

Serial No. 318,456

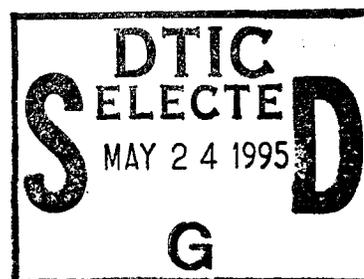
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Inventor Arthur W. Snow  
Michael E. Boyle

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# APPLICATION FOR LETTERS PATENT

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT Michael E. Boyle and Arthur W. Snow, both  
citizens of the United States of America,  
and residents of Burke, Virginia and Alexandria, Virginia,  
respectively

have invented certain new and useful improvements in GLASSY  
ORGANIC-DYE BASED OPTICAL MATERIALS AND THEIR METHOD OF PREPARATION

of which the following attached pages are a specification:

Prepared by: Ajay Pathak  
Reg. No. P-38,266  
(202) 767-2246  
(202) 767-3427  
(202) 404-7380 FAX

Naval Research Laboratory  
Office of Counsel (Patents)  
4555 Overlook Avenue, SW  
Building 28, Room 260, Code 3008.2  
Washington, DC 20375-5325

This application is a continuation-in-part application of co-pending U.S. Patent Application, Serial No. 08/239,068, filed May 6, 1994, which co-pending application is incorporated herein by reference in its entirety and for all purposes.

#### BACKGROUND OF THE INVENTION

Organic dyes are typically employed as colorants usually by adsorption onto solid surfaces from solution in which case their spectral reflectance is the desired optical property. In some instances the spectral transmission is the desired property and the dye is employed in a liquid solution. In other situations, such as those involving laser based technologies, emission from the dye molecule is the desired optical property, and, again, the dye is used in the form of a liquid solution. To take advantage of transmission optical properties in a solid state, a morphology free of optical scattering centers or optical discontinuities (solid and liquid crystallites, anisotropic domains, microscopic phase separations, etc.) is a rigid requirement. Organic dye compounds fall short of this requirement.

In the solid state, organic dyes are highly colored polycrystalline masses and very opaque to visible light. This is a consequence of their molecular structure. Organic dye molecules have a delocalized, highly conjugated structure frequently incorporating rigid fused rings and heterocycles

which provide for the strong optical absorption. To make a dye soluble in water or polar solvents, ionic substituents (e.g. sulfonic acid and its salts) are functionalized to the periphery of the planar rigid structure. For nonpolar solvents, larger conformationally free substituents (e.g. alkyl groups) are employed, and the solubility is entropically instead of enthalpically driven.

However, even in solution the tendency for a dye to aggregate is very strong. This aggregation is a parallel association of the planar molecules arising from extraordinarily strong Van der Waal forces between the highly conjugated structures. With increasing concentration, the aggregates become larger as a result of incorporation of more dye molecules and eventually become optical and physical discontinuities as solvent is entirely removed. Films cast in this manner display far too much scattering for applications requiring optical transmission. In some cases, where the substituent groups are flexible and conformationally free, it is possible to achieve melting before decomposition, but the aggregate structural discontinuity is still present. When these materials are viewed under crossed polarizers, liquid crystallinity is observed, and the optical scattering is unacceptable.

The current technical approach to incorporating organic dyes in glassy matrices is that of blending the organic dye

molecule into a glassy polymeric host. This requires very demanding conditions of molecular compatibility between dye and host in order to achieve molecular dispersal and prevent phase separation. The concentration of the dye in the polymeric host is frequently limited to a threshold of less than 1%. Above the threshold of 1%, phase separation occurs. In the case of a thermoset glass, the presently claimed invention eliminates this difficulty by direct covalent bonding of the dye with the host. For the organic glass, the host is completely eliminated. In addition, both the organic glass and the thermoset glass are one package systems, offering significant advantages to processing.

Peripherally substituted phthalocyanines have been shown to be useful materials for non-linear optical applications as indicated in related patent application Serial No. 08/239,068. Soluble phthalocyanines have previously been synthesized for solution studies of their non-linear optical properties. However, there have been few studies of these materials in the solid state because of increased optical losses due to light scattering and birefringence. This low optical quality is related to an inherent tendency for phthalocyanine macrocycles to stack co-facially into anisotropic molecularly organized structures which are similar to those found in common liquid crystalline systems.

