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13. ABSTRACT (Maximum 200 words) Although materials with high third order susceptibilities demonstrate optical switching or limitation in response to critical input intensity, application in devices for sensor protection (to include that of the human eye) has not yet been brought to practicable fruition. Devices such as goggles require an optically clear carrier of high transparency and good mechanical properties for the NLO material. Our goals are directed toward development of such a material by incorporation of $\chi^3$ -active materials into a polymeric carrier which is strong and transparent. Although $\chi^3$ properties do not require noncentrosymmetry, the NLO behavior frequently is enhanced by alignment which removes the symmetry element. In addition, the structural integrity of polymers is frequently improved by alignment. Thus, a central theme of our Phase I study is the alignment of the guest/host systems as a route to development of protective materials. Promising $\chi^3$ -active materials will be processed into films using polycarbonate (PC) relying on its requisite optical and mechanical properties as the host polymer. Three NLO-active components will be evaluated: (1) a tetrabenzoporphyrin (TBP), (2) a polyaniline (PANI), and (3) a sol complex. Thus, a full range of both molecular and polymeric NLO-active substances will be surveyed in Phase I. (This report has been developed under an STTR contract.)				
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# **SENSOR PROTECTION FROM LASERS**

## **Final Phase I STTR Technical Report (August 12, 1996 - February 11, 1997)**

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# Sensor Protection from Lasers

## 1. PROJECT SUMMARY

The overall objective of this SBIR project is the development of high  $\chi^3$  materials with optical clarity and mechanical strength for sensor and eye protection. One specific end-product of the proposed investigations is a material suitable for protection of the human eye against laser irradiation. Such a material must not only have a reasonable optical limiting response, but also have optical clarity, thermal stability, and high impact strength. To develop this material, promising  $\chi^3$ -active materials were processed into films using polycarbonate (PC) relying on its requisite optical and mechanical properties as the host polymer. Three NLO-active components were evaluated: (1) a tetrabenzoporphyrin (TBP), (2) a polyaniline (PANI), and (3) a sol complex. Thus, a full range of both molecular and polymeric NLO-active substances were initially targeted for the Phase I survey.

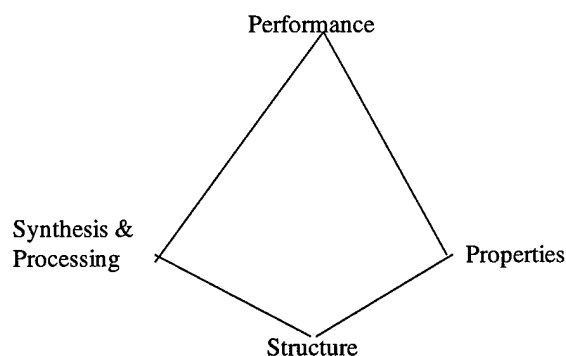
Although materials with high third order susceptibilities demonstrate optical switching or limitation in response to critical input intensity, application in devices for sensor protection (to include that of the human eye) has not yet been brought to practicable fruition. In addition to the physics requirements for translation of input laser energy, devices such as goggles require an optically clear carrier of high transparency and good mechanical properties. Thus, our Phase I determination of feasibility was directed toward development of such a material by incorporation of  $\chi^3$ -active materials into a polymeric carrier which is strong and transparent focusing almost exclusively on the materials processing constraints of a valid protection system. In addition to the first order translation of solution chemistries to solid phase materials, a supporting theme of our Phase I study was the investigation of the alignment of the guest/host systems as a route to development of protective materials exploiting our patented system for in-plane poling to determine the feasibility of the proposed approach. Although  $\chi^3$  properties do not require noncentrosymmetry, the NLO behavior frequently is enhanced by alignment which removes the symmetry element. In addition, the structural integrity of polymers is frequently improved by alignment.

We report herein on the preparation and characterization of guest/host polymer thin films. Results of our Phase I work suggest that solid phase NLO materials can be prepared, thus demonstrating their potential for sensor protection from lasers. The results are very encouraging. We have obtained excellent optical power limiting results for the films that we manufactured. In summary, (1) we have developed techniques to fabricate RSA films; (2) various NLO materials can be processed using these techniques; (3) the techniques are suitable for the development of multilayer limiters; and (4) we have developed a sound agenda for the development and improvement of solid multilayer optical power limiters.

## 2. PROJECT RATIONALE

The thrust of the Phase I work was to demonstrate high  $\chi^3$  values in composite films of a host polymer into which  $\chi^3$ -active materials have been incorporated. It was reasoned that, while a single material might eventually meet optical, mechanical and processing criteria, a viable approach would be to explore hybrid, multicomponent and multifunctional materials with each component serving one or more specific needs. Specifically, doped polymer systems were investigated where the host or matrix offered the desired optical transparency and mechanical toughness, with molecularly dispersed dopants providing the requisite optical limiting behavior. It was anticipated that the host polymer would serve to "matrix-isolate"  $\chi^3$  chromophores, thus reducing the potential for both phase segregation of the guest molecules and photophysical processes among them which might be undesirable.

Our efforts have been guided by the "materials tetrahedron" shown below, which emphasizes that the ultimate goal of performance is realized through the linkage to structure and properties which are in turn dictated by synthesis and processing.



### • THE HOST POLYMER

The host polymer may be  $\chi^3$  inactive but must have excellent mechanical and optical properties. Polycarbonate (PC) is the host of choice, having high impact strength, optical clarity, and processability. PC (Lexan<sup>®</sup>, GE Plastics) is optically clear due to the absence of crystallinity, and is rather easily processed from solution (methylene chloride is a commonly used solvent) or the molten state ( $T_g$  ca. 150<sup>o</sup>C). Also, the polymer is tough as a result of short-range segmental motions which act as energy absorbers. Lucite<sup>®</sup> or poly(methylmethacrylate), PMMA, was also investigated as a host. PMMA is amorphous and has good optical transparency and easy processability into films but lacks the toughness of polycarbonate.

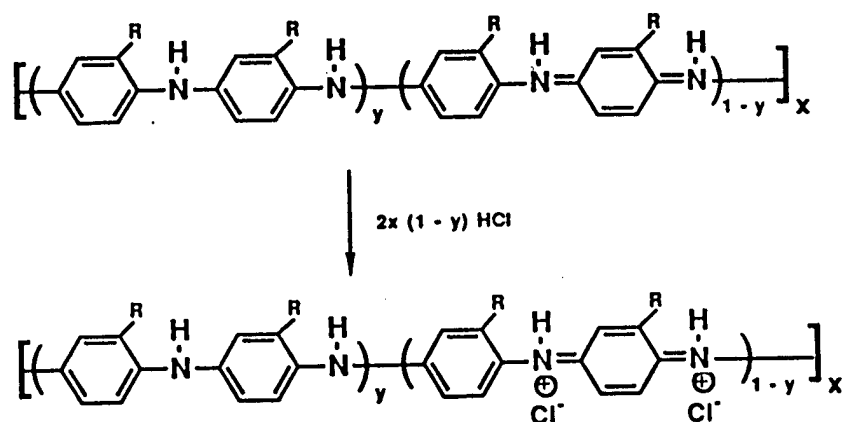
It would be ideal to identify a host which was also  $\chi^3$ -active. An enzymatically synthesized polyaniline (PANI) was examined in this context both as a free standing film and as a composite with PC. The initial plan considered that if PANI was film-forming,

the  $\chi^3$  guests (TBP and a tricyanovinyl aniline (TCVA) coated silver sol (TCVA/Ag)) would be incorporated directly into the PANI; should film formation not be practicable, PANI was to be incorporated into PC prior to introducing the TBP and sol guests.

- *GUEST NLO-ACTIVE MATERIALS*

Three classes of the guest  $\chi^3$  materials were chosen in order to afford flexibility in the design of the guest-host systems. The three materials were (i) polyaniline, (ii) a zinc tetrabenzporphyrin derivative, and (iii) a silver sol-organic chromophore complex.

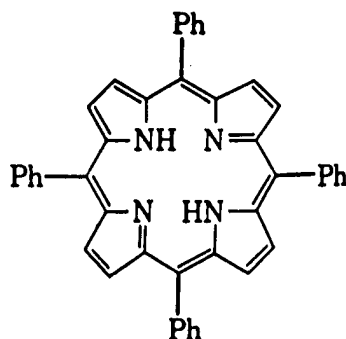
1. Polyanilines



Conducting polymers are typically characterized by at least modest  $\pi$ -electron delocalization, and this coupled with the high polarizability of these electrons makes conjugated polymers interesting candidates for applications relying on third-order nonlinearities. Moreover, the optical and electrical properties of these polymers are readily modulated by redox reactions of the backbones. Polyaniline ( $R = \text{H}$ , above) is one of the most widely studied conducting polymers due to the easy conversion of neutral to cationic and conducting forms by protonation (with a concomitant change in optical absorption), the excellent environmental stability of both forms, the opportunity to control the processability via the choice of conjugate base of the acid, and the ability to control the processability and optical and electronic properties by the choice of the  $R$  group. For example, when  $R = \text{methyl}$ , the polymer (poly-*o*-toluidine) is more soluble in common solvents (Focke et al., 1989), and it was reasoned that such substituents would also afford enhanced solubility in polymeric host such as Lexan<sup>®</sup> polycarbonate.

Polyaniline and derivatives are typically prepared by oxidation of aniline with, for example, persulfate in the presence of HCl. However, it is also possible to polymerize aniline via enzymatic catalysis, and this may be advantageous if the polymer chain structure is more polarizable than that obtained by typical wet chemical conditions.

## 2. Tetrabenzoporphyrin Derivatives



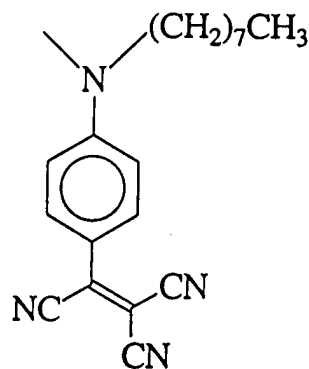
Metal-containing tetrabenzoporphyrins were selected as active materials for sensor protection for several reasons. First, they, like related phthalocyanines (Miles, 1994), have strong optical absorptions and, complexed with selected metals, can show efficient intersystem crossing and hence large triplet-triplet absorptions which afford optical limiting. Second, both the metal and the substituent group on the porphyrin ring can be changed, offering tunability of optical properties and enhanced solubility in host polymers. Third, porphyrins are redox-active and it should be possible to tune the optical absorption of metal-containing porphyrins by altering the redox state of the metal.

It is of course important to achieve a high chromophore density to maximize the optical response but, as shown in our Phase I results, chromophore aggregation has an undesirable effect on the optical limiting capability of zinc tetrabenzoporphyrin. However, we believe that we have the ability to control host-guest interactions, and thus it should be possible to achieve a good balance of chromophore loading without significant interchromophore interactions.

## 3. Silver Sol/Chromophore Complexes

Earlier work by Korenowski and Wnek (LaPeruta et al., 1991; Kitipichai et al., 1992) demonstrated that silver sols dispersed in a polymer containing p-tricyanovinylaniline units exhibited large third order NLO responses from four wave degenerate mixing experiments. Noble metal nanoparticle systems are of interest because of their intrinsically large third order nonlinear susceptibilities (LaPeruta et al., 1991; Kitipichai et al., 1992). When combined in a composite, interactions between the polymer host bearing NLO chromophores and metal colloids were shown to yield enhanced third order nonlinear susceptibilities. A proposed model for the enhancement is shown in Figure 1.

Further work in Wnek's laboratory demonstrated that Ag sols to which p-tricyanovinylanilines having a long alkyl tail at the aniline nitrogen are dispersable in DMF. For example, a grey-black powder of Ag in alcohol, prepared from reduction of silver salts with  $\text{NaBH}_4$ , immediately disperses to form an optically clear, magenta solution upon addition of a small amount of compound 1.



1

Replacement of ethanol as it evaporates with DMF preserves the Ag colloid. This suggests that the NLO chromophores need not be present as part of a polymer into which the sols might be dispersed. Rather, we believed that it would be possible to disperse homogeneously Ag sols modified with 1 into a variety of polymer hosts. These hosts may confer mechanical stability with the Ag colloid, absorbed 1 being the NLO-active entity. As will be discussed in the following, only a limited amount of work was done on the Ag sol system, principally because of the promising results obtained from the Zn tetrabenzoporphyrin/Lexan<sup>®</sup>.

### 3. PHASE I EXPERIMENTAL METHODS AND RESULTS

#### 3.1 Introduction

The thrust of the Phase I was to demonstrate high  $\chi^3$  values in composite films of a host polymer into which  $\chi^3$  active materials have been incorporated. The host polymer may be  $\chi^3$  inactive but must have excellent mechanical and optical properties. Polycarbonate (PC) was the host of choice, having high impact strength, optical clarity, and processability. It was a supporting goal to identify a host which was also  $\chi^3$  active. Polyaniline (PANI) was examined in this context both as a free standing film and as a composite with PC. If PANI was processable into a film, other  $\chi^3$  active materials would be incorporated into it.

The experimental program included preparation of  $\chi^3$  active PANI, and incorporation of PANI into a PC. This program utilized the most common commercial PC synthesized from bisphenol A, 2,2'-bis(4-hydroxyphenol) propane, known as Lexan<sup>®</sup>. PC composites were also prepared using two other  $\chi^3$  materials, a TBP and an Ag sol, thus surveying a range of molecular offerings to address requirements for both optical efficiency and materials processing.

The tasks of the Phase I work program are summarized as follows:

- Task 1.* Preparation and Characterization of Polyaniline
- Task 2.* Acquisition of TBP and Preparation of Silver Sols
- Task 3.* Preparation of PANI Films and PANI/PC Films
- Task 4.* Alignment of PANI and PANI/PC Films
- Task 5.* Spectral Characterization: UV/Vis and IR Absorption
- Task 6.* Polymer Characterization: DSC and TGA
- Task 7.* Mechanical Characterization: Tensile Strength and Modulus
- Task 8.* NLO Characterization: Degenerate Four Wave Mixing
- Task 9.* Reporting

### **3.2 Materials**

- Aniline (Sigma Chemical Co.)
- 4-n-Butylaniline (TCI, Tokyo, Japan)
- 4-sec-Butylaniline (TCI, Tokyo, Japan)
- 1,4-Dioxane (Fisher Scientific)
- Dimethylformamide, HPLC grade, used as received (Aldrich Chemical Co.)
- Formaldehyde solution, 37.1% (Fisher Scientific)
- Gelatin (from porcine skin, approx. 300 bloom) (Sigma Chem. Co.)
- HEPES, N-(2-hydroxyethyl)piperazine-N'-ethane sulfonic acid (Sigma Chemical Co.)
- Horseradish peroxidase, Type II, 150-200 units/mg solid (Sigma Chemical Co.)
- Hydrogen peroxide, 30% (w/w) (Sigma Chemical Co.)
- Methylene Chloride, HPLC Grade (Sigma Chemical Co.)
- Polycarbonate, PC, Lexan 9034 Sheets (General Electric)
- Silver nitrate, ACS (Bradford Scientific)
- Zinc meso-tetra-p-methoxyphenyl-tetrabenzoporphyrin (ZnOCH<sub>3</sub>TBP) and zinc meso-p-hydroxyphenyl-tetrabenzoporphyrin (ZnOHTBP) were kindly supplied by Dr. Masato Nakashima of the US Army Natick Labs.



- N-methyl-N-dodecyl-4-tricyanovinyl aniline, TCVA, was kindly supplied by Professor Gary E. Wnek of Virginia Commonwealth University

### 3.3 Synthesis of Polyanilines (PANI)

(The PANI syntheses were done in collaboration with Dr. Joseph A Akkara of the US Army Natick Labs.)

#### *POLYANILINE HOMOPOLYMERS (n-PANI)*

The HEPES buffer (20% aq HEPES (250 mM)/80% dioxane, v/v) was prepared by dissolving 5.9575 g HEPES in distilled H<sub>2</sub>O and bringing the volume to 100ml. The concentration of this solution is 250 mM. Twenty ml of this solution was then dissolved in 80ml of 1, 4-dioxane. The pH was adjusted to 7.5.

The 30% H<sub>2</sub>O<sub>2</sub> (1.1 g) was dissolved in a small portion of the buffer; fifty mgs of HRP was dissolved in a small portion of the buffer; and the aniline (0.91g) was dissolved in the remaining buffer.

The HRP solution was added to the aniline solution followed by the addition of the H<sub>2</sub>O<sub>2</sub> solution. This mixture was allowed to react at room temperature for up to 24 hrs with gentle stirring. PANI forms and can be separated by centrifugation at 5000g for ~ 10 min.

