This project involves a collaborative synthetic, polymer processing, and physico-chemical program directed at exploiting the unique properties of the high modulus/high strength polymers poly(p-phenylenebenzobisthiazole) (PBT) and poly-(p-phenylenebenzobisoxazole) (PBO) for electronic charge transport and nonlinear optical (NLO) properties. In the former area, we have continued our successful studies of directly doping these polymers by electrochemical means and of processing phthalocyanine/polymer hybrid materials. In the NLO area, we have continued exploration of the properties of NLO chromophore/PBT hybrid materials and of glassy macromolecules with such chromophores covalently bonded to the backbone. Initial studies of oriented NLO chromophores embedded in crosslinkable matrices have also been carried out. Approaches to inorganic/organic hybrid NLO materials via intercalation processes are also under investigation.

Keywords:
PBT, Conductive polymers; Phthalocyanine; Nonlinear Optical properties; Polymer doping,
PBT,PBO-Based Hybrid Polymers with Nonlinear Optical Properties or High Electrical Conductivity

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INTRODUCTION

As materials, polymers offer unexcelled diversity and tailorability in terms of light weight, strength, elasticity, plasticity, chemical and corrosion resistance, toughness, thermal stability, lubricity, and processability with regard to forming films, foils, fibers, coatings, etc. Traditionally, however, the application of polymers in optics technology has been limited largely to inexpensive lenses, prisms, fiber wave guides, anti-reflection coatings, filters, etc. In electronics technology, the attractive properties of polymers have typically been exploited only in insulator fabrication, with little attention being devoted to applications based on charge transport. It is very clear, however, that in both areas the traditional pictures are rapidly changing, and recent discoveries in the areas of polymeric/organic materials with high electronic conductivity\(^1\) or with highly nonlinear optical properties\(^2\) signal that new generations of advanced materials for optics and electronics technology await synthesis, characterization, and application.

Progress in both of the above areas requires an integrated, multidisciplinary attack involving synthesis, processing, and physical measurements. In both areas, there is a key, dominant synthetic/architectural requirement of microstructural control to afford the tailored arrays of molecular subunits necessary for facile charge transport or enhanced electronic nonlinear optical polarization response. There is also the requirement that the resulting polymers have superior processing, mechanical, and environmental stability characteristics. In terms of technology, realistic consequences of breakthroughs in polymeric materials with nonlinear optical properties include new advances in optical telecommunications, optical information processing, and integrated optics. In the area of processable conductive polymers, realistic
consequences include new types of photoconductive sensors, EMP/EMI shielding materials, RAS/RAM components, extreme service plastic conductors, electronic device components, and energy cell (battery) components.

The present research effort involves a collaborative, interdisciplinary project aimed at developing new types of macromolecular electronically conductive and nonlinear optical materials based upon a unique class of polymers developed through the Air Force Materials Laboratory Ordered Polymers Program. These polymers are poly(p-phenylenebenzobisthiazole) (PBT, I) and poly(p-phenylenebenzobisoxazole) (PBO, II). These robust, rigid-rod macro-molecules can be processed from acid solution to form very high modulus/high strength fibers and films. For example, proper processing of PBT yields fibers with a modulus over four times that of Kevlar-29 (III). Despite the many attractive properties of PBT and PBO and the great deal that has been learned about these materials, we suggest that untapped opportunities await exploitation of PBT and PBO in the areas of electrically conductive polymers and nonlinear

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{III}
\end{align*}
\]
optical materials. This research program thus capitalizes both upon the unique characteristics of PBT and PBO as well as demonstrated strength and productivity at Northwestern in collaborative synthesis, spectroscopy, polymer characterization, and charge transport measurements. We have also collaboratively drawn upon the expertise developed at the Polymer Branch of the Air Force Materials Laboratory (WPAFB) on PBT/PBO synthesis, structure, characterization, and processing. Our objectives with PBT and PBO are:

1. To determine whether strong, flexible, processable, electrically conductive macromolecular/macromolecular and molecular/macromolecular hybrids can be produced with phthalocyanine-based electrical conductors.