The present invention is concerned with the design and synthesis of phthalocyanines and lead derivatized phthalocyanines which form optically clear glasses and exhibit no birefringence or liquid crystallinity. The preparation of monomeric phthalocyanine organic glasses is also desirable for facile processing and material repair. The instant invention involves functionalized phthalocyanine and lead derivatized phthalocyanine monomers and examples of their properties as organic glasses and their polymerization into optically transparent glasses.

The non-linear optical measurements of a lead derivatized polyphthalocyanine film of the present invention show enhanced third-order nonlinear optical properties. The combination of the optical properties derived from the phthalocyanine structure with the processing and transparency properties of organic glasses and polymerized thermoset glasses produces a new material for use in optical devices.

Previously reported amine substituted phthalocyanine monomers have involved phthalocyanine formation from nitro substituted phthalonitriles followed by reduction to the amine substituted phthalocyanine as noted in POLYHEDRON 6, 1463 (1987); MAKROMOL. CHEM., 189, 1001 (1988), each article incorporated herein by reference in its entirety and for all purposes. Achar et al., *supra*, substituted a simple amino

group at the four benzo rings of the phthalocyanine structure. This group is quite small in size and does little to promote solubility. It was found that the reduction of the nearly insoluble tetranitrophthalocyanine precursor proceeded with difficulty and the lack of solubility of the tetraaminophthalocyanine product precluded its use as a thermoset comonomer as well as satisfactory solution characterization such as NMR. Wöhrle et al., *supra*, substituted four aminophenoxy groups at the phthalocyanine periphery by reducing the nitrophenoxy analog with  $\text{SnCl}_2$ . This aminophthalocyanine is related to part of the present invention; however, the present synthesis differs in that the use of metallic reagents is avoided.

#### SUMMARY OF THE INVENTION

Accordingly, one object of the current invention is to transform organic dye compounds into glassy materials with processing and optical properties suitable for practical applications. Another object of the present invention is achieving material processibility (i.e., melt, solution or thermoset polymer formation) while retaining the optical properties of the glass (i.e., non-optically scattering and non-birefringence) and dye (optical adsorption, reflection and emission characteristics). The advantages and new

features of the present organic dye glasses are many. One such advantage is the fact that a single component organic material that is both an optically transparent dye and a structural glass is provided. Melt processibility and incorporation into conventional glassy thermoset materials (epoxies, cyanates, bismaleimides) with direct molecular bonding are additional advantageous features. Furthermore, in contrast to the prior methods wherein a dye is occluded in a host polymer, the following features of higher optical density/lower scattering glass; no phase separation because of the one component system; more facile recovery and recycle; and increased laser damage threshold are accomplished.

These new materials are optically clear, non-birefringent phthalocyanine glasses having thin film optical properties which may be utilized in various optical devices, for example, but not limited to, optical limiters. The synthetic design of these new materials involves introducing functionality at the periphery of a phthalocyanine molecule or a metal containing phthalocyanine molecule with a design for hydrogen bonding, stereochemical interaction and irregular symmetry to promote glass formation by inhibiting molecular organization. Additionally, the peripheral functionality depresses the glass transition temperature to a practical processing range. The thin film nonlinear optical

properties of these materials exhibit excited state absorption characteristics which give rise to a non-linear optical response useful for optical limiting.

BRIEF DESCRIPTION OF THE DRAWINGS

5            Several terms and abbreviations are used in this application which have meaning as described below:

          PbPc(PGE3Ap)<sub>4</sub>                    Lead Tetrakis (N,N-Bis(3-phenoxy-2-hydroxy-1-propyl)-3-aminophenoxy)phthalocyanine;

          H<sub>2</sub>Pc(PGE3Ap)<sub>4</sub>                    Tetrakis (N,N-Bis(3-phenoxy-2-hydroxy-1-propyl)-3-aminophenoxy)phthalocyanine;

10

          PbPc(AP)<sub>4</sub>                        Lead tetrakis-(3-aminophenoxy)phthalocyanine.