#### *PANI COPOLYMERS (PsBAA and PnBAA)*

(Our Natick collaborators suggested a PANI copolymer based on their observations relating to ease of synthesis and characterization. Two derivatized anilines were used in the syntheses, sec-butyl and an n-butyl aniline, each being copolymerized with an equimolar ratio of aniline. These syntheses are thus reported below.)

The reaction was carried out at room temperature in a solution of dimethylformamide (DMF) and succinate buffer (0.1M at pH 5.5) in the ration of 1:1 (v/v). The monomers, aniline (5.0g) and 4-n-butylaniline (8.0g) were dissolved in 200 ml of DMF. Horseradish peroxidase (120mg) was dissolved in 200 ml succinate buffer (pH 5.5, 0.1M), and added slowly to the aniline DMF solution with constant stirring via stirring bar. With continued stirring, the polymerization reaction was initiated by the dropwise addition of hydrogen peroxide (30%) to the above reaction solution; 16 ml of hydrogen peroxide was added over an eight-hour period. The reaction was allowed to proceed with stirring to a total reaction time of 20 hours. Formation of a PANI is evidenced by the formation of a precipitate. The precipitate was isolated via centrifugation (30 minutes at 5000g), washed with water and air-dried. To increase the yield, the reaction supernatant was reduced in volume via rotary evaporation. This viscous residue and the primary precipitate were dried under vacuum at 50<sup>0</sup> C. (Reaction yields were generally ~ 60%.)

"PsBAA" is the copolymer of a 1:1 mole ratio of 4-sec-butylaniline and aniline (Sample # JA-31). PnBAA is the copolymer of n-butylaniline and aniline. The initial PANI experiments were done using the PsBAA. Although this sample was not highly purified, it enabled us to explore its film forming capacity and to develop techniques for incorporating the polymer into a polycarbonate (PC) support.

### 3.4 Preparation of Silver Sols

Previously, we had prepared silver sols by reduction of silver nitrate with sodium borohydride (Trantolo et al, 1996). The silver colloid was prepared via a chemical method (rather than a laser ablation method). Silver nitrate can be reduced to silver metal with an alkali aluminum hydride. Several aspects of the complete system, including the solubility of the reactants used (here, N-methyl-N-dodecyl-4-tricyanovinyl aniline, TCVA) as well as the reactivities of the two organic compounds towards the reducing agent, had to be understood before choosing the solvent system. A main issue in the preparation of the colloid, its isolation, and subsequent use in the film preparations requires a cognizance of both the colloidal dispersion and solubility. Ultimately, the colloid should be isolable and then suspendable in a solvent which dissolves the polycarbonate (PC) host. The inorganic reagents are soluble in water, methanol, and 95% ethanol but insoluble in most organic solvents (ether, chloroform, etc.). On the other hand, PC is insoluble in those same solvents while TCVA is only partially soluble in ethanol.

In our earlier work, it appeared that a silver colloid was obtained when 96% ethanol was used as a solvent and the excess borohydride was decomposed with acetic acid before adding TCVA to the colloid. A solution of silver nitrate (9 mg in 100 ml ethanol) was added dropwise to a solution of sodium borohydride (14 mg in 100 ml ethanol). The borohydride solution immediately becomes yellow and as more silver nitrate was added the color progresses to red, then dark gray. At the end of the addition (~ 15 minutes), one drop of glacial acetic acid was added followed by 14 mg TCVA. (If TCVA is added to the colloid without decomposing the excess  $\text{NaBH}_4$ , its color changes from red to yellow, indicating that TCVA gets reduced by hydrides.) However, within a short time, a dark-gray suspension precipitates with the formation of a shiny silver layer on the glassware.

At this point, the TCVA/silver mixture is in ethanol solution. In our initial preparations, this mixture was then transferred to a DMF-based medium. DMF is one solvent for film formation. In order to transfer from the ethanolic colloid, ten grams of DMF were added to the suspension and slowly evaporated with a stream of air until no more than 3 grams of the total suspension remained. Here, the solvent composition is predominantly DMF.

In another embodiment of the colloid preparation, it appeared that the mixture could be isolated directly from the ethanol solution. The ethanol solution was evaporated to dryness yielding a dark magenta particulate. Preliminary investigations suggested that this TCVA/silver "colloid" could be resuspended in methylene chloride. This is an attractive solvent for film preparation because it is a good solvent for PC and has a reasonable vapor pressure.

We attempted to determine the 'stoichiometry' of this silver/TCVA complexation. The colloid preparation was followed spectrophotometrically anticipating that the TCVA absorbance would be different than that of the TCVA/silver complex. This had the potential to offer additional direction to the colloid preparation. However, attempts to follow the color progression during colloid preparation (i.e., the progression from yellow to red) were not successful. Even without further addition, the yellow color develops at a rate too fast to allow sampling for spectral analysis.

With minor modification, this is the technique used by Creighton et al. (1979). We repeatedly observed a progression of color from yellow through red to blue gray with final precipitation of particulate silver. Although addition of stabilizing agent such as TCVA produces a relatively stable sol in that the particle growth as judged by the color progression was slower, the stability was still judged insufficient for further processing into PC-based films.

We have therefore explored an alternative method which appears to merit continued use. If the reduction is carried out with formaldehyde rather than with the borohydride the reaction is slower as is the progression of color changes. Silver nitrate was dissolved in an aqueous gelatin solution. To this was added the formaldehyde. A deep red color developed which, at this writing, is stable for at least 21 days. The solution appears clear when viewed directly against a light source but hazy when viewed perpendicular to the light. This qualitative observation indicates light scattering by small particles. A spectrum of the diluted suspension (taken at day 21) has an absorption band at 427 nm which does not shift on further dilution by a factor of 2.5, (The spectra are displayed in Figure 2.) The diluted solutions were yellow to yellow-brown, and the absorption at 427 nm is characteristic of silver particles substantially smaller than the wavelength of light. Creighton (1979) reports an absorption at about 380 nm for a silver sol but on addition of pyridine this peak diminished with appearance of longer wavelength absorptions.

(The use of gelatin to stabilize gold sols was reported by Michael Faraday (1857). The sols were prepared by striking an arc between two gold electrodes immersed in water. The sols are still stable and are on display in the British Museum.)

Although gelatin is a very effective stabilizing agent, its NLO activity is not known to us. Thus, the use of the NLO-active TCVA's as outlined in our Phase I Workplan was still included in the program.

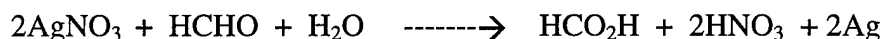
To plan on the outcome of the revised sol preparation, TCVA was treated with an excess of formaldehyde with no noticeable change. (This is being confirmed by absorption measurements.) Although gelatin can be crosslinked by dialdehydes (e.g., glutaraldehyde), the reaction is too slow with formaldehyde to permit stabilization of the sol.

Several experiments were conducted using formaldehyde reduction of silver nitrate without gelatin to form the sol. In one series of these experiments, TCVA and silver nitrate were co-dissolved in aqueous ethanol followed by addition of formaldehyde. No immediate reaction was observed, although, over the course of several days, silver slowly precipitated. These experiments showed that TCVA is fairly effective in stabilizing silver ion, and may significantly slow the growth of the sol particles.

In another experiment, an aqueous silver nitrate solution was treated with formaldehyde. When the yellow color was beginning to turn red, an alcoholic TCVA solution was added. After 5 minutes, the solution appeared slightly hazy and red brown in color, but no precipitate of silver had formed. After 4 days, a slight silver coating formed on the inside of the test tube. The solution was red-brown with a very slight haze.

We tentatively conclude from these experiments that TCVA is fairly effective at stabilizing the silver ion and somewhat effective in stabilizing the sol. However, stability must be improved before further processing into films can be undertaken.

The stoichiometry of the reduction process is shown below:



Reduction of 50 mg of AgNO<sub>3</sub> should thus require 11 µl of 37.1% HCHO solution. A further advantage of this approach is that the reduction can be stopped by oxidizing excess HCHO with dilute hydrogen peroxide without destroying the sol and without oxidizing the TCVA.

### **3.5 PANI Film Preparation and UV/VIS Characterization**

#### *PANI COPOLYMERS*

A solution of PsBAA in methylene chloride (4.3 mg/ml) was cast on a glass microscope slide and allowed to evaporate. The resulting deposit of PsBAA was not a film. Films were formed, however, from co-solutions of PC and PBAA. A solution of PsBAA in methylene chloride (4.3 mg/ml) was mixed with a solution of PC in methylene chloride (8.6 mg/ml) in a volume ratio of 1:2. This co-solution was cast on a glass microscope slide and allowed to evaporate to form a film with a 4:1 weight ratio of PC:PsBAA. A second film was cast from a co-solution containing a 1:4 volume ratio of the two stock solutions to form a film with a PC:PsBAA ratio of 8:1. Both films were flexible and transparent although under optical microscopic examination each showed minor inclusions of some foreign insoluble material, probably impurities in the original sample.

Visible spectra were taken of a PsBAA solution in methylene chloride over the concentration range of 7.9 µg/ml to 63.4 µg/ml. The spectra are displayed in Figure 3. Absorbance versus wavelength data is given in the following.

<i>Concentration, mg/ml</i>	<i>Absorbance (wavelength, nm)</i>		
0.0634	2.4274 (331)	1.0976 (420)	---- (532)
0.0317	1.6871 (318)	0.5468 (422)	0.1709 (532)
0.01585	0.9602 (314)	0.2995 (420)	0.0959 (532)
0.007925	0.4992 (313)	0.1554 (424)	0.0507 (532)

Absorbance vs. wavelength is plotted in Figure 4. Two peaks appear in the visible region of the spectrum. The short wavelength peak (313-331 nm) exhibits a pronounced hypochromic displacement (blue shift) at increasing concentrations. This effect is much less noticeable at the longer wavelength peak at 420 nm. Although no peak appears at 532 nm, absorbances were noted. Linear regressions in the linear regions are given below, the slopes of which are the extinction coefficients in AU/mg/ml (AU = absorbance units).

<i>Wavelength</i>	<i>Conc. range, mg/ml</i>	<i>Linear regression*</i>	<i>Correlation Coeff.</i>
313-331	0 - 0.01585	$A = 0.00637 + 60.580C$	0.99974
420	0 - 0.0634	$A = 0.01302 + 17.112C$	0.99965
532	0 - 0.0317	$A = 0.00528 + 5.343C$	0.99974

\* Includes 0,0 point

Two spectra were also taken of the 8:1 PC:PsBAA film by fixing it to the face of a quartz cuvette in two positions with respect to the beam (Figure 5). The film thickness was approximately 10  $\mu\text{m}$ . Peaks were observed at 421 nm (Abs = 0.4884, 0.4728) and at 315 nm (Abs = 1.0725, 1.1922). The absorbance at 532 nm was 0.2514 and 0.2267. A control of pure Lexan film of about the same thickness showed no absorbance in the visible region.

It is interesting to compare the ratio of absorbances of the short wavelength peak to that at 420 nm. The ratio decreases with increasing concentration, and at the highest concentration the ratio is very close to that observed for the PBAA/PC film.

<i>Conc, mg/ml</i>	<i>Ratio</i>
0.0079	3.213
0.0159	3.206
0.0317	3.085
0.0634	2.211
film	2.196, 2.522* (Average = 2.359)

\*Two measurements at different orientations of the film in the cell

Polycarbonate (from bisphenol A, 4,4'-dihydroxy-diphenyl-2,2'-propane) has a heat distortion temperature of 138-143°C at 66 psi (Billmeyer, 1962) and a glass transition temperature reported variously as 144-145°C (Bandrup, 1989) and 150°C (O dian, 1981). Odian reports its crystalline melting point as 270°. Two sheets of PC (General Electric Lexan 9034, 2mm thick x approx 1 in<sup>2</sup>). were placed between two stainless steel cylinders with flat polished surfaces. This assembly was placed in a hydraulic press and heated by

heating tapes wrapped around the cylinders. At a temperature of 132-142°C and a pressure of approximately 2000 psi, the sheets fused to form a solid transparent composite without significantly compromising its optical clarity. A spectrum of this composite in the visible was taken for base line data and is shown as the lower curve of Figure 6. As seen in this figure, PC is transparent to 400 nm; below 400 nm the absorbance increases rapidly.

The 8:1 PC/PsBAA film was sandwiched between two of the 1" square Lexan sheets and a fused composite prepared as described above. A spectrum of this composite is also shown in Figure 6. The maximum of the of the 420 nm peak is not clearly defined due to the slight absorbance of the PC. Absorbances of the fused PC plates with and without the PsBAA are shown below. (All spectra of PC/PsBAA film and Lexan plates were taken against air as a reference.)

<i>Absorbance</i>	420 nm	532 nm
<i>Fused PC Plates*</i>	0.1089	0.0990
<i>Fused PC Plates with PsBAA</i>	0.3409	0.2254
<i>Ratio of Absorbances</i>	0.319	0.4392

\* thickness of the fused lexan plates is 4 mm.

Spectra were taken of a second thin (10 um) PC/PsBAA film with an 8:1 ratio of PC:PsBAA. Spectra were taken both before and after heat treatment at 132-142°C to look for evidence of thermal degradation (Figure 7). Absorbances at both wavelength maxima and at 532 nm were recorded.

<i>Wavelength, nm</i>	<i>316</i>	<i>421</i>	<i>532</i>	<i>A<sub>316</sub>/A<sub>421</sub></i>
Before heat treatment	1.143	0.462	0.202	2.474
After heat treatment	0.798	0.361	0.168	2.211

The ratios of absorbances at 315 and 421 nm before and after heat treatment were 2.474 and 2.211. Although there is a 10.6% reduction in the ratio, this does not necessarily indicate thermal degradation, although this point must be addressed more fully by infrared spectroscopy. Again, the differences in the spectra are probably due to variation in placing the film against the face of the quartz cuvette rather than to changes in chemical composition. Figure 7 displays the thin film spectra before and after heat treatment.

These results are very encouraging in that it appears quite possible to fabricate with ease structurally strong composites of good optical quality by this technique. The optical density of the PC/PBAA film can be adjusted by controlling the ratio of the two polymers and the film thickness, a function of the solution concentration and surface area over which the solution is cast.

## PANI HOMOPOLYMERS

The UV/Visible spectra of the n-PANI in MeCl<sub>2</sub> solutions are displayed in Figure 8. Three peaks were observed at wavelengths of 236, 290, and 338 nm. Absorbance versus concentration data is given in Table 1 and is plotted in Figure 9. The extinction coefficients of n-PANI at these wavelengths were computed from the slopes of the plots, and are reported in Table 2.

Conc. of n-PANI, $\mu\text{g/ml}$	Absorbance		
	at 236 nm	at 290 nm	at 338 nm
64.1	3.1802	1.9455	1.5743
32.0	1.9158	1.0396	0.8465
16.0	0.9802	0.5198	0.4307
8.0	0.4901	0.2525	0.2228

Table 1 Absorbance of n-PANI in MeCl<sub>2</sub>

Wavelength, nm	Conc. Range, $\mu\text{g/ml}$	Linear Regression	Correlation Coeff. ( $R^2$ )
236	8.0-64.1	A=0.0495C+0.1241	0.9880
290	8.0-64.1	A=0.0304C+0.0209	0.9986
338	8.0-64.1	A=0.0245C+0.0268	0.9983

Table 2 Results of Linear Regression for n-PANI/MeCl<sub>2</sub> Solutions

It is interesting to compare the extinction coefficient of the n-PANI in MeCl<sub>2</sub> to the extinction coefficient in the composite film. UV/Visible spectra of Films 79-36-5 and 79-43-1 to 79-43-4 were taken by mounting the film in the spectrophotometer perpendicular to the beam path. One peak was observed at 337-342 nm (see Figure 10). Absorbance versus weight ratio data is reported in Table 3, and the plot of these data is displayed in Figure 11. (Note that the weight fractions of n-PANI in the films have been converted into units of mg/cm<sup>3</sup>; the density of PC is 1.2 g/cm<sup>3</sup>.) Again, a linear regression was performed on the points to obtain the slope, from which the extinction coefficient can be calculated. The results of the linear regression are summarized in Table 4.