2. To determine whether these polymers can be rendered electrically conductive using electrochemical techniques.

3. To advance our general understanding of structure/performance relationships in both of the above areas.

4. To determine whether strong, flexible processable highly efficient nonlinear optical materials can be obtained by appropriate "doping" and orientational processing.

5. To determine whether strong, flexible, processable, highly efficient nonlinear optical materials can be obtained by modifying the polymer backbone and orientational processing.

6. To advance our general understanding of structure/performance relationships in both of the above areas.

7. To advance our understanding of how to employ electrical fields in the processing of stiff chain polymer systems.
I. PROCESSING STUDIES

A central theme in all PBT,PBO studies described herein is the ability to accurately and reproducibly fabricate macroscopic polymer structures with optimized orientational, electrical, mechanical, and optical properties. An in-house capability to process PBT in unusual forms (e.g., containing added "molecular metals," or molecular nonlinear optical chromophores), in unusual solvents, in unusual environments (e.g., in a poling field), or with a considerably modified backbone architecture, was planned as a major first objective. Extensive collaboration with the Ordered Polymers Group at Wright-Paterson has been an essential part of this effort.

Work accomplished under AFOSR funding has aimed to: 1) master the handling of PBT in polyphosphoric acid (PPA) or triflic (trifluormethanesulfonic) acid, and 2) bring to full operation a highly-automated, computer-controlled, state-of-the-art fiber wet-spinning apparatus for producing fibers of stiff-chain materials such as PBT, Kevlar, etc. In large measure, these objectives have been achieved. The consultation of Marilyn Hunsacker of Wright-Paterson has been invaluable in this connection. With regard to the handling of PBT in solutions, it was found that satisfactory fibers could be wet-spun from triflic acid but that their mechanical properties were slightly inferior to those spun from PPA. The desirability of triflic acid lies in its unique ability to dissolve many substances which, when co-processed with PBT, will usefully modify the electrical and/or optical characteristics (vide infra).

Although the mechanical properties of PBT fibers spun to date from triflic acid may be an inherent consequence of using a non-polymeric solvent (such as is the case with PPA), it may alternatively be due to the use of spinning dopes having nonoptimal PBT concentrations. Thus, one aim of our work in the past
contract period has been to carry out a thorough study of the solution physical chemistry of these solutions. We are carrying out this effort following the approach of Flory and Frost.\textsuperscript{4,5} A very significant aspect of this approach has been the ability to establish the molecular weight partitioning between the lyotropic and isotropic phases in PBT solutions. The reason for this lies in the fact that only the long chains will exhibit much self-alignment as the solution passes through the wet-spinning process.

It is expected, then, that these calculations will lead naturally to the following proposed optical microscopy work. The objective here will be to observe directly the relative amounts of isotropic and lyotropic phases that develop in PBT solutions with triflic acid. It is to be remembered that chemical degradation will limit how long we can work on these solutions (approximately 4 hours). It is hoped that we can obtain PBT's with different levels of conversion (polydispersity is not controllable; it remains near 1.98). This optical microscopy will also launch a novel line of studies with PBT, viz., the direct observation of the precipitation process. We have been modeling this aspect of our proposed work after that of Koenhen,\textsuperscript{6} who published extensively on the coagulation of polymers into reverse osmosis membranes. We expect to find out with this study which processing parameters lead to fully-dense (and therefore having maximal properties) solids as opposed to micro-porous precipitates. We point out, however, that highly novel linear and/or nonlinear optical properties may be achieved in PBT solids by proper exploitation of coagulation into microporous microstructures.

The other area of work relates to proper control of hydrodynamics of the solution in the spinnert and in the jet. Here, we focus on the geometry of the hole through which the pressurized PBT passes. Fortunately we have acquired good
connections with the Courtaulds Co. in England. They have fabricated for us dies whose shape changes in instructive ways that will allow us to spin fibers with high and low degrees of chain orientation preserved during passage out of the cylinder. Unpublished work done in another laboratory at Northwestern will serve to guide our analysis here.

II. PBT, PBO-BASED ELECTRICALLY CONDUCTIVE POLYMERS

Efforts to synthesize and characterize processable, environmentally stable conductive polymers based upon PBT and PBO have progressed along two lines: 1) electrochemical doping of pure PBT and 2) preparing molecular/macromolecular hybrid materials based upon PBT and PBO.

