by the Karasz–MacKnight Mean Field Theory treatment. Their formalism states that the opportunities for preparing miscible blending pairs is greatly enhanced where at least one of the components is a random copolymer and that further enhancement occurs when both components are copolymers—rather than homopolymers.

As indicated in the hypothetical phase diagram of *Figure 16*, blends of inherently compatible polymer pairs can be prepared in a choice of three basic morphologies: miscible, discrete particle phase within a continuous matrix (binodal phase decomposition) and co-continuous phases (spinodal phase decomposition). *Figure 17* shows how the *LCST* (lower critical solution temperature) or phase boundaries of *Figure 16* can be shifted vertically for copolymer blends with small changes in composition to obtain one of the three morphologies.

Under an AFOSR–DARPA funded research program at University of Massachusetts, Celanese Research Corporation (CRC) and the National Bureau of Standards, a new family of high performance, miscible polymer blends based on aromatic polybenzimidazoles and aromatic polymides has been discovered by applying these principles. Preliminary evidence, obtained with commercially available, soluble polymers suggests that polymers of these generic types may be miscible over a wide range of compositions and structural variations. Blend miscibility was evidenced in the form of single T_g's and well-defined single tan δ relaxations intermediate to those of the component polymers, the formation of clear films and, in one case, enhanced solvent resistance.

Recently Buckly, Stamatoff, Calundann, Khanarian, and Jaffe of CRC and Garito found that these blends had large third order susceptibility by third harmonic generation measurements. In addition, in 2-methyl 4-nitroaniline (MNA)-poly(methyl methacrylate) (PMMA) polymer alloys they have clearly demonstrated the importance of molecular design to obtain materials with large Kerr constraints. In this case the major contribution to the d.c. Kerr effect comes from the orientation of molecules in the electric field. Karasz has also demonstrated the importance of blending to electroactive polymers utilizing polyphenylene vinylene via water-soluble precursor polymers.

The historical chronology of the evolution of the science of polymer blends toward multifunctional structures and composites at the University of Massachusetts is presented in *Table 5*.

In conclusion, the theme for this conference can be best expressed as multifunctional polymer structures (*Table 6*). The content of the papers of the conference suggests that history will record it as being a milestone in fostering new directions for the design and processing of multifunctional composites. Examples have been given in this talk showing that ordered, oriented ultrastructural features of multiphasic materials will play an important role in electroactive polymer device design.

New devices will be designed based on the

Table 5 Evolution of science of polymer blends toward multifunctional polymers

Chronology	
1967.	Inception of AFOSR Support Main Theme: Thermal Properties of Polymers
1972.	Emphasis on Polymer Blends
1977.	Mechanical, Phase Behavior of Blends Lower Critical Solution Temperatures Found
1979.	Copolymer Effects Discovered
1980.	First Molecular Level Polymer Alloy
1981.	Conducting Polymers/Blends/Light Scattering
1982.	Copolymer Theory for Blends
1984.	DARPA Program Started, Using These AFOSR Results
1986.	—Transition to Industry —Industrial Investment in U. Mass Blends Program —Program DARPA 6.2 Industrial Contracts With Subcontracts to U. Mass

Table 6 Future directions for electroactive polymer device design

Future
• Multifunctional Composites
• Ordered, Oriented Ultrastructural Features of Multiphasic Materials in Electroactive Polymer Device Design
• Multidirectional, Anisotropic Advantages
• Intelligent Processing of Materials (IPM) Research on Control of These Features

multidirectional, anisotropic advantages of these structures. The Intelligent Processing of Materials (IPM) will become an important area of research to control the orientation, ordering, and distribution of ultrastructures in the processing of new macromolecular multifunctional structures.

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