Sample no.	Wt. Ratio of n-PANI to PC	Absorbance at 337-342 nm
79-36-5	1:48.5	1.2103
79-43-1	1:20.8	1.7339
79-43-2	1:12.5	2.1458
79-43-3	1:101	0.7325

Table 3 Absorbance of n-PANI in PC Composite Films

Wavelength, nm	Conc. Range, w/w%	Linear Regression	Correlation Coeff., ( $R^2$ )
337-342	0.98-7.4	$A=0.0186C+0.6078$	0.9781

Table 4 Results of Linear Regression for n-PANI/PC Composite Films

The extinction coefficient of the composite film is 0.0186 in an unit of AU/[(mg/cm<sup>3</sup>)(20 μm)] (see Table 4), or 9.3 AU/(mg cm<sup>-3</sup> cm). This number was compared to the extinction coefficient of n-PANI in MeCl<sub>2</sub> (24.5 AU/(mg ml<sup>-1</sup> cm) reported in Table 2). The absorbance of n-PANI in PC composite films is 2.63 times lower than the absorbance in MeCl<sub>2</sub> at 338 nm wavelength.

### 3.6 Alignment of PANI/PC Composites

The PC/PBAA solutions were evaporated in the presence of electric fields of up to approximately 10 kV/cm. It was thought that given a field direction parallel to the film surface, there should be some degree of alignment of the polymers. Although the dipole moment of the PBAA is not known, PC has a reported dipole moment of 0.67 Debye, which may confer some alignment to the PANI. As pointed out by Prasad and Williams (1991) alignment may enhance  $\chi^3$  values, and polymer alignment also potentially could add strength to the polymer composite. Alignment can be detected by polarized infrared spectroscopy as changes in the intensity of bands with transition moments aligned parallel or perpendicular to the field direction.

PANI and PC were co-dissolved in MeCl<sub>2</sub> to form solutions with certain PANI/PC ratios. The solutions were cast on glass embedded in a Teflon well using our cell configuration designed for electric field alignment. An electric field was applied parallel to the solution surface after the solution was cast. Thus, the polymer films were formed on the glass after the solvent flashed off. The field strength was 2.63 kV/cm for the aligned films; the control films were prepared at zero field strength. Typically, the films were strong enough to be recovered from the glass with gentle pulling. The films were placed in desiccators under vacuum to remove the residual solvent. All of the films were flexible and transparent; however, film integrity was proportional to the concentration of PC in the film. The sample information is tabulated in Table 5 which gives the n-PANI/PC ratios, the field strengths, and the film thickness.



<i>Sample No.</i>	<i>n-PANI to PC Ratio</i>	<i>Field Strength, kV/cm</i>	<i>Thickness, <math>\mu\text{m}</math></i>
79-36-2	1:48.5	2.63	20
79-36-5	1:48.5	0	20
79-43-1	1:20.8	0	20
79-43-2	1:12.5	0	20
79-43-3	1:101	0	20
79-43-4	0:1	0	20

*Table 5 Sample Data*

### 3.7 IR Characterization of the Aligned n-PANI/PC Films

Films 79-36-2 and 79-36-5 were examined for the degree of alignment due to the applied electric field during the film preparation. Figures 12 and 13 show the IR spectra of Film 79-36-5 polarized at 0 and 90 degrees, respectively. From these spectra, no significant difference was observed in absorbance, suggesting that there was little or no alignment in an electric field. This was our expectation since no strong dipole exists in both PC and n-PANI. In addition, the spectrum of Films 79-36-2 and 79-36-5 were compared to the spectrum of Film 79-43-4 (100% PC film) (see Figure 14). There was no absorbance from n-PANI observed in the spectrum, implying that the content of n-PANI in PC matrix is too low to be detected in the IR.

### 3.8 Preparation of TBP/PC Composites

In the initial experiments with TBP, composites similar to those in Section 3.5 were prepared using a TBP in PC. The TBP used was a  $\text{ZnOCH}_3\text{TBP}$ . A film was first formed in PC using solutions of both in methylene chloride. The final TBP/PC film was in the weight ratio of 10.6:89.4. This film was then laminated between two 1" square Lexan sheets, again as described previously (Sample 79-26).

### 3.9 Optical Characterization

- *DEGENERATE FOUR WAVE MIXING (DFWM)*

The DFWM measurements follow the techniques described by our collaborator, Prof. D. Rao of UMassBoston (1994). All measurements were done using a Quantel Nd:YAG frequency doubled laser at 532 nm with a picosecond pulse. We report first on some of our initial measurements. In Sections 3.5 and 3.7, the preparation and characterization of these composites was described. The NLO measurements are tabulated in the following:

<i>SAMPLE #</i>	<i>Sample Description</i>	<i><math>\chi^3</math>, esu</i>
79-23	PsBAA/PC	$4.8 \times 10^{-12}$
79-43-1	n-PANI/PC (1:20.8)	$1.3 \times 10^{-11}$
79-36-2	n-PANI/PC (1:48.5)	$4.8 \times 10^{-12}$
79-34-4	ZnTBP/PC (1:50)	$1.2 \times 10^{-10}$
83-FA-1	ZnTBP/PC (1:50)	$6.6 \times 10^{-14}$
83-FA-2	PC only	$6.2 \times 10^{-11}$

*Table 6. Sample DFWM Measurements*

These initial results were very encouraging in that it appeared that some NLO activity can be retained in the composite. At this point in the project, it seemed possible to and mechanical resilience. It was quite possible to fabricate with ease structurally strong composites by this technique. Theoretically, the optical density of the PC film can be adjusted by controlling the ratio of the two materials and the film thickness, a function of the solution concentration and surface area over which the solution is cast.

- *Z-SCAN MEASUREMENTS*

The Z-scan technique is a single beam technique which allows the determination of the real and imaginary parts of the third-order susceptibility. In the Z-scan experiments the transmittance of the nonlinear medium through a finite aperture in the far field is measured as a function of the sample position Z to determine the real part of the susceptibility. A schematic of the Z-scan technique is shown in Figure 15. On the other hand the transmittance of the nonlinear medium without an aperture is measured as a function of the sample position Z to determine the imaginary part of the susceptibility. The zero position for Z is taken to be that of the focal plane.

Open aperture Z-scan measurements of solutions of ZnTBP and thin films of PMMA and PC doped with ZnTBP exhibit reverse saturable absorption demonstrating that the idea of doping the polymer with the dye is essentially sound and works. Two traces, one for THF solution and the other for a PMMA film, are shown in Figures 16 and 17.

- *POWER LIMITING MEASUREMENTS*

Power limiting measurements were obtained with a standard f/5 experimental setup. The center portion of an expanded beam is chosen as the input in order to simulate a distant source. The laser source used in the experiments is a Q-switched Nd:YAG laser frequency doubled to give 10 nanosecond pulses at 532 nanometer wavelength at a repetition rate of 10 Hz. The output power is plotted versus input power. The power limiting curve is shown in Figure 18. We obtained a power limiting curve for ZnTBP doped film where the host was PC. The free standing film was sandwiched between transparent Lexan (PC) sheets. The impact strength for the sandwiches is that of PC (12-16 ft-lb/in). The tensile strength is 8500-9500 psi. Water (moisture) absorption for a 1/8

of an inch bar in 24 hours is of 3.0 %. The linear transmission of the film is 32%. The experimentally observed limiting threshold is of 1  $\mu\text{J}$  which corresponds to a fluence of about 35  $\text{mJ}/\text{cm}^2$ . Obviously there is much room for improvement concerning the limiting threshold if the sensor is a human eye. The experimentally observed damage threshold is 100  $\mu\text{J}$  which corresponds to a fluence of about 3.5  $\text{J}/\text{cm}^2$ . It is noteworthy that beyond the damage threshold, the transmission drops sharply and irreversibly which is a more desirable outcome than the opposite effect. The ratio of high fluence transmission (1  $\text{J}/\text{cm}^2$ ) to linear transmission is 0.02. The presence of the film between a laser source and a sensor or eye would increase the dynamic range of the sensor by at least two orders of magnitude as evidenced by the width of the limiting region in the graph.

Power limiting curves displaying the dependence of the power limiting on wavelength (Figure 19) and solvent for ZnTBP (Figure 20), as well as curves comparing C60, a liquid crystal and ZnTBP solutions are also included for reference (Figure 21).

## 4. CONCLUSIONS AND DISCUSSION

### 4.1 Processing of Solid Phase $\chi^3$ Materials

In this Phase I project, our focus has been on the processing of  $\chi^3$  materials in mechanically strong polymeric hosts. We have chosen PC as the host material. The objective is to combine the  $\chi^3$  material into a host such that the resulting composite maintains the NLO activity that the starting chromophore displays in solution.

A number of film preparation techniques have been investigated in this project. Again, the objective is to put each of the three  $\chi^3$  materials, PANI, TBP, and the silver sol, into a mechanically strong host. Early on, it was clear that the PANI, as received from the US Army Labs in Natick, would not be a candidate host because its low molecular weight precluded its use as a supporting film. PC is a good film-former and has demonstrated adequate performance as a host for the  $\chi^3$  materials. Films were made by casting a solution of the chromophore and PC either directly on a 2mm PC sheet or on Teflon. Those films cast on the PC sheet are then covered with another layer of 2 mm PC and effectively sandwiched by placing two stainless steel cylinders and heating to 132-142  $^{\circ}\text{C}$  at 2000 psi. Those films cast on Teflon are removed from the casting surface and then laminated between the PC sheets using the same assembly.

### *SOLVENTS*

We have observed that the use of appropriate solvents is of utmost importance in the processing of the samples. Samples of TBP in methylene chloride show the highest sensitivity towards photodegradation. Methylene chloride is compatible with both the TBP dyes and PMMA and PC, but the damage threshold is reached very early for both films as well as solutions (less than 100 laser shots at 532 nm wavelength with 30 mJ and 25 picosecond pulses at a repetition rate of 7 Hz).

THF is a particularly good solvent for TBP's but is incompatible with both PMMA and PC. Methyl ethyl ketone, 1,4-dioxane and toluene were also tried because they are compatible with both TBP's and PMMA. Of these candidates, the most promising two are 1,4-dioxane and toluene. In these cases, it takes around 10000 laser shots to photodegrade the TBP and TBP solutions evaporate slowly enough to form good surface quality evaporated films. Furthermore, the evaporated films adhere well to polycarbonate substrates, thus allowing the fabrication of multilayer sandwiches.

### *AGGREGATION*

The TBP dyes form aggregates. We studied the effect of aggregation by measuring Langmuir-Blodgett films of TBP. The films show no reverse saturable absorption. A possible mechanism for this occurrence is that in the aggregates there are many more pathways for de-excitation compared to the single molecules. The effects of aggregation are evident in the linear absorption spectrum of the samples where a blue shifted and broadened Soret band is evidenced.

### *MOISTURE*

The effects of moisture (water) in the samples is very dramatic. With increased concentration of water, the otherwise sharp and intense Soret band first broadens and blueshifts and eventually splits up. Measurements of intensity dependent transmission on THF solutions and THF/water (1:1 by volume) made at the onset of reverse saturable absorption clearly indicate that the increasing absorption observed in the THF solutions completely disappears in the case of the THF/water mixtures. The reason is that water induces the formation of TBP aggregates.

The above remarks are of serious concern in the choice of a processing technique that is suitable for obtaining multilayer optical limiters. It is useful, then, to summarize the solvent preparation methods en route to recommending solvent-free composite processing.

### *SOLVENT PROCESSING*

- To summarize,
- The solvent must be compatible with both the nonlinear material and the polymer host.
- Substrate on which evaporation takes place must have a smooth surface.
- One must be able to detach film from substrate after evaporation.
- Free standing film is then sandwiched between uniformly thick, optically clear and transparent Lexan (Polycarbonate) sheets.

- Sandwich is placed in a press with a heating sheet surrounding the sandwich.
- Temperature is controlled to induce adhesion of the sandwich by going slightly above and below the glass transition temperature of the host.
- Contacts between press and sandwich must be smooth and uniform surfaces to prevent deformation of the sandwich.

Problems:

- Control of uniformity of thickness
- Difficult to attain an optically smooth surface.
- Bubble formation
- Evaporation rate (non uniform distribution of NLO molecules).

Advantages:

- Solutions are very homogeneous blends.

*RECOMMENDATIONS FOR SOLVENT-FREE COMPOSITE PROCESING*

- Mill polymer host into a fine powder (variation: mill dry solid formed from solution of host and NLO material).
- Dry powder for 48 hours in oven at a temperature below glass transition temperature of host to get rid of any moisture or remaining solvent.
- Dust host powder with NLO material to the target proportions.
- Shake and coat host powder pellets
- Extrude mixture through a pellet die to form blended pellet.
- Extrude as many times as necessary to form uniform blend.
- Add pellet to a laboratory size injection molder.
- Inject blended pellets into an optically smooth, hot, metal mold (die) to form film samples.

### Problems:

- Processing temperatures must be compatible with both the host and the NLO material. (PC and PMMA are compatible with TBP's and phthalocyanines but may not be with other NLO materials)
- Drying and processing may require gas atmosphere other than air.

### Advantages:

- Uniform thickness throughout film.
- Ability to control of thickness.
- Optically smooth surfaces.
- Solvent incompatibilities may be avoided.
- Different shapes can be given to the finished material by simply changing the metal mold (die).

## **4.2 Nonlinear Absorption**

The imaginary part of the third order susceptibility is responsible for nonlinear absorption. Two-photon absorption (TPA), saturable absorption (SA), and excited-state absorption (ESA) are the most relevant types of nonlinear absorptive processes. Transitions that involve one photon and transitions that involve two photons have different selection rules; two photon processes involve the simultaneous absorption of two photons to excite a material. Saturable absorption (SA) involves the saturation of a given transition, by populating an excited state of the material so that the material which initially absorbed at that wavelength becomes more transparent. Excited state absorption involves a sequential process in which a photon is initially absorbed and the molecule remains in an excited state for a finite length of time so that a second photon that arrives during that time is also absorbed to put the molecule into an even higher excited state.

The basic difference between two-photon and excited state transitions is that the former involve intermediate extremely short-lived virtual states, while the later involve intermediate real states whose lifetime is not determined by the Heisenberg uncertainty relations but instead their lifetimes are determined by the electronic structure of the molecules in the materials. Two-photon absorption (TPA) processes are dependent on the intensity (energy per unit time per unit area) of the incident light whereas excited state absorption (ESA) processes are dependent on the fluence (energy per unit area) of the incident light. The two processes can be resolved by obtaining measurements of the samples for different incident pulsewidths. For optical power limiters, we are mostly interested in a fluence dependent material because if the nonlinear transmission

characteristics of the material were intensity dependent that would make the amount of power limiting dependent on the incident laser pulse's pulsewidth which is undesirable.

For an ESA material the ground state absorption cross section is smaller than the excited state absorption cross section. Thus a suitable material for optical power limiting must have as large as possible a ratio of excited state absorption cross section to ground state absorption cross section. Materials that meet this requirement are the tetrabenzporphyrins (TBP), the phthalocyanines (Pc) and the buckminsterfullerenes. The largest ratios have been observed for the tetrabenzporphyrins for which  $\sigma_{\text{eff}}/\sigma_0$  is around 30 at 532 nm wavelength. For the phthalocyanines, it is between 10 and 18 at 532 nm wavelength. For the buckminsterfullerenes (C60), it is one order of magnitude larger but only at 694 nm wavelength which is a region of low sensitivity for the human eye.

In summary, we require a material with large excited to ground state cross section ratio in the regions of the visible spectrum where the eye is most sensitive. During the day, that is around 560 nm wavelength due to cone cells and during the night it is around 510 nm wavelength due to the rod cells. The maximum absorption for the excited state of both TBP's and Pc's is centered close to these wavelengths. This justifies our choice of pursuing these materials as our guest NLO system in future work. Nevertheless, the proposed methodology for processing solid films can be used for any other material that may be of interest for power limiting.

Our optical characterization of films which we prepared suggests that solid phase NLO materials can be prepared, thus demonstrating their potential for sensor protection from lasers. The results are very encouraging. NLO activity, as measured by DFWM, is retained in the composite; open aperture Z-scan measurements of solutions of ZnTBP and thin films of PMMA and PC doped with ZnTBP exhibit reverse saturable absorption, and power limiting measurements yielded a power limiting curve for ZnTBP/PC films. These power limiting experiments are particularly important. The experimentally observed limiting threshold was 1  $\mu\text{J}$  which corresponds to a fluence of about 35  $\text{mJ}/\text{cm}^2$ . While there is much room for improvement concerning the limiting threshold if the sensor is a human eye (the experimentally observed damage threshold is 100  $\mu\text{J}$  which corresponds to a fluence of about 3.5  $\text{J}/\text{cm}^2$ ), it is important to note that beyond the damage threshold the transmission dropped sharply and irreversibly, a desirable outcome. Our results can be compared with those reported by Kost et al.(1993) for optical power limiting at 532 nm wavelength with 8 ns pulses. Although Kost used a different experimental setup and did not report damage thresholds, they report ratios of high fluence transmission (1  $\text{J}/\text{cm}^2$ ) to linear transmission for films of several RSA materials doped in PMMA. They report 0.28 for C60, 0.40 for chloroaluminum phthalocyanine, 0.67 for N-methylthioacridone and 0.94 for King's complex. Our results represent a one order of magnitude improvement over their best result. This supports the Phase I project concept of doping the high impact polymers with NLO dyes.