The chemical structure of the PBT repeat unit suggests an electron-rich π system with a low ionization potential. This property along with a highly regular, extended architecture is an almost universal prerequisite for an organic electronic conductor. Thus, initial efforts to "dope" (i.e., to bring the electronic structure into a π radical cation state) PBT fibers and films involved treating as-spun PBT fibers with Br₂ solutions for varying amounts of time. This resulted in a dark-red coloration and a slight increase in electrical conductivity. The resonance Raman spectrum exhibited a band attributable to Br₅⁻, suggesting that some oxidation of the polymer backbone had occurred. However, these materials were found to slowly lose Br₂ upon standing. Experiments with stronger oxidizing agents such as nitrosonium salts (e.g., NO⁺Br₄⁻, NO⁺PF₆⁻) and high-potential quinones (e.g., DDQ, tetrafluoro-TCNQ) have also met with only limited success.

Electrochemical techniques offer an alternative, highly efficient technique for creating polymer structures with partially filled metal-like bands. Indeed,
we find that PBT can be reductively doped either as a coating on an electrode or as a free-standing film. Cyclic voltammetry experiments in Bu₄N⁺BF₄/THF (Figure 1) demonstrate that the doping process is completely reversible and reveal capacitive currents diagnostic of appreciable electrical conductivity. We find that the black-coppery films, although somewhat air-sensitive, exhibit conductivities as high as 30 Ω⁻¹ cm⁻¹ at room temperature. Coulometric measurements indicate a fully doped stoichiometry of 0.57 electron/polymer repeat unit. Complementary electrochemical studies of the simplest PBT fragment (IV) demonstrate considerable stabilization of the negative charge by the polymer.

Figure 1. Cyclic voltammogram of a PBT film on a Pt electrode. The pattern is typical of a conductive polymer which undergoes reversible redox processes.
Another approach to preparing processable, environmentally stable conductive polymeric materials has been to "alloy molecular conductors (e.g., doped metallophthalocyanines, M(Pc)) or macromolecular conductors (e.g., doped poly(metallophthalocyanines)) with high-modulus aramids such as Kevlar and Nomex. We find that strong, flexible, environmentally stable, electrically conductive fibers can be spun from solutions of PBT and Ni(Pc) in triflic acid, followed by doping of the fibers in iodine solution. During the past contract period, we have carried out detailed studies of mechanical and electrical properties as a function of Ni(Pc)I content. Some of these results are shown in Figure 2. We have also obtained preliminary evidence from X-ray diffraction

![Figure 2. Comparison of tensile and electrical properties as a function of Ni(Pc)I content for a series of PBT/Ni(Pc)I fibers.](image)
of some phase separation into discrete PBT and Ni(Pc)I phases, with the latter composed of very small or highly disordered crystallites. The dependence of the conductivity on Ni(Pc)I content is suggestive of percolation behavior, and the temperature dependence of the conductivity can be best fit to a fluctuation-induced tunneling mechanism which is typical of a composite. The variable-temperature thermoelectric power of the most conductive PBT/Ni(Pc)I fibers is characteristic of a p-type molecular metal.

Iodine doping is by no means the optimum approach to bringing about conductivity, and detailed studies of the electrochemical properties of the PBT/M(Pc) hybrids will be carried out. Preliminary cyclic voltammetry investigations have already found that PBT/Ni(Pc) films can be reversibly doped (either p- or n-). Crucial questions concern the kinetics of doping and the doping levels which can ultimately be achieved, as well as the suitability of free-standing films and fibers for this approach. The thermal properties and stability of all PBT/Ni(Pc) hybrid materials are being scrutinized by TGA and DSC techniques.