          Figure 1 is a Differential Scanning Calorimetry thermogram for a) PbPc(PGE3Ap)<sub>4</sub> and b) H<sub>2</sub>Pc(PGE3Ap)<sub>4</sub>. The only feature observed for those materials are distinct glass transitions at 65°C and 80°C respectively.

15

          Figure 2 is a comparison of H<sub>2</sub>Pc(PGE3Ap)<sub>4</sub> electronic spectra in the Q-band region for a) a thin film cast from solution on a glass microscope slide (161->154°C & 55°C), and b) a dilute solution (10<sup>-6</sup> M in CHCl<sub>3</sub>). Also shown is a comparison of PbPc(PGE3Ap)<sub>4</sub> electronic spectra in the Q-band region for c) a thin film on quartz and d) a dilute solution (10<sup>-5</sup> M in CHCl<sub>3</sub>).

20

          Figure 3 shows the change in optical density of a thin film of PbPc(PGE3Ap)<sub>4</sub> glass measured with a 1.2 psec duration

25

white light continuum 1 nsec after excitation of the sample with a 1 psec pulse at 590 nm, in the wing of the Q-band. The second spectrum, centered at  $\Delta Q = 0$  was recorded ~ 10 psec before the pump pulse.

5           Figure 4 shows the IR spectra of (a) 4-(3-aminophenoxy)phthalonitrile (1); (b) 4-(3-phthalimidophenoxy)phthalonitrile (2); (c) tetrakis(3-phthalimidophenoxy)phthalocyanine (3).

10           Figure 5 shows the  $^1\text{H}$  NMR spectra of (a) 4-(3-aminophenoxy)phthalonitrile (1), 0.056 M,  $\text{DMSO}-d_6$ ; (b) 4-(3-phthalimidophenoxy)phthalonitrile (2), 0.054 M,  $\text{DMSO}-d_6$ .

          Figure 6 shows the IR spectra of (a) tetrakis(3-aminophenoxy)phthalocyanine (4) and (b) lead tetrakis (3-aminophenoxy)phthalocyanine.

15           Figure 7 shows the UV/VIS spectra of (a) tetrakis (3-aminophenoxy)phthalocyanine (THF); (b) lead tetrakis (3-aminophenoxy)phthalocyanine (THF) and (c) thin film of the polyurethane/lead-tetrakis (3-aminophenoxy) phthalocyanine copolymer (5.9% of phthalocyanine by weight).

20           Figure 8 shows the  $^1\text{H}$  NMR spectra of (a) tetrakis (3-aminophenoxy) phthalocyanine (0.03 M,  $\text{THF}-d_4$ ) and (b) lead tetrakis (3-aminophenoxy) phthalocyanine (0.01M,  $\text{THF}-d_4$ ).

Figure 9 shows the Differential Scanning Calorimeter trace of the polyurethane/lead-tetrakis (3-aminophenoxy) phthalocyanine copolymer (5.9% of phthalocyanine by weight).

5 Figure 10 shows the Differential Scanning Calorimeter trace of 4-(3-aminophenoxy) phthalonitrile detailing the melting point at 175°C and the subsequent self-reaction at 263°C.

10 Figure 11 shows the absorption spectrum of a film of the PbPc(Ap)<sub>4</sub> urethane-butanediol copolymer. The nominal thickness of this film is 25 μm.

Figure 12 observes the change in absorbance (ΔO.D.) as a function of wavelength at 40 ps and 1.2 ns after excitation at 675 nm of the thin film of PbPc(Ap)<sub>4</sub> urethane-butanediol copolymer.

15 Figure 13 shows the transmission of a ~45 μm film of the PbPc-(Ap)<sub>4</sub> urethane-butanediol copolymer as a function of laser intensity for 1.2 ps pulses at 590.5 nm.

20 Figure 14 shows the DFWM Signal S<sub>xxxx</sub> (all beams polarized parallel to each other) as a function of the delay time of the back probe beam.

Figure 15 shows the expanded time scale of the data in Fig. 14.