### **4.3 Conclusions**

In summary,

- We have developed techniques to fabricate RSA films.
- Various NLO materials can be processed using these techniques.
- The techniques are suitable for the development of multilayer limiters.
- The films have excellent mechanical characteristics.
- We have developed a sound agenda for the development and improvement of solid multilayer optical power limiters.
- We have obtained excellent optical power limiting results for the films that we manufactured.

## **5. FUTURE DIRECTIONS**

### **5.1 Modeling of Thermal Responses**

The thermally induced nonlinear optical behavior of the films developed in Phase I, both the thermally induced defocussing and self focussing effects and the thermal damage, can be predicted from a simulation code that has been developed and verified for nonlinear optical liquids and organic molecules. This code can be used for the solid films once the nonlinear optical properties and mechanical properties of the films have been measured. While the thermal effects may be small for the picosecond measurement techniques used in Phase I, the algorithm provides a means of extrapolating the results to longer pulse widths or to picosecond pulse trains that extend for milliseconds or nanoseconds. Operating versions of the code are available at Northeastern University (our STTR partner) and the US Army Natick Research, Development and Engineering Center (Kowalski 1995, 1996a, 1996b).

The simulation code or computer algorithm is a three dimensional, transient thermal response model that is solved using a finite difference technique. The algorithm predicts the temperature of the material and the phase change and refraction of the laser radiation as it travels through the material. The inputs to the algorithm are the geometry of the system, characteristics of the incident laser radiation and thermal and optical properties of the material. The algorithm includes a simultaneous numerical solution for the electromagnetic wave equation using a ray trace technique. In the ray trace technique, the incident radiation is divided into a set of plane waves which travel through the film. This electromagnetic wave model has been verified to be an accurate approximation in thin liquid cells (thickness up to 2 mm). A modified Euler integration method is used to solve the finite difference formulation. The modified Euler integration method allows the



nonlinear variation of the properties, especially the dependence of the absorption coefficient and the index of refraction on the laser radiation intensity and the density of the material. The density of the material is related to the temperature and pressure fields within the film through the equation of state. The algorithm includes the traditional Fourier conduction and continuum equation of state for pulses that are on the order of nanoseconds and microscale heat transfer and absorption coefficient models for laser pulses in the picosecond range. User specified models are included in the algorithm for the absorption coefficient and index of refraction that are based on reversed saturable absorption processes or other  $\chi^3$  processes reported in the literature. The preprocessor subroutine included in the algorithm allows the user to specify the temporal and spatial variation of the incident radiation. These choices include the gaussian spatial and temporal laser radiation, ramp and square wave inputs.

The algorithm has been verified by comparing the predictions to experimental results reported in literature citations. The algorithm is capable of reproducing thermally induced Z-scan behavior in  $\text{CS}_2$  exposed to laser radiation at 532 nm and 10.6 micron wavelengths. The algorithm has also been shown to be able to predict the thermal reflectance effect in nickel films that are exposed to picosecond laser pulses. These successes of the algorithm for predicting thermally induced nonlinear optical behavior suggest that it can be used as a development and design tool for the films being developed in this STTR project. Using the framework that has been established in the algorithm, the effects of the substrate or of the residual solvent on the threshold of thermal damage can be determined. The thermally induced nonlinear behavior can also be calculated based on test data to further supplement the design of the protection system.

## 5.2 Multicomponent Multiphase Materials

The promising results obtained for molecularly dispersed Zn TBP in PC suggest that the multicomponent guest-in-host approach is viable. However, there are broader implications from this work. For example, it should be possible to extend the multicomponent approach to multiphase materials, where individual phases confer specialized properties to the composite material (Figure 22).

For example, two different chromophores with different optical characteristics can be bound in adjacent domains. Alternatively, one domain might contain the optically active molecules and the other may serve a mechanical/structural role. This idea was recently exploited in the preparation of light-emitting polymer thin films based on the comb fluoropolymer Nafion<sup>®</sup>, where ionic domains bind either luminescent or carrier transport molecules and fluorocarbon domains offer mechanical integrity (Karasz and Wnek, 1996). It is of course important for the phase sizes to be small so as not to scatter light, and this is easily possible with, for example, block copolymers where the average domain size is ca. 10-30 nm (Bates and Fredrickson, 1990). Moreover, the domain shape (spheres, cylinders, sheets) can be controlled in block copolymer films by the relative block lengths and processing conditions.

### 5.3 A Comprehensive Protection System

The achievement of reverse saturable absorber (RSA) properties in a polymer composite needs to be combined with other laser protection materials to provide a total system with increased protection. This combination can be a hybrid construction with layers of different laser protection materials, including the RSA materials of this Phase I project and new types of materials. It can also be the use of multifunctional materials where each have more than one laser protection property, i.e., RSA, NLO refractive, new types, etc.

An example of a new type of laser protection mechanism to be combined with the baseline RSA material is the "picosecond photochromic approach." It is based on using an absorber which absorbs photons and forms a colored or photochromic product in a one picosecond timescale. Most photochromic processes take more than one second to form the colored product, and thus are not suited for laser protection. Typical properties of the picosecond photochromic materials in a polymer composite roughly developed for the RSA materials is as follows:

NO LASER	LASER EXPOSURE AT 1MW/cm <sup>2</sup> FOR 0.4J/cm <sup>2</sup>
50% transmission	13% transmission
40% transmission	8% transmission
17% transmission	1% transmission
10% transmission	0.14% transmission

These properties are short of the reduction to the 0.01% transmission that is desired for laser protection. It should be possible to improve the picosecond photochromic properties as a single laser protection system to a higher level, but even greater improvements should be possible by hybrid construction with other types of NLO systems, such as RSA materials of this Phase I project, and by selecting materials for the picosecond photochromic system that are multifunctional and simultaneously exhibit other NLO properties, such as RSA.

The optimization and combinations of the RSA materials, of other NLO materials, and of the new types of NLO-like materials, such as the picosecond photochromic materials, should be the best laser protection that can be achieved with NLO-related materials as a whole.

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**APPENDIX**  
**REPORT FIGURES**

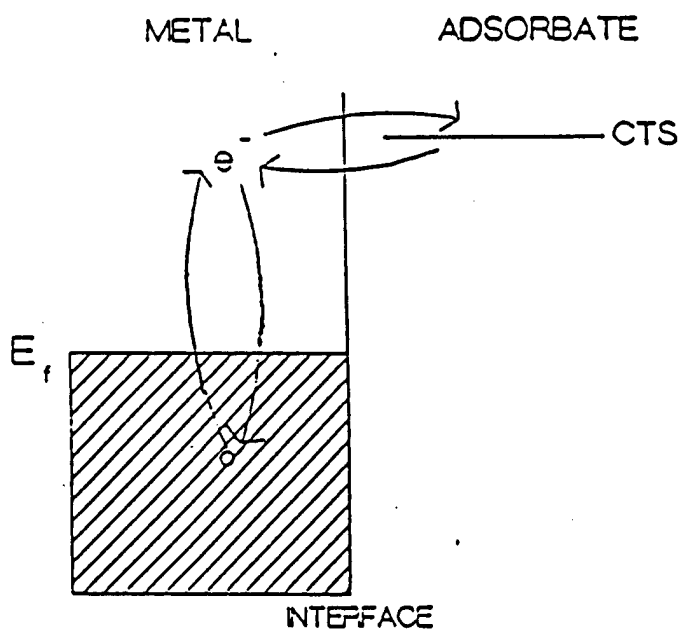


FIGURE 1

Charge Transfer Scheme. The diagram shows the photon induced promotion of a valence electron (below the Fermi level) to the conduction band. The promoted electron can then couple to an uncoupled molecular orbital state or charge transfer state (CTS) of the adsorbate/metal complex. The electron is then transferred back to the conduction band followed by recombining with the hole in the valence band.

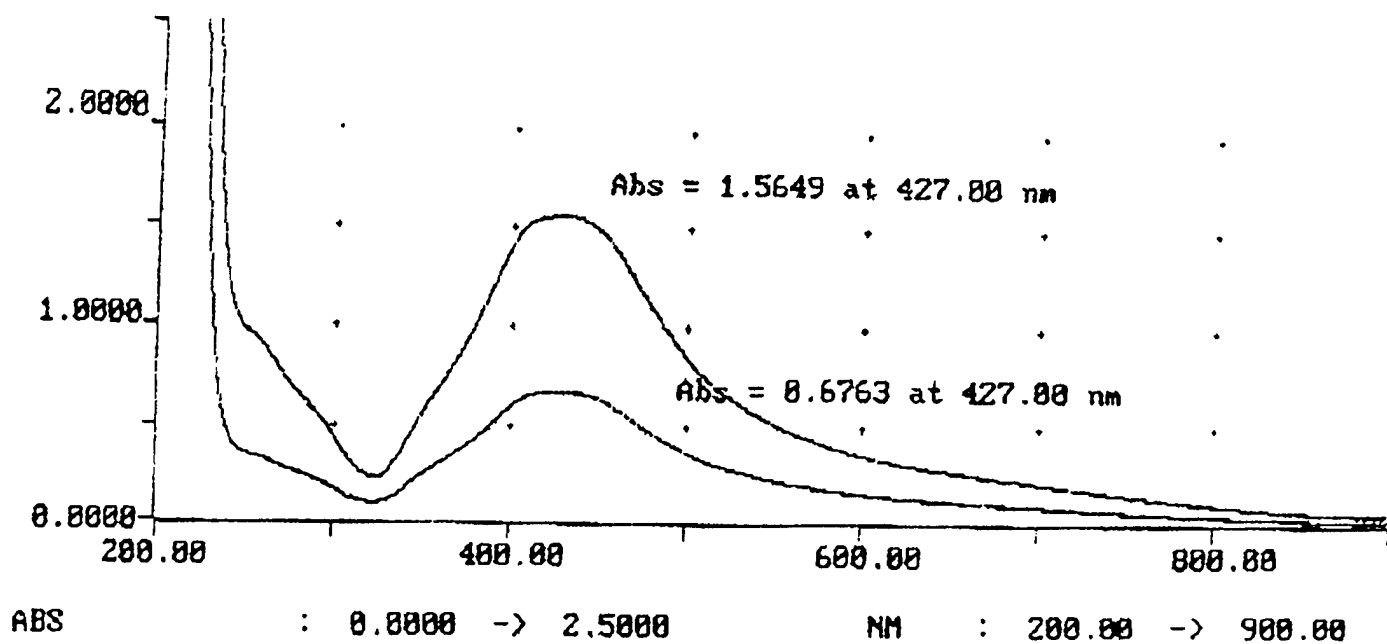


FIGURE 2

Silver Sol Complexed with Gelatin  
Upper curve = 2.5X concentration of lower curve  
(Sample 82-7)

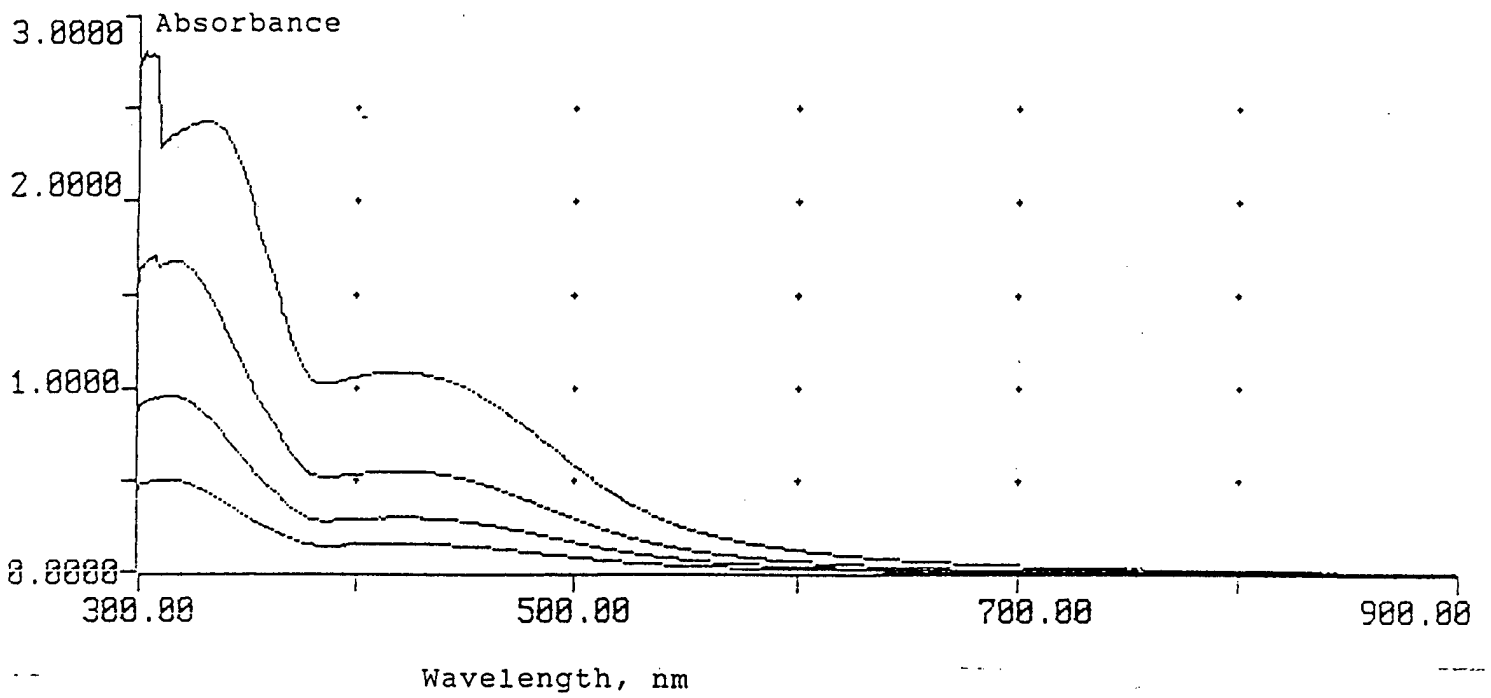
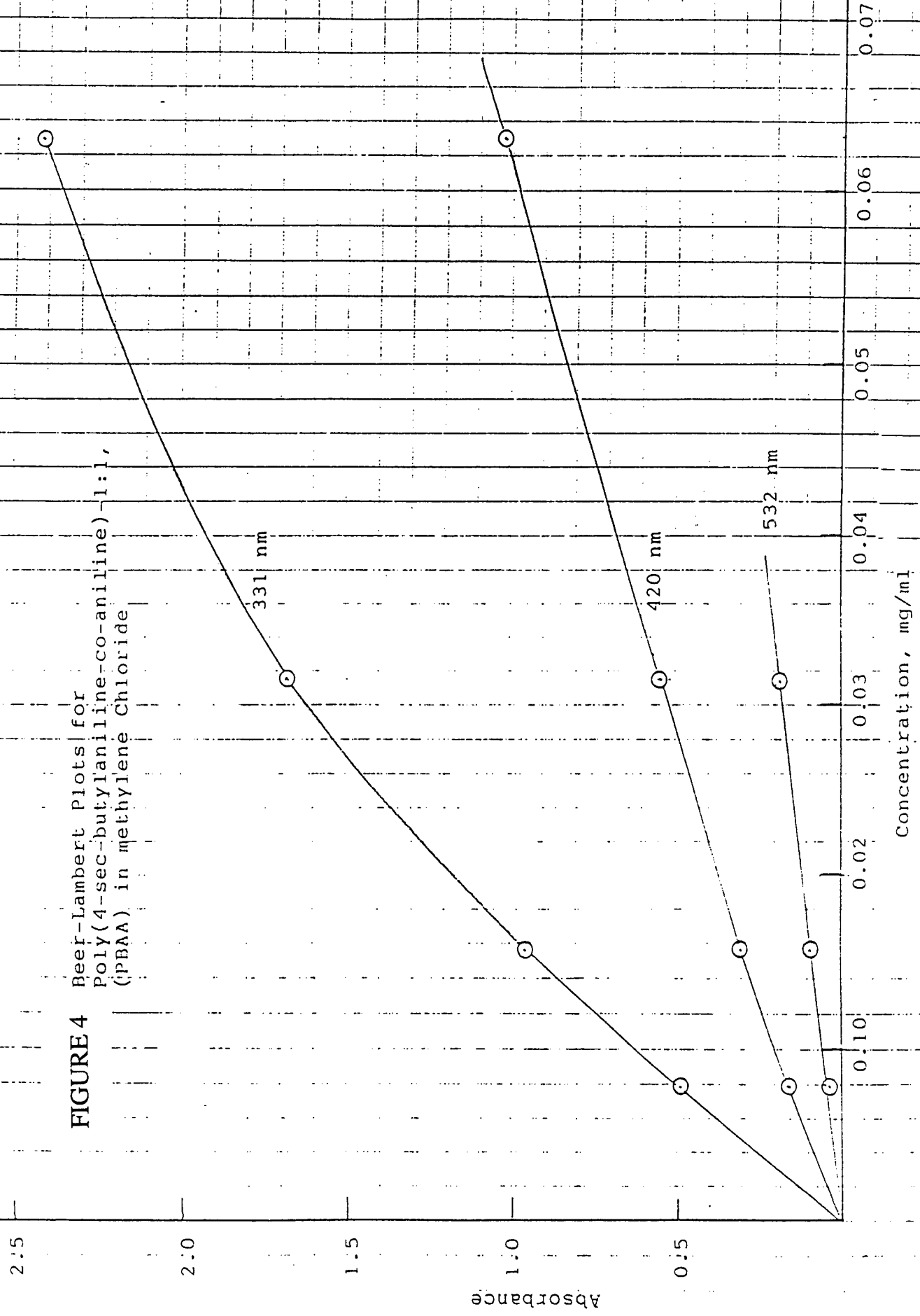