III. RATIONAL DESIGN AND CONSTRUCTION OF HIGH-PERFORMANCE NONLINEAR OPTICAL MATERIALS.

A. Background

The fundamental relationship describing the change in molecular dipole moment (polarization, $\mathbf{P}$) due to interaction with an external electric field (as in the oscillating electric vector of electromagnetic radiation) $\mathbf{E}$ can be expressed in a power series (eq.1). Here $\alpha$ is the linear polarizability, $\beta$

$$P = \Delta \mu - \alpha \mathbf{E} + \beta \mathbf{E}^2 + \gamma \mathbf{E}^3 + \cdots$$  (1)
the quadratic hyperpolarizability, and \( \gamma \) the cubic hyperpolarizability; these coefficients are tensor quantities. The even order coefficient \( \beta \), which is responsible for second harmonic generation (SHG), vanishes in centrosymmetric systems. There are no symmetry restrictions on the odd order tensors. The analogous macroscopic polarization arising from an array of molecules is given in eq. (2). An important consequence of these relationships is that light

\[
\psi = \chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{EE} + \chi^{(3)} \mathbf{EEE}
\]  

waves of frequency \( \omega \) passing through an array of molecules can interact with them in such a way to produce new light waves at double (2\( \omega \), SHG), triple (3\( \omega \), THG), etc. the original frequency (a nonlinearity in the polarization).

Significantly, it has been found that up-conversion efficiencies can be very high for certain classes of extensively conjugated organic molecules—far higher than for traditional inorganic solids (e.g., LiNbO\(_3\), KDP, GaAs).\(^2\) Moreover, the \( \pi \) electron character of the phenomena in the organic materials implies response times (ca. 10\(^{-14}\) sec) which are far shorter than in conventional inorganic materials.

In regard to developing materials with maximum \( \chi^{(2)} \), the crucial problems are designing the optimum chromophore and enforcing stable noncentrosymmetry in a processable material having a large chromophore density. Success in the area of chromophore design would greatly benefit from chemically-oriented theoretical models which would allow testing of ideas prior to laborious synthetic efforts.

In collaboration with Professor M. Ratner, we have developed a computationally efficient perturbation theoretical approach using the Pariser, Parr, Pople (PPP) model Hamiltonian.\(^{15}\) This methodology allows detailed examination of how molecular \( \beta \) tensors depend on chromophore architecture and substituents. It also provides valuable information on chromophore optical absorption (crucial for
chromophore/laser matching) and dipole moment (crucial for electric field poling experiments—vide infra). The excellent agreement between theory and experiment in known systems is illustrated in Figure 3.15c. We are now using this theoretical approach routinely in materials design.

From the standpoint of enforcing molecular organization in a controlled fashion as well as offering a ready means for producing mechanically stable films, fibers, and other desirable geometries for device applications, combining nonlinear optical chromophores with the properties of selected polymeric materials would appear to be highly desirable. Two broad classes of motifs are doped guest-host assemblies (V) and chromophore-functionalized polymers (VI,VII). The success of any approach depends critically on: i) maximizing chromophore/polymer compatibility so that phase separation does not occur, ii) achieving and maintaining maximum chromophore orientation so that maximum noncentrosymmetry and optical nonlinearity are attained and preserved.

Figure 3. Frequency dependence of $\beta_{\text{vec}}$ for para-nitroaniline: experimental $\beta_{\text{vec}}$ (solid line), and theoretical $\beta_{\text{vec}}$ (dashed line).
Variants of approaches V and VII are presently under investigation in our laboratories and are discussed in the following sections. The principal means of chromophore orientation have been by poling in a strong electric field. To this end, a versatile poling apparatus has been constructed which allows precise monitoring of temperature, poling under vacuum or inert atmosphere, and accurate monitoring of any current passing through the sample during poling. In addition, we have acquired a great deal of practical experience in regard to film fabrication and electrode attachment. NLO measurement techniques have been developed and are being carried out in collaboration with Professor G. Wong.