#### DETAILED DESCRIPTION OF THE INVENTION

25 This invention is concerned with the conversion of organic dyes into processible organic glasses and involves

covalent attachment of a substituent group at the periphery of the dye chromophore. This substituent group counters the dye's tendency to aggregate and makes the dye a processible glass by either modulating the dye's glass transition

5 temperature into a practical processing range (i.e. 50 to 250°C) or by converting it into a monomer which is subsequently cured into a glassy thermosetting solid. To counter the dye aggregation tendency the peripheral group structure is designed to have symmetrical irregularity, poor

10 packing efficiency and secondary bonding forces that inhibit molecular ordering. In practice this means selecting isomer structures of mixed and low symmetry, e.g., racemic and geometrical isomer mixtures and numerous hydrogen bond sites, e.g. polyfunctional alcohols and amines. The substituents

15 incorporated onto the phthalocyanine molecule at the ring periphery counteract the strong tendency of the phthalocyanine structure to form ordered aggregates. The macroscopic results of such features are a non-scattering non-birefringent optical transparency due to a lack of long

20 range order and a glass transition temperature that allows processing at elevated temperature (100° - 200°C).

Processibility is achievable in two forms. The first form is a reversibly melting organic glass. In this case the dye chromophore is functionalized with several large and

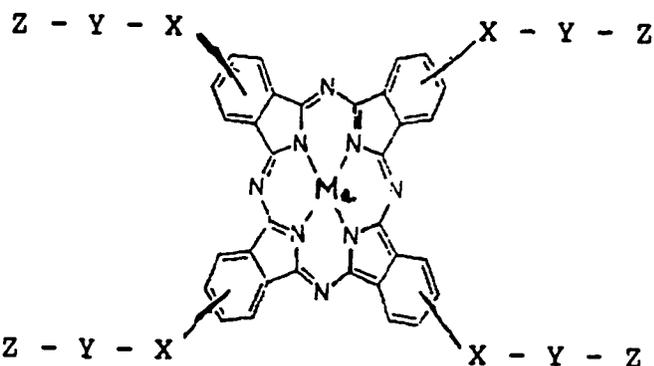
25 molecularly flexible peripheral groups. The molecular

flexibility and conformational freedom regulates the glass transition temperature. A preferred embodiment utilizes a phenyl glycidyl ether amine adduct which is cyclotetramerized with hydroquinone. The second form is that of a thermoset polymer and is formed by an irreversible transformation from a monomer melt. In this case, the dye's peripheral substituent group is further functionalized by a polymerizable functional group responsible for network formation. Thermoset monomer repeat units include epoxy, isocyanate or  $\delta$ -valerolactone adducts. A preferred embodiment of the instant invention utilizes bisphenol-A diglycidyl ether adduct. Other preferred embodiments utilize isophorone diisocyanate adduct (IPDI) or toluene diisocyanate adduct (TDI) as the thermoset monomer repeat unit.

15

Accordingly, the present invention involves peripherally peripherally functionalized phthalocyanine compound, having a phthalocyanine ring, for organic glasses selected from the group consisting of formulas I and II:

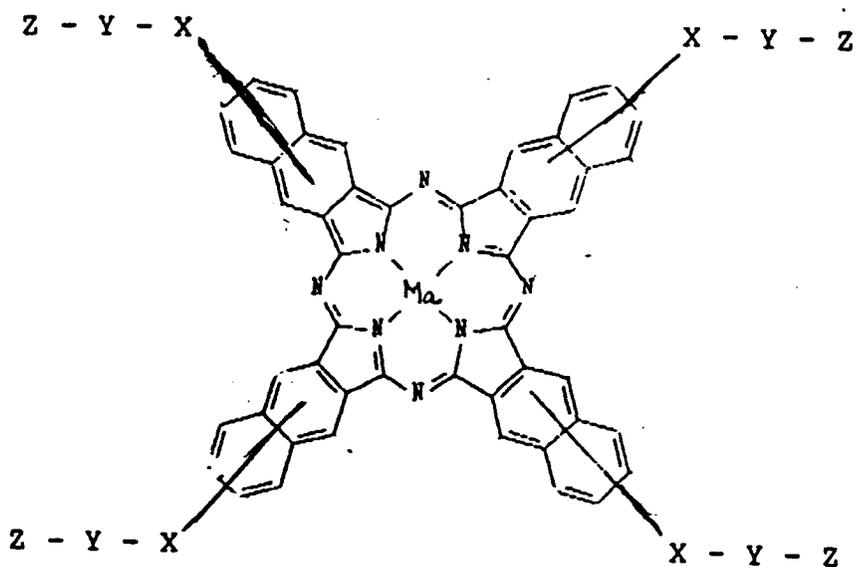
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I.