FIGURE 3

Spectra of PBAA in Methylene Chloride



**FIGURE 4** Beer-Lambert Plots for  
POLY(4-sec-butylaniline-co-aniline)-1:1,  
(PBAA) in methylene chloride



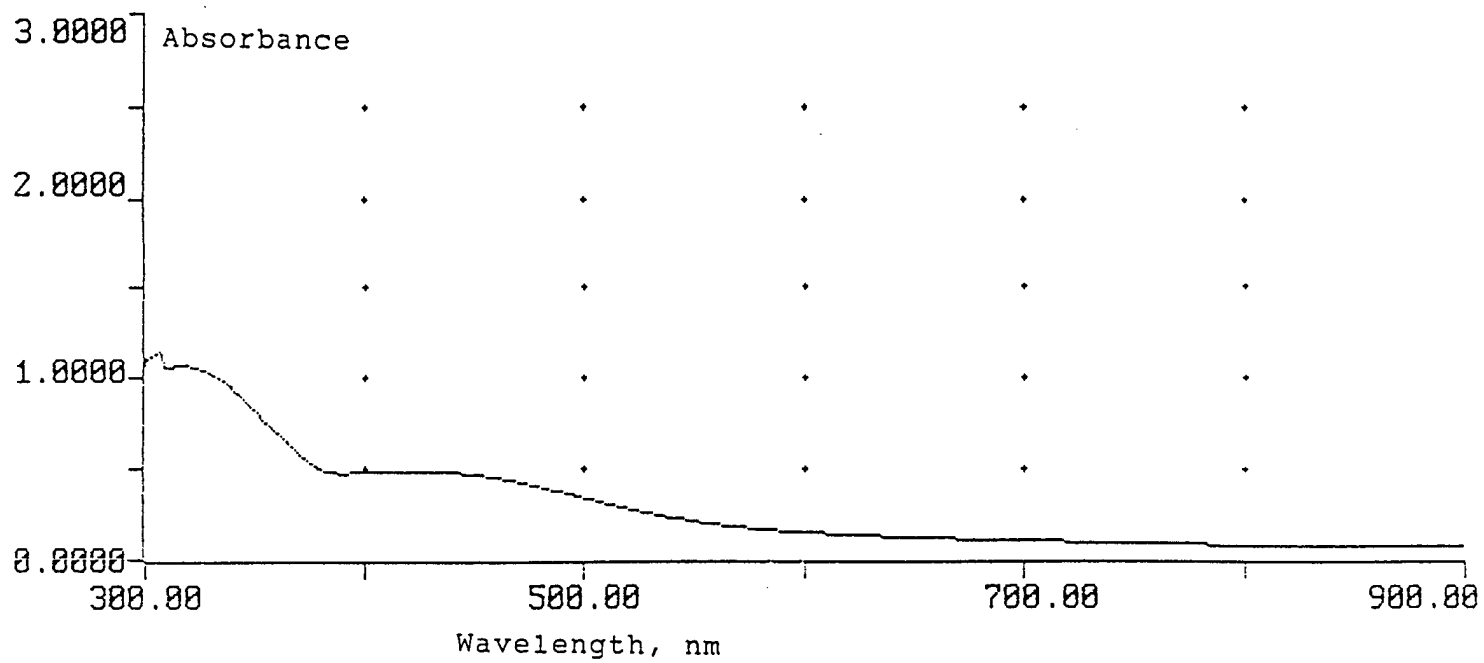


FIGURE 5

Absorbance of a PC/PBAA (8:1) Thin Film

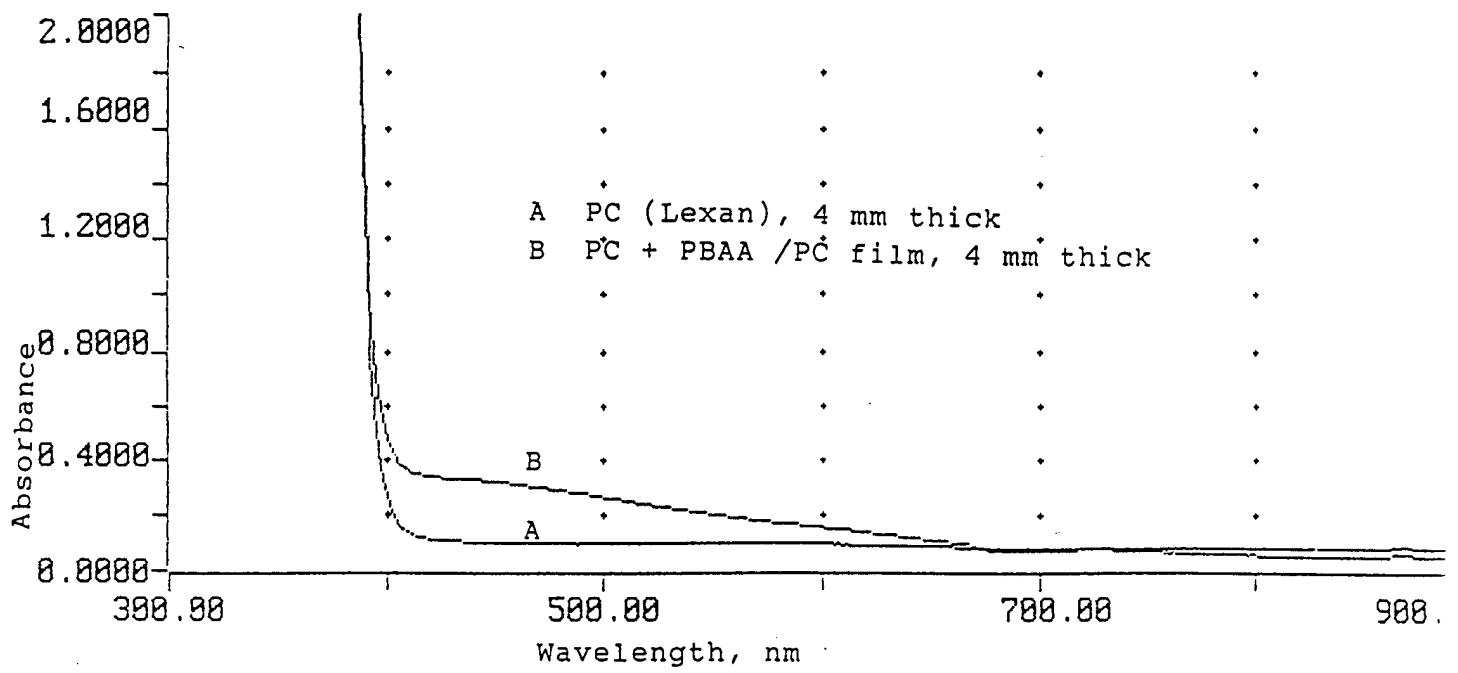


FIGURE 6

Spectra of Lexan Plates, 4mm (A), Lexan Plates with PC/PBAA Film (B)