B. PBT-PBO-Based and Other Guest-Host Approaches

Approach V offers advantages in terms of synthetic simplicity and stoichiometry control. However, an unanswered question in all such guest-host systems is whether the simple Langevin isolated molecule description of the preferential orientation achievable by poling (eq. (3)) will limit SHG orientation.

\[
\text{orientation} = \frac{\mu \cdot E}{kT}
\]  
(3)
efficiency. Here $\mu$ is the molecular dipole moment and $E$ is the electric field strength. One approach to maximize preferential orientation would be to imbed rod-like guest chromophores in the aligned lattice of rigid-rod polymers such as PBT and PBO. One-dimensional "head-to-tail" alignment of chromophores should promote very high preferential orientation (cf. eq.(3), in effect, a single molecule with a very large $\mu$) for modest electric fields. Initial studies have involved PBT and a guest NLO chromophore (VIII) designed to maximize guest-host compatibility (Figure 4). We find that PBT can be doped with VIII to yield films which give substantial SHG signals after poling in an electric field. Interestingly, unpoled films and neat powders of VIII also give SHG signals! At present, microstructural characterization of the doped films by X-ray diffraction (are small crystallites of VIII present?), uv-visible, infrared, Raman, and high resolution CP Mas NMR spectroscopy are in progress. Poling studies will focus on developing electrode geometries (e.g., annular) which maximize the SHG signal.

Figure 4. Synthesis of a PBT guest chromophore.

The simple doping of NLO chromophores into glassy polymers (e.g., poly(methylmethacrylate) was the first successful guest-host synthetic approach.
to frequency-doubling polymer films. We find that this approach is severely limited by the solubility of the guest in the host, diffusion of the guest out of the host, and most significant of all, long-term instability of the chromophore preferential orientation that was induced in the poling process (relaxation of the guest-host structure). This structural relaxation might be minimized in structures where the polymer guest matrix could be crosslinked during or immediately after poling. We are at present investigating the straightforward and technically attractive approach of blending NLO polymers with a newly available optical grade epoxy cement and then poling during the epoxy curing process. It has been of interest to determine to what degree the chromophore orientation can be "locked in" by the curing process (eq.(4)).

First experiments have been carried out with nonfunctionalized chromophores such as p-(dimethylamino)nitrobenzene and 4-dimethylamino-4'-nitrostilbene. We find that such hybrid materials give efficient long-lived SHG if the epoxy matrix is sufficiently cured. At a later stage, hydroxyl- or amino-functionalized chromophores, which would be chemically incorporated into the crosslinked host matrix, will also be examined.

C. Chromophore-Functionalized Polymers

To circumvent the aforementioned disadvantages of simple chromophore-doped guest-host materials, we have investigated the approach of covalently linking NLO chromophores to glassy, film-forming macromolecules. Polystyrene
(PS) was chosen as the initial backbone because of its excellent transparency, low dielectric constant, relatively high $T_g$ (to stabilize chromophore alignment), and amenability to many kinds of functionalization and processing. Details of the synthesis (chloromethylation, etherification) and electric field processing are shown in Figure 5. It was anticipated that the salt-like character of the pyridinium-functionalized polymer (PS)CH$_2$-X would offer several unique possibilities. First, the ionic structure should raise $T_g$. Second, electrophoretic ion migration under the influence of the poling field could conceivably produce very large chromophore preferential orientations.

Research on the functionalized polystyrene NLO materials is still in the early stages, however it is already apparent that large SHG coefficients can be readily attained. Thus, films of (PS)CH$_2$-IX with 12.5% styrene functionalization give $d_{33} = 2.7(3) \times 10^{-9}$ esu, which is more than twice the corresponding parameter for KDP. Representative data are shown in Figure 6. Films of (PS)CH$_2$-X with rather low (4.5%) functionalization levels also exhibit high SHG coefficients as well as interestingly nonlinear $d_{33}$/poling field behavior. Present efforts are directed at achieving higher chromophore functionalization levels, increasing poling fields by improving film and electrode contact quality, and at characterizing the time-dependence of the frequency doubling capacity (what factors stabilize chromophore orientation?). These issues will be thoroughly addressed in the coming contract period.