15



20

II.

25

wherein

M = Be, Mg, Al, Si, Ti, Mn, Fe, Co, Ni, Cu, Zn, Ge, Rh,  
Pd, Ag, Cd, In, Sn, Pt, Au, Hg, Pb, Bi or VO  
(vanadyl oxide);

5 a = 0, 1 (if no metal is present, a=0);

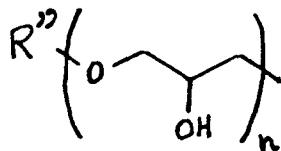
X = oxygen, sulfur;

Y =  , siloxyl, alkoxy, or alkyl  
chain (C<sub>1</sub> to C<sub>16</sub>) including linear, branched,  
10 saturated, unsaturated, substituted, unsubstituted,  
cyclic;

Z = H, OH, OCN, SH, NH<sub>2</sub>, NHR, NR<sub>2</sub>, carboxylic acid,  
ester, anhydride, OR', SR', NHR', NR'<sub>2</sub>, OCOOCOOR'  
wherein R is alkyl or aryl and wherein R' is a  
15 monomeric repeating unit selected from the group  
consisting of:

(i)

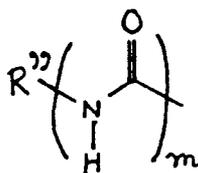
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wherein  $n = 1, 2, 3,$  or  $4$  and  $n$  specifies the number of branches attached to  $R''$  and  $R''$  is selected from the group consisting of alkyl, aryl and mixtures thereof;

(ii)

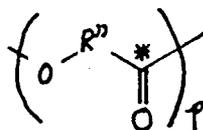
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wherein  $m = 1, 2, 3,$  or  $4$  and  $m$  specifies the number of branches attached to  $R''$  and  $R''$  is selected from the group consisting of alkyl, aryl and mixtures thereof;

10

(iii)



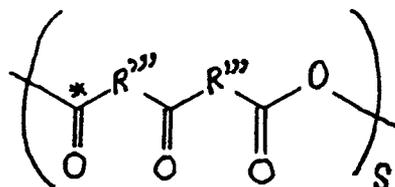
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wherein  $R''$  is selected from the group consisting of alkyl, aryl and mixtures thereof and attachment to the phthalocyanine ring is via the carbonyl carbon marked with an asterisk (\*) and  $p$  is an integer from 1 to 100,

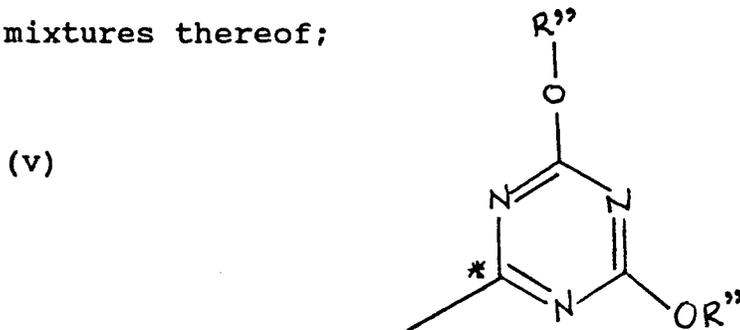
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inclusive;