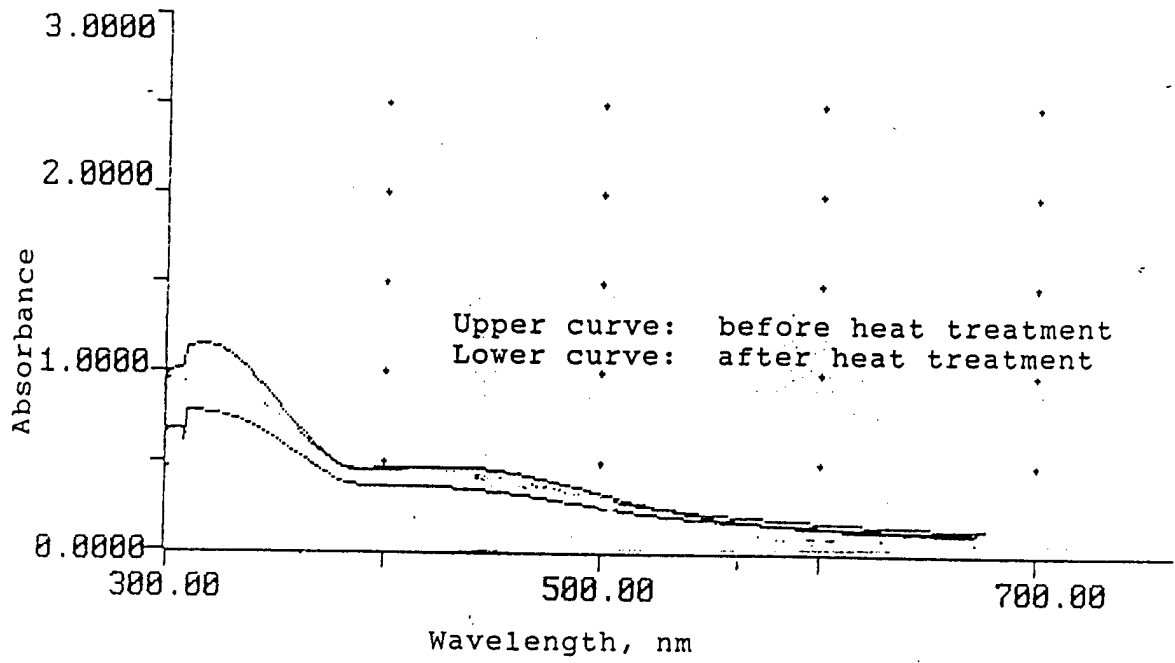


FIGURE 7

Spectra of PC/PBAA Thin Film Before and After Heat Treatment

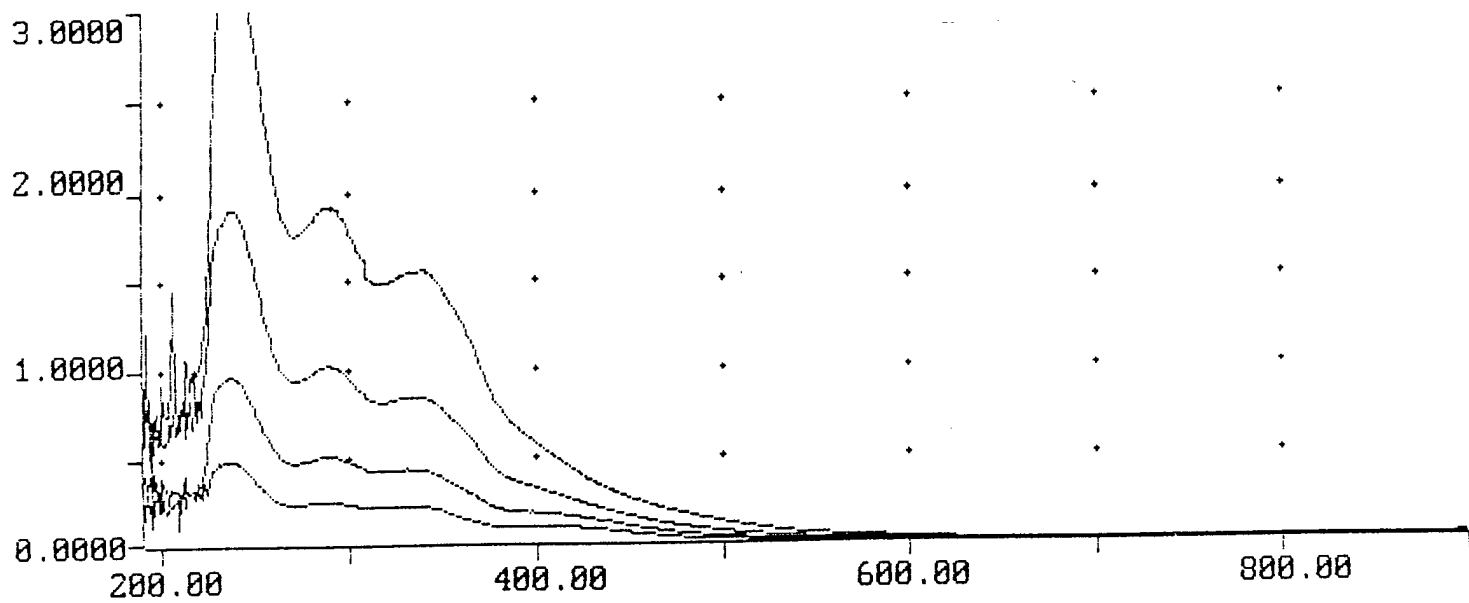


FIGURE 8

Spectra of n-PANI in Methylene Chloride

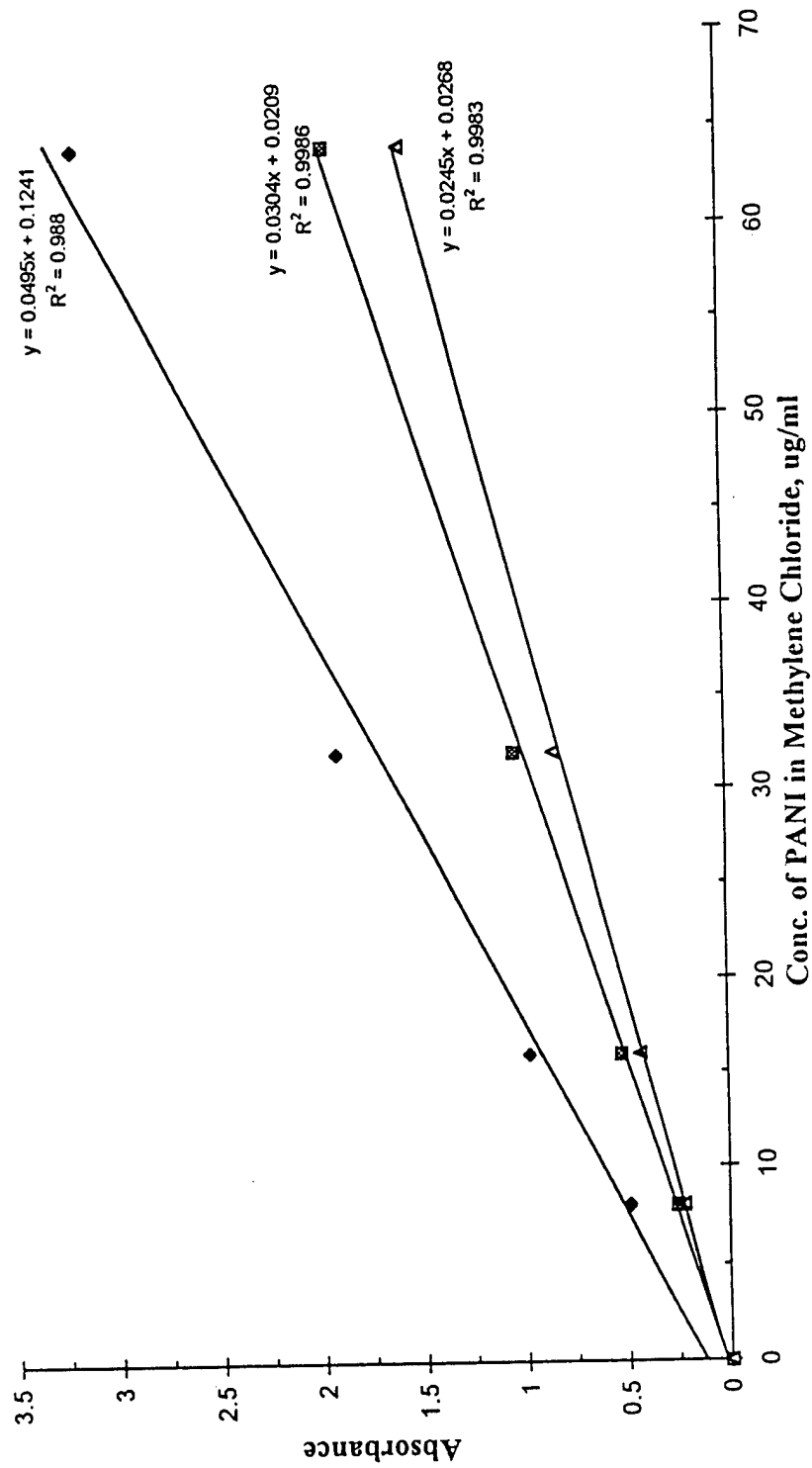


FIGURE 9

Beer-Lambert Plot for n-PANI in Methylene Chloride

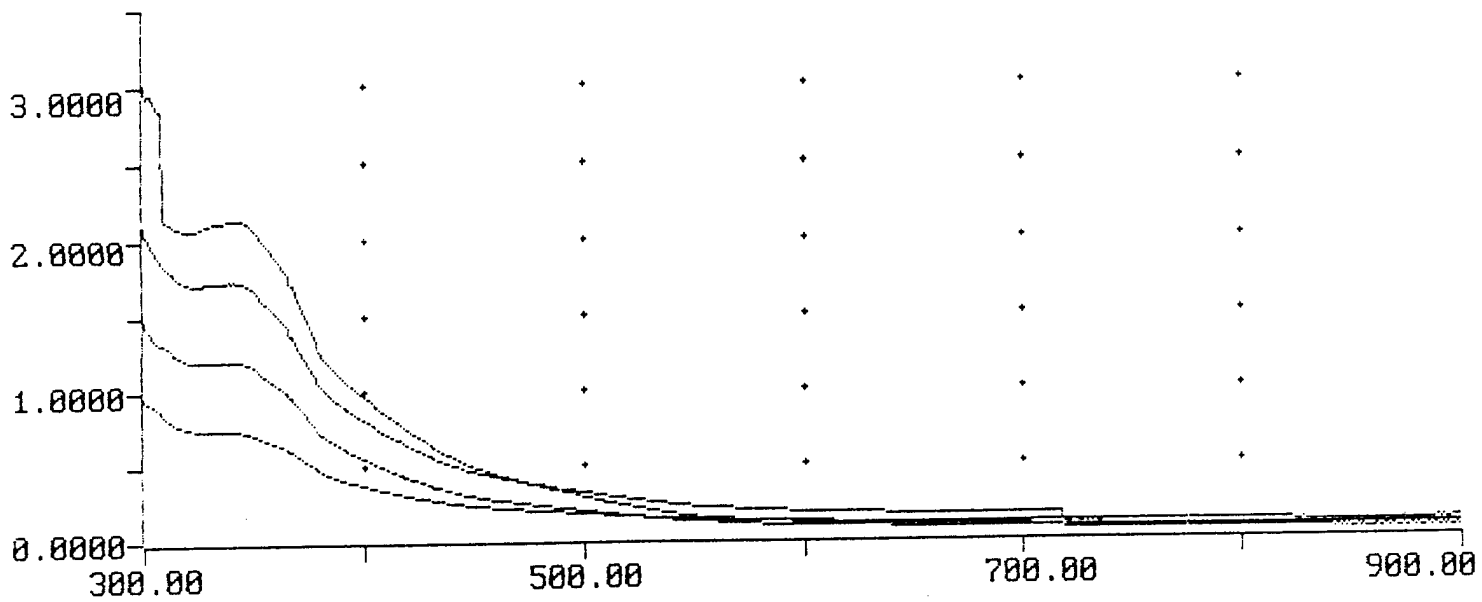


FIGURE 10

Spectra of n-PANI/PC Composite Films

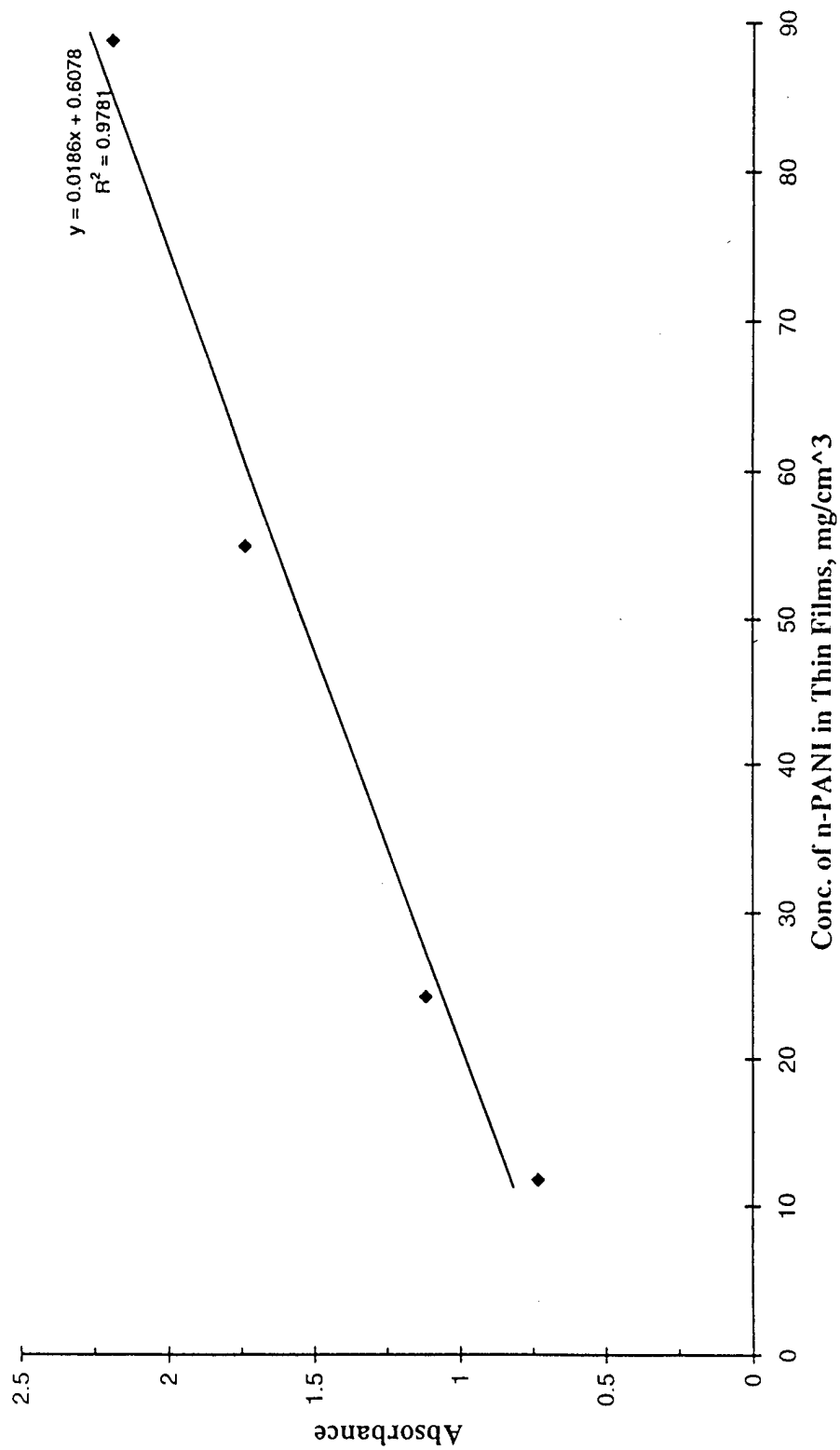


FIGURE 11

Beer-Lambert Plot for n-PANI/PC Composite Films



PERKIN ELMER

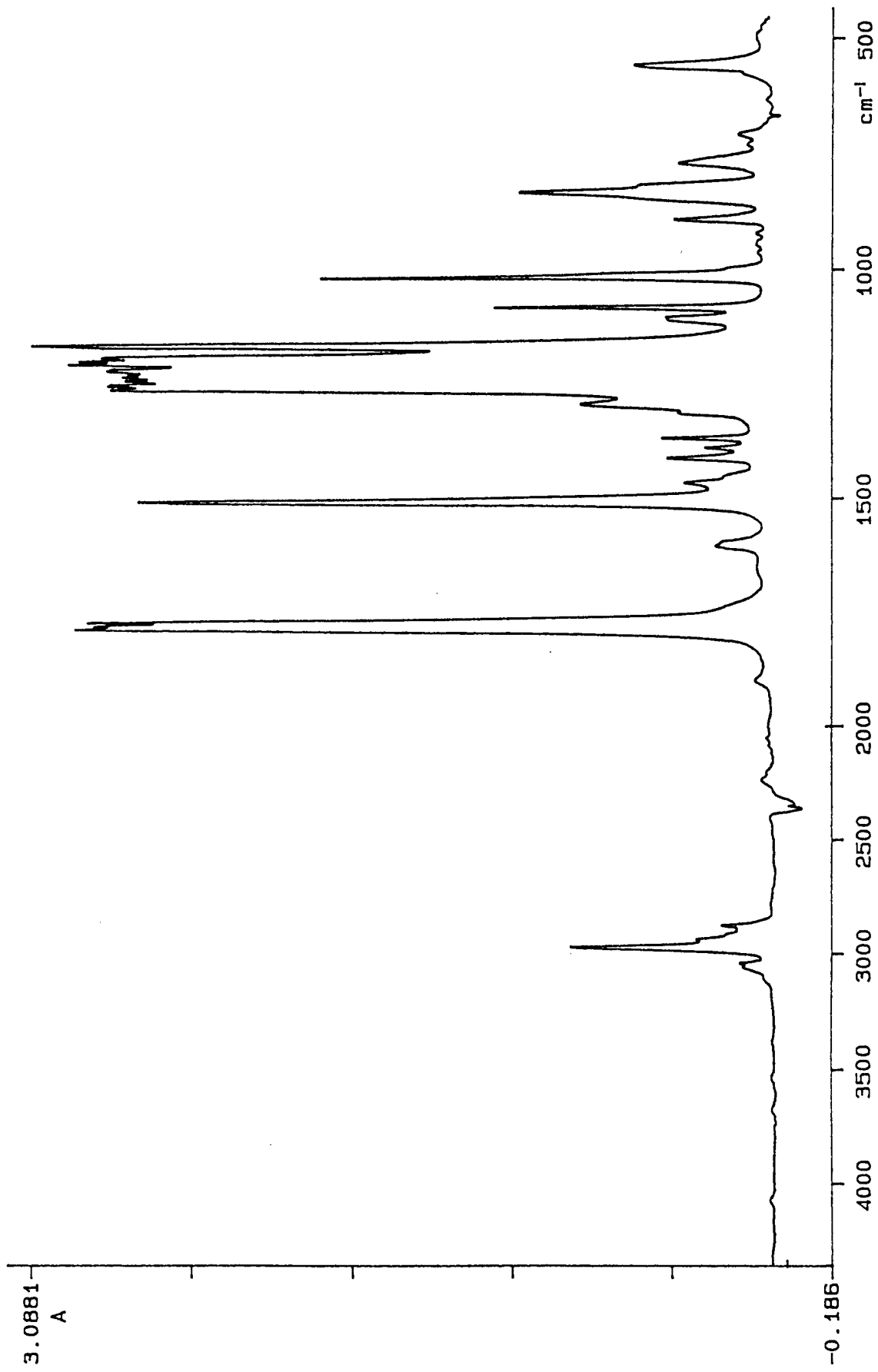


FIGURE 12

IR Spectrum of n-PANI Thin Film (Polarized at  $0^\circ$ )  
(Sample 79-36-2)

PERKIN ELMER

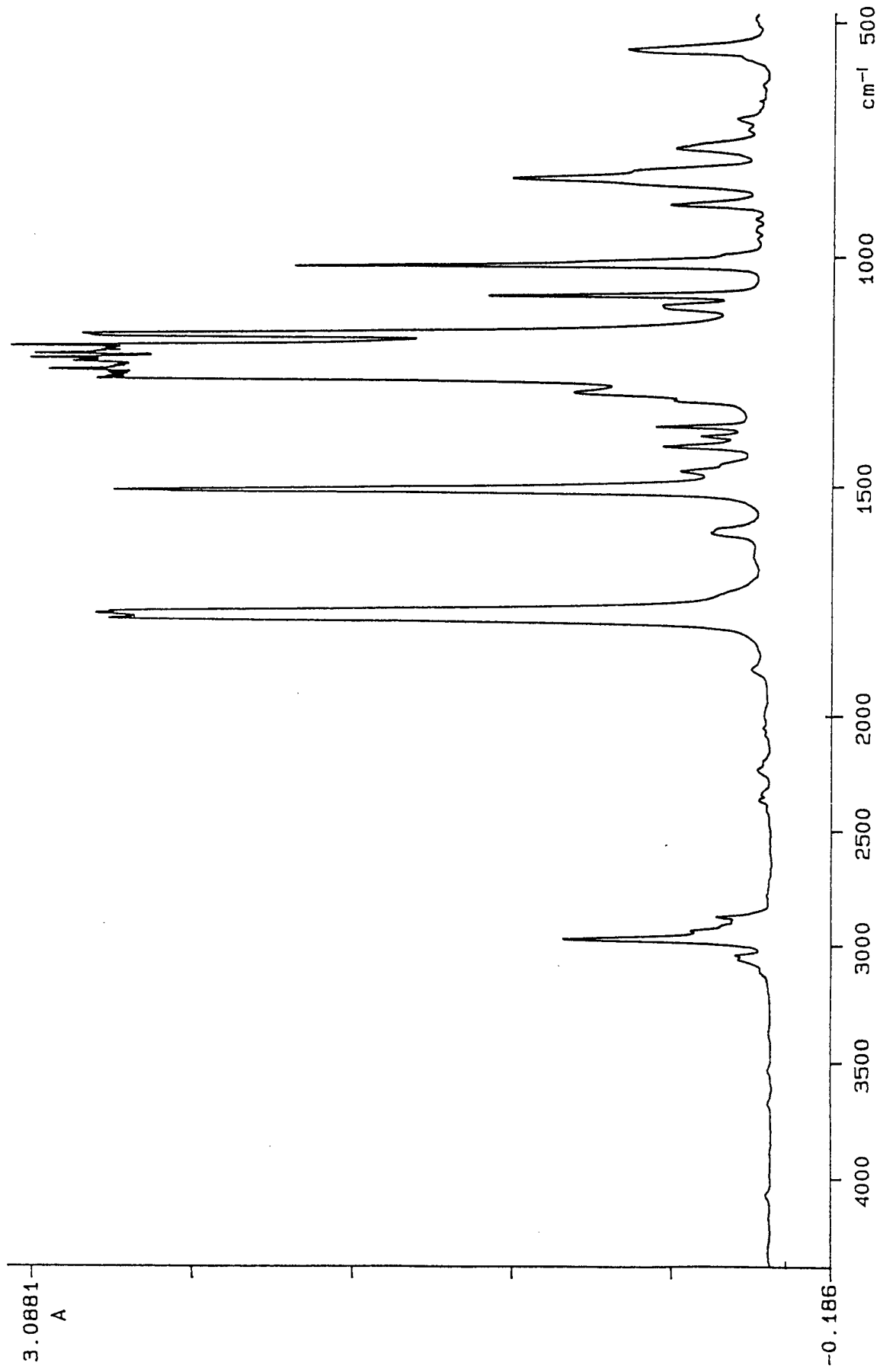


FIGURE 13

IR Spectrum of n-PANI Thin Film (Polarized at 90°)  
(Sample 79-36-2)