Glassy backbone polymers with high glass transition temperatures and the possibility of even higher levels of chromophore functionalization would be of great interest ($I^{2\omega}$-(chromophore number density)$^2$). Presently under investigation is poly(p-hydroxystyrene), (PS)-OH, which has $T_g = 180^\circ$, a very high density of reactive functional groups, as well as good solubility, processing,
SYNTHESIS AND POLING OF COVALENTLY-FUNCTIONALIZED POLYMERS FOR FREQUENCY DOUBLING

I. FUNCTIONALIZATION

A. Alcohol Chromophores

\[
\text{ROH} + \text{TIOEt} \xrightarrow{\text{benzene}} \text{TIDR} \rightarrow \text{EtOH}
\]

\[
(\text{PSICH}_2) + \text{TIDR} \rightarrow (\text{PSICH}_2 \text{OR} + \text{TIL}_2)
\]

B. Pyridinium Chromophores

\[
\text{ROH} + \text{HNO}_2 - \text{H} \rightarrow \text{H}_2\text{N} - \text{O} \rightarrow \text{H}_2\text{N} - \text{NO}_2
\]

\[
(\text{PSICH}_2) + \text{Ov} \xrightarrow{\text{MeOH}} (\text{PSICH}_2\text{OV}^+)^-
\]

\[
\text{Ov} \rightarrow \text{H} - \text{N} - \text{CH} - \text{CH}_2 - \text{NMe}_2
\]

II. ALIGNMENT

(Random) \rightarrow \text{E} \rightarrow \text{Preferential}

Figure 5. Methodology for the synthesis and electric field processing of polystyrene covalently functionalized with NLO chromophores.
Figure 6. Second harmonic intensity of typical film of (PS)CH$_2$-IX versus that from a quartz reference crystal for 1.064 μm incident laser light. The linear relationship demonstrates that $I^{2\omega}$ depends quadratically upon $I^{\omega}$.

and adhesive characteristics. We find that (PS)-OH can be readily functionalized as shown in eqs. (5) and (6). Chromophore functionalization

\[
\text{(PS)}-\text{OH} + \text{OH}^+ \rightarrow \text{(PS)}-\text{O}^- \quad (5)
\]

\[
\text{(PS)}-\text{O}^- + \text{ROTs} \rightarrow \text{(PS)}\cdot\text{OR} + \text{OTs}^- \quad (6)
\]

ROH = chromophore IX, Figure 5

\[
\begin{array}{c}
\text{HO} \\
\text{NO}_2
\end{array}
\quad (XI)
\]

OTs$^-$ = p-toluenesulfonate
levels in the 50-60% range can be readily achieved, and excellent films can be cast from ethereal solvents. SHG coefficients \( (d_{33}) \) as high as \( 18 \times 10^{-9} \) esu have been measured. In regard to chromophore orientational stability, it appears that the hydrogen bonding network provided by (PS)-OH and chromophore functional groups help to "lock" poled orientations in place. SHG decay time constants as long as 360 days have been recorded. An informative contrast to the above results and an illustration of the advantage of functionalized polymers is provided by studies of guest-host doped materials prepared from (PS)-OH and chromophores IX or XI. In this case, polymer-chromophore phase separation occurs at all but the lowest doping levels.

Another attractive approach to the construction of polymeric NLO materials is the functionalization of macromolecule backbones with rod-like chromophores which would give rise to sidechain liquid crystal polymers (XII). The lyotropic nature of the sidechains ensures efficient orientation by an electric field. Historically, however, the low \( T_g \) values achievable in such materials and the accompanying instability of the optical characteristics has made them impractical as NLO materials. This picture has now changed, and Professor A. Griffin (U. of Southern Mississippi) has recently prepared a class of sidechain liquid crystal polymers with \( T_g = 90^\circ \text{C} \). We are collaborating with him in the
NLO characterization of these polymers. Samples are now in hand and film fabrication experiments are under way.

D. Intercalative Routes to Nonlinear Optical Materials

Numerous classes of chemical transformations are now known in which organic molecules can be inserted ("intercalated") into the van der Waals gaps of layered inorganic solids (eq.(7)). In most cases, the geometry of the host layer structure largely dictates the resulting orientation of the guest molecules. In regard to the construction of NLO materials, the intercalation of high-β NLO chromophores into the crystal structures of acentric layered materials suggests a new route to crystalline inorganic/organic hybrid structures with highly oriented chromophore assemblies. Our initial studies are focusing on optically transparent mica-like kaolinite and dickite materials in which aluminosilicate layers form acentric ABCABCABC patterns. Such materials undergo intercalation reactions, and guest molecules can be oriented by networks of hydrogen bonds (e.g., the single crystal diffraction results in Figure 7).
Figure 7. Projection of the structure of the dickite-formamide intercalate perpendicular to the layer planes. Single crystal diffraction results from ref. 24.