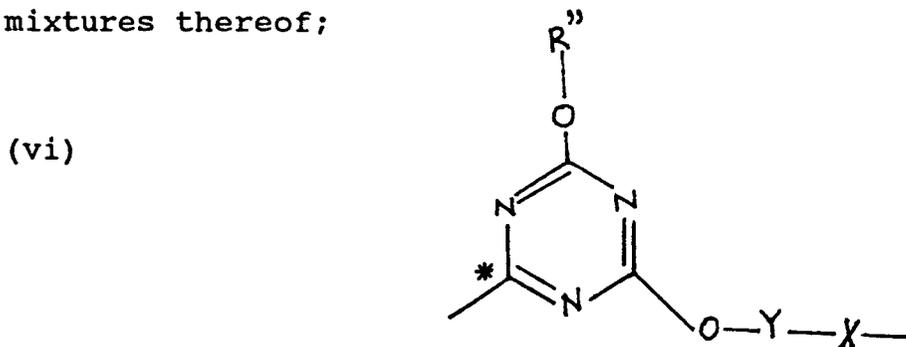
(iv)



wherein  $s$  is an integer between 1 to 100, inclusive and attachment to the phthalocyanine ring is via the carbonyl carbon marked with an asterisk (\*) and  $R'''$  is selected from the group consisting of alkyl, aryl and mixtures thereof;

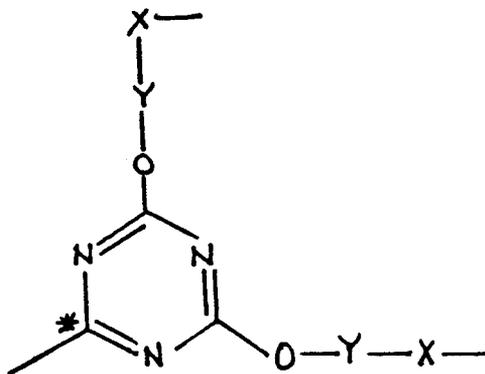


wherein attachment to the phthalocyanine ring is via the carbon atom marked with an asterisk (\*) and  $R''$  is selected from the group consisting of alkyl, aryl and mixtures thereof;



wherein attachment to the phthalocyanine ring is via the carbon atom marked with an asterisk (\*) and  $R''$  is selected from the group consisting of alkyl, aryl and mixtures thereof;

(vii)



5 wherein attachment to the phthalocyanine ring is via the carbon atom marked with an asterisk (\*) and R'' is selected from the group consisting of alkyl, aryl and mixtures thereof;

10 with the proviso that when Y =  and Z is NH<sub>2</sub>, then Y is not substituted in the para position.

The examples presented below pertain to phthalocyanine dyes and various peripheral groups. This invention is logically and readily extendible to other classes of dyes and glass formation promoting peripheral groups by those skilled and knowledgeable in the art of organic chemistry.

EXAMPLES

EXAMPLE I  
REVERSIBLY MELTING ORGANIC DYE GLASS

The chemical synthesis of the reversibly melting organic dye glass, is presented in Scheme I. Procedures for synthesis of compounds not commercially available are described below.



4-(3-Aminophenoxy)phthalonitrile. A mixture of 10.54 g (60.9 mmol) 4-nitrophthalonitrile and 7.00 g (64.1 mmol) 3-aminophenol were dissolved in 50 ml dimethylsulfoxide and 14.85 g anhydrous potassium carbonate was added over 6 hr period in 1 g quantities with stirring. The reaction mixture was filtered, then added dropwise to 700 ml water to precipitate 10.0 g (70%) product. The product was recrystallized from methanol (MP 172°C).

10 3-N,N-Bis(3-phenoxy-2-hydroxy-1-propyl)  
aminophenoxyphthalonitrile. A mixture of 0.200 g (0.852 mmol) 4-(3-Aminophenoxy)phthalonitrile and 0.275 g (1.83 mmol) phenyl glycidyl ether were reacted at 150°C for 3 hr. The product is a viscous liquid which solidifies to a hard glass on cooling. This product may be purified by alumina column chromatography or it is possible to proceed directly to the phthalocyanine forming reaction.

20 Tetrakis (N,N-Bis(3-phenoxy-2-hydroxy-1-propyl)-3-  
aminophenoxy)phthalocyanine. A mixture of 0.450 g (0.852 mmol) 3-N,N-Bis(3-phenoxy-2-hydroxy-1-propyl) aminophenoxyphthalonitrile. and 0.0246 g (0.224 mmol) hydroquinone were reacted at 175°C for 18 hr. to