PERKIN ELMER

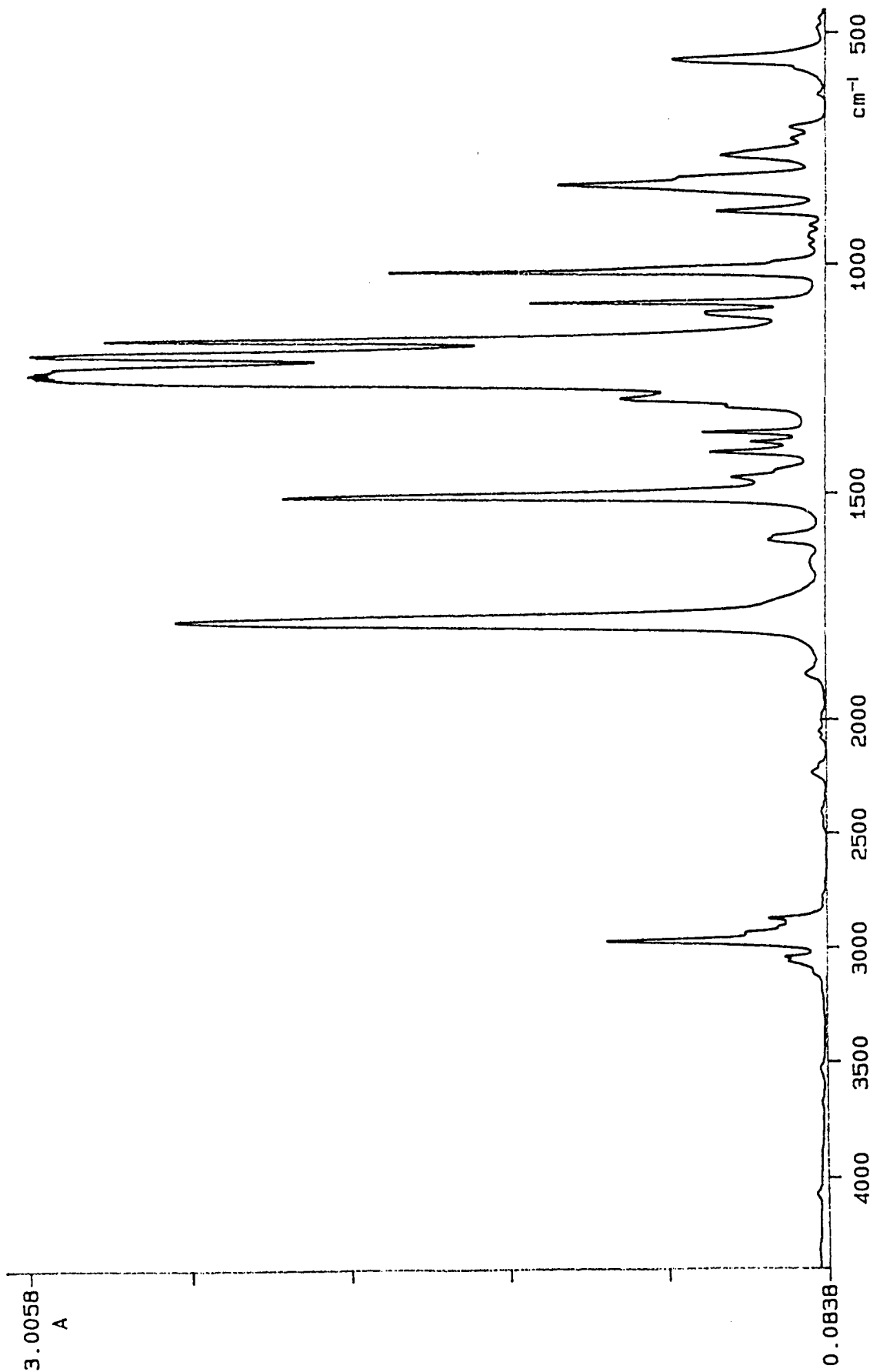


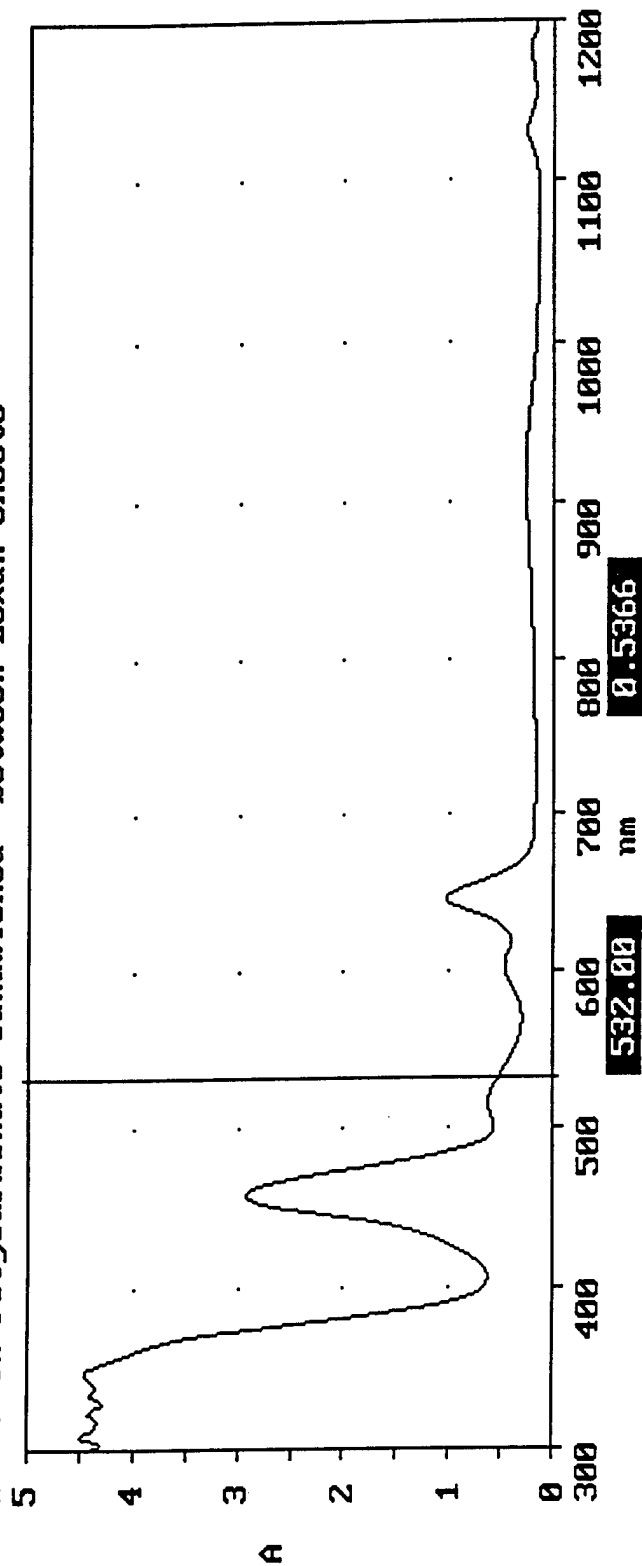
FIGURE 14

IR Spectrum of PC Thin Film  
(Sample 79-43-4)

FIGURE 15

ZnTBP/PC in Lexan Laminate

X: USER003; 1200.0 - 300.0 nm; pts 901; int 1.00; ord 0.1503 - 4.5181 A  
Inf: Zn TBP in Polycarbonate sandwiched between Lexan sheets



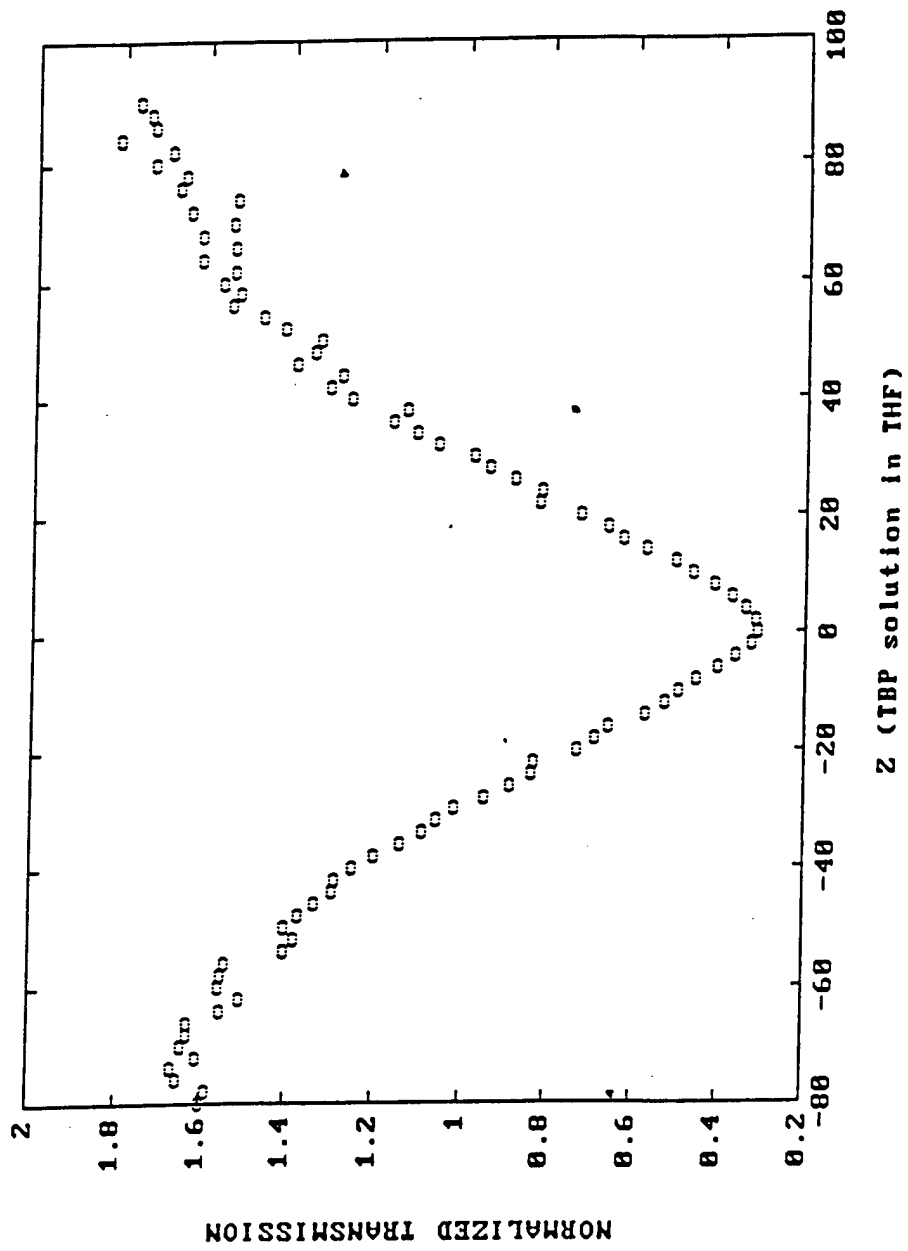


FIGURE 16

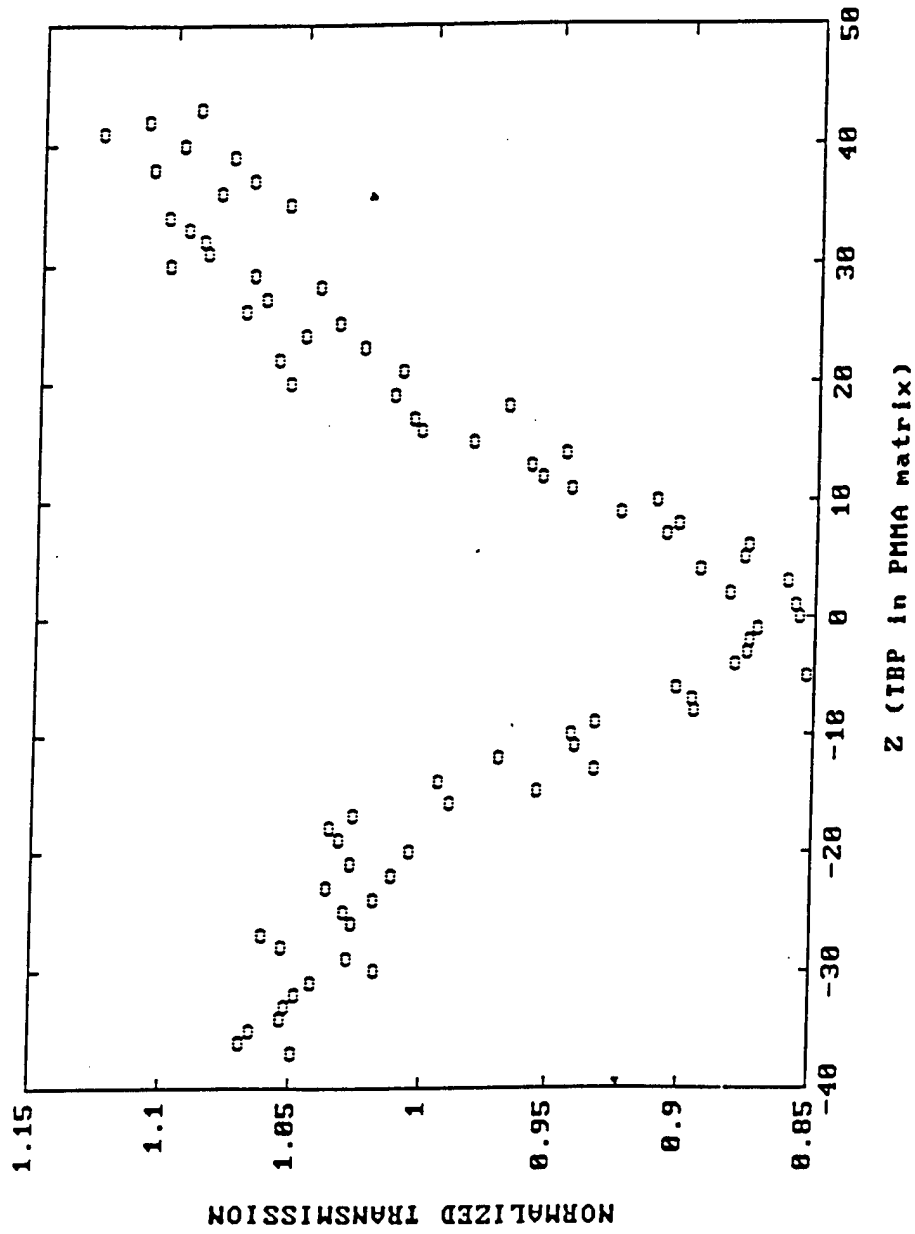


FIGURE 17

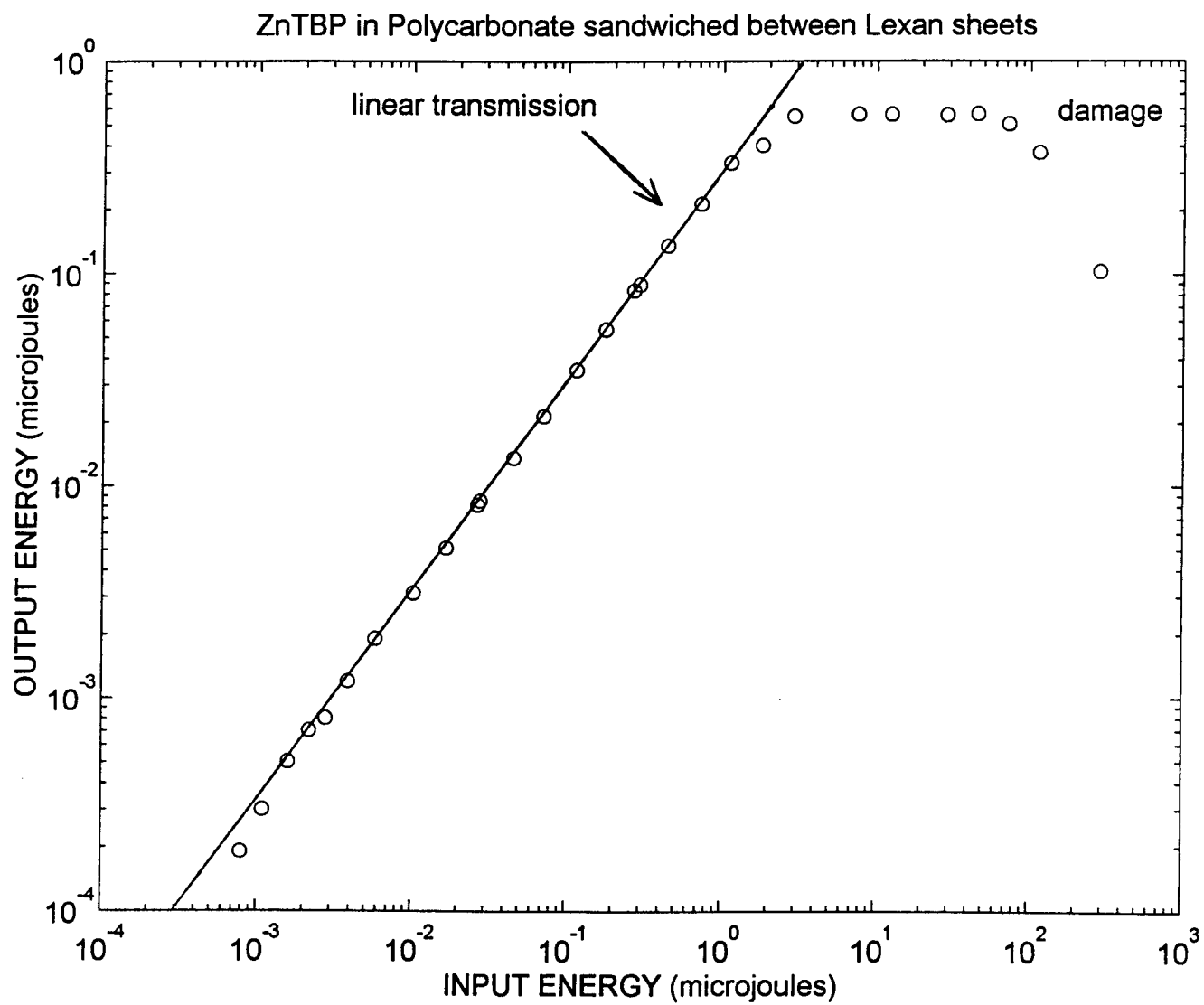


FIGURE 18

FIGURE 19

**POWER LIMITING  
WAVELENGTH EFFECT**

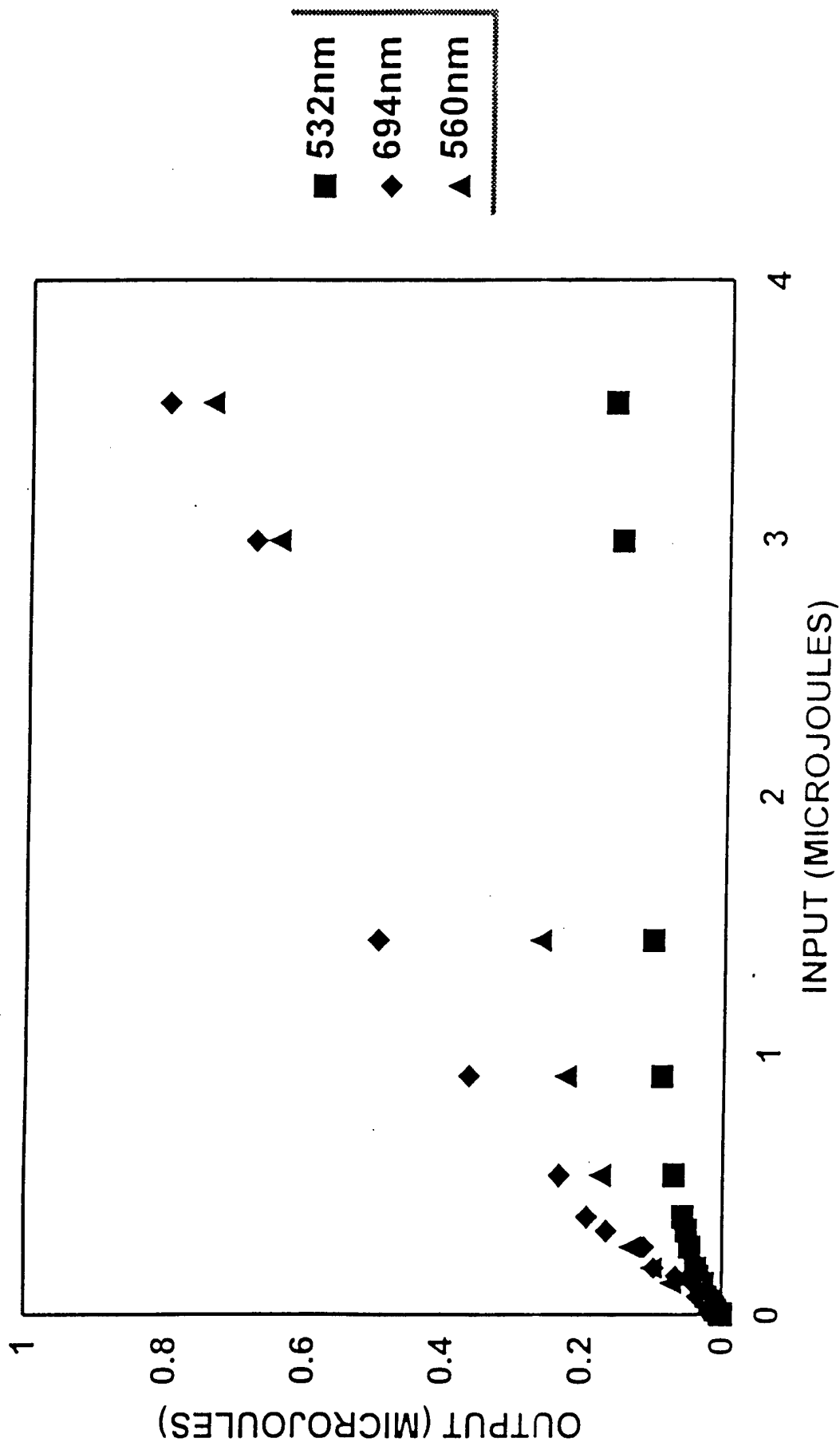
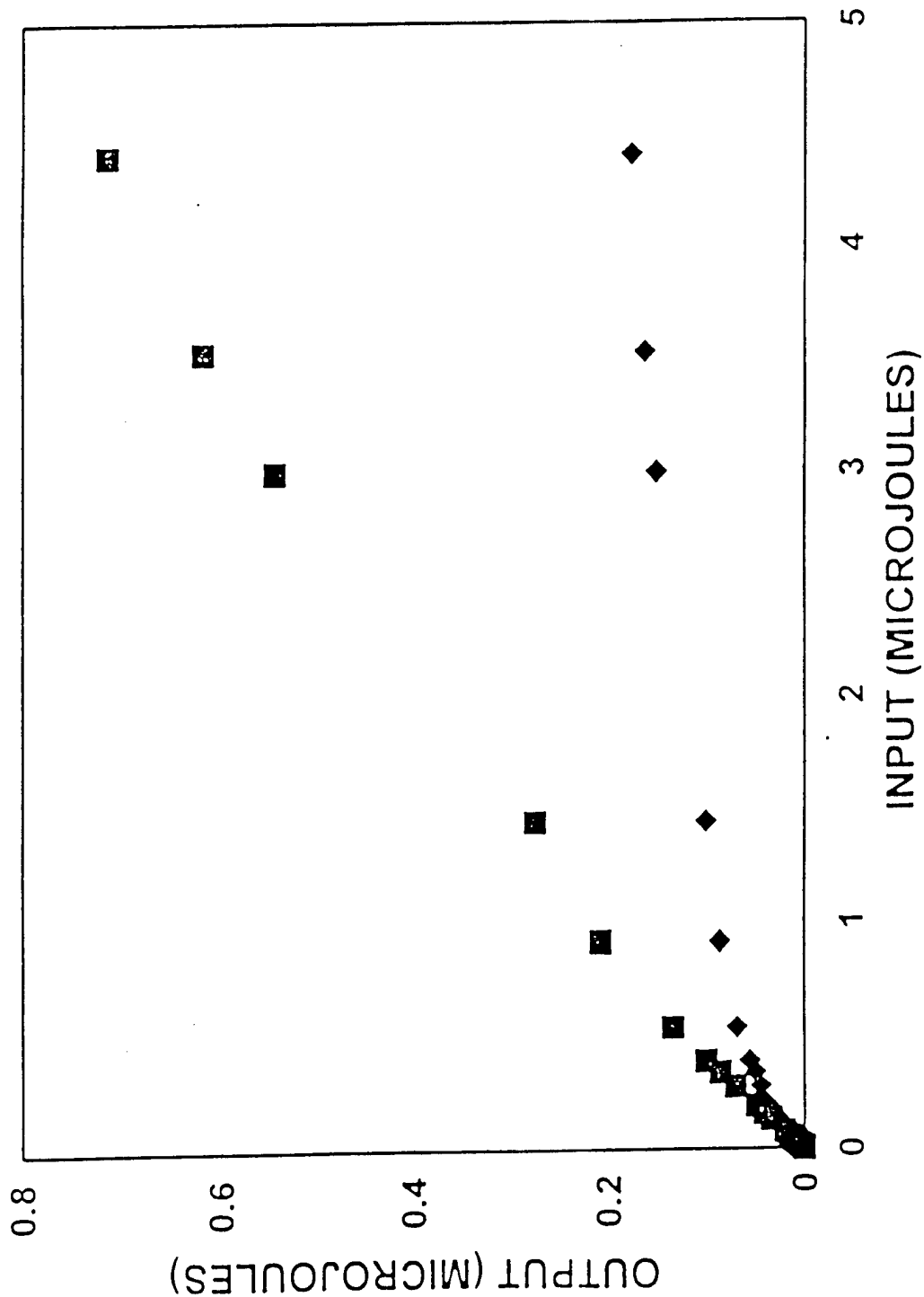




FIGURE 20

**POWER LIMITING  
SOLVENT EFFECT**



ZnTetrabenzporphyrin

■ THF

◆ TOLUENE

FIGURE 21

# POWER LIMITING COMPARISON

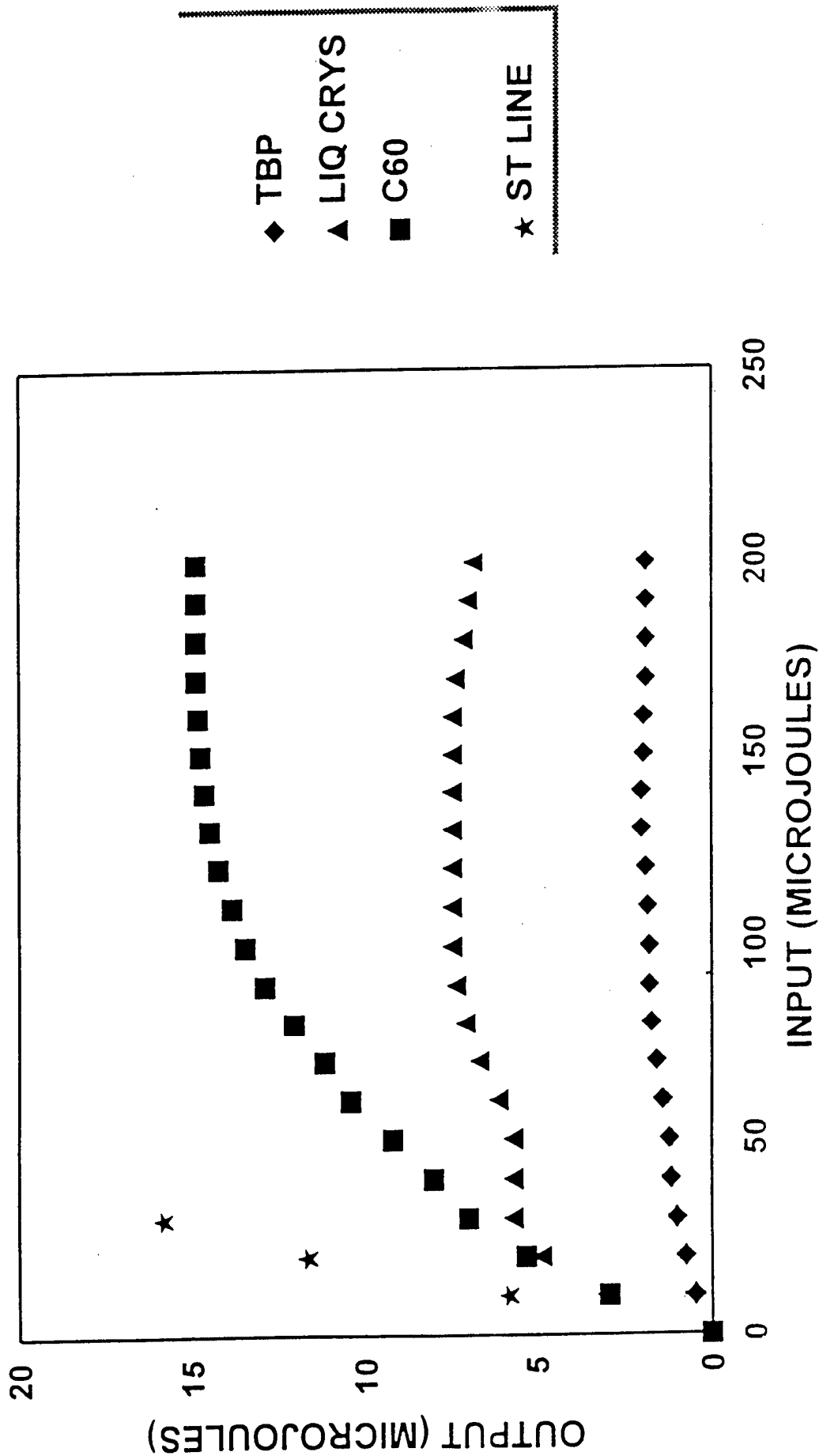
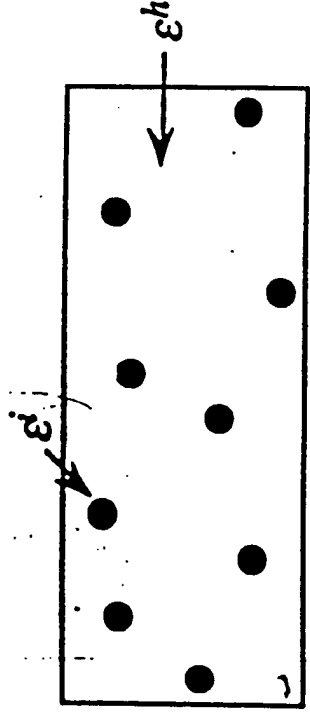


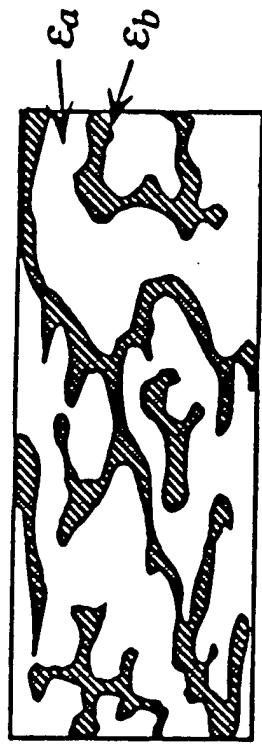
FIGURE 22  
(from Boyd, 1996)

# Composite Geometries

- Maxwell Garnett



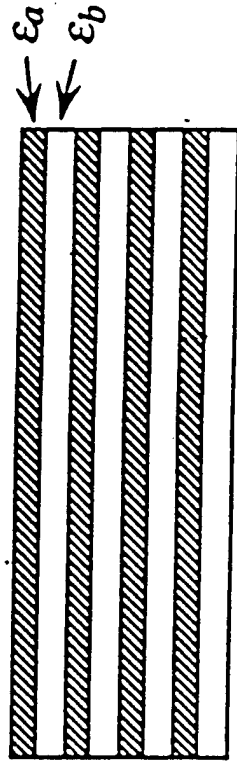
- Bruggeman (interdispersed)



- Fractal Structure



- Layered



scale size of inhomogeneity  $\ll$  optical wavelength

**APPENDIX**  
**PROJECT TEAM**

**Phase I STTR**  
**“Sensor Protection from Lasers”**  
**THE STTR PROJECT TEAM**

- **CAMBRIDGE SCIENTIFIC, INC.**

Debra J. Trantolo, Principal Investigator  
Joseph D. Gresser, Technical Director  
Y.Y. Scott Hsu, Program Manager  
Donald L. Wise, Responsible Corporate Official  
Steve Carlson, Commercialization Advisor  
Robert Langer, MIT, Technical/Business Advisor  
Alexander M. Klibanov, MIT, Technical/Business Advisor

*Polymer processing and characterization; materials science; polymer matrix systems; applications to electrical, optical, and biomedical materials.*

- **NORTHEASTERN UNIVERSITY, STTR UNIVERSITY PARTNER**

Gregory Kowalski, Principal Investigator  
Franciso J. Aranda, Technical Associate

*Modeling of NLO systems; polymer characterization and analysis.*

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Franciso J. Aranda, Post-Doc, UMassBoston

*$\chi^3$  materials and characterization (In collaboration with Natick Labs).*

Jayant Kumar, Prof. of Physics, UMassLowell

*$\chi^2$  materials and characterization.*

Gary E. Wnek, Prof. and Chair, Chemical Engineering, VCU

*Polymer design, synthesis, and characterization for electrical and optical applications.*

- **PROFESSIONAL COLLABORATORS**

Joseph A. Akkara, US Army Natick Labs

*Polyaniline NLO materials*

Masato Nakashima, US Army Natick Labs

*Porphyrin NLO materials*

(Joseph F. Roach, US Army Natick Labs)

(Barry Decristofano, US Army Natick Labs)