We find by X-ray diffraction and elemental analysis that kaolinite undergoes intercalation by pyridine-N-oxide chromophores (XIII) to yield yellow or orange powders. The structure of the intercalate is shown in the figure. Preliminary powder SHG experiments reveal significant frequency doubling which is not discharged by extensive sample washing (i.e., which is not likely due to the chromophore being simply adsorbed on the surface). Presently in progress are infrared and ultraviolet-visible studies of the intercalate to obtain information on layer-chromophore interactions and synthetic work with other chromophores. More quantitative SHG experiments using
the Kurtz powder technique will begin shortly. At a later stage, single crystal synthetic efforts will begin.
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3. For leading references, see:


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(d) Li, D.; Ratner, M. A.; Marks, T. J., submitted for publication.

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(b) Li, D.; Yang, J.; Wong, G. K.; Marks, T. J., unpublished results.


19. Hubbard, M. A.; Marks, T. J., research in progress.


21. (a) Ye, C.; Marks, T. J., unpublished results.


23. Hubbard, M. A.; Marks, T. J., research in progress.


25. Hubbard, M. A.; Yang, J.; Marks, T. J.; Wong, G. K., research in progress.
COMPLETED PROJECT SUMMARY

1. **PBT,PBO-Based Hybrid Polymers with Nonlinear Optical Properties or High Electrical Conductivity**

2. **PRINCIPAL INVESTIGATORS:**
   - Tobin J. Marks
   - Stephen H. Carr
   - Department of Chemistry
   - Department of Materials Science and Electrical Engineering
   - Northwestern University, Evanston, IL 60208

3. **INCLUSIVE DATES:** March 15, 1986-August 15, 1988

4. **CONTRACT/GRANT NUMBER:** AFOSR-86-0105

5. **COSTS AND FY SOURCE:** $300,000

6. **SENIOR RESEARCH PERSONNEL:** C. Ye
   - N. Minami

7. **JUNIOR RESEARCH PERSONNEL:** P. DePra
   - J. Giesler
   - Y. Jin

8. **PUBLICATIONS:**


9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project involves collaborative synthetic, polymer processing, and physicochemical work aimed at exploiting the unique properties of the high modulus/high strength polymers, poly(p-phenylenebenzobisthiazole) (PBT) and poly(p-phenylenebenzobisoxazole) (PBO), for electronic charge transport and nonlinear optical NLO applications. In the former area, we are exploring the properties of macromolecular/macromolecular and molecular/macromolecular hybrid materials constructed from PBT, PBO, and phthalocyanine metallomacrocycles. In the second thrust we are exploring the combination of judiciously selected processing strategies with NLO chromophore doping or direct incorporation in the polymer backbone.

10. INTERACTIONS

Invited Lectures on the Subject of This Grant (T. J. Marks)

7/86 Gordon Research Conference on Solid State Chemistry
9/86 American Chemical Society National Meeting (Anaheim)
1986-1987 Phi Lambda Upsilon Lecturer, University of Nebraska
1986-1987 Mack Awardee and Lecturer, Ohio State University
1/87 University of Chicago
1/87 University of Wisconsin
2/87 Tulane University
3/87 University of Idaho
4/87 American Chemical Society National Meeting
10/87 Boomer Lectures, University of Alberta
10/87 Merck-Frosst Lectures, University of British Columbia
11/87 University of Chicago Polymer Symposium
1/88 Gordon Research Conference on Electrochemistry
3/88 Louisiana State University
4/88 Georgetown University
4/88 Iowa State University
5/88 University of Utah
5/88 Syracuse University
5/88 Learmakers Symposium
8/88 SPIE NLO Symposium

**Awards (T. J. Marks)**

Editorial Advisory Board, *Chemistry of Materials*
Advisory Board, *Progress in Inorganic Chemistry*
1989 American Chemical Society Award in Organometallic Chemistry

**Patents**

C. Ye and T. J. Marks, "Functionalized Polymers for Nonlinear Optical Applications" (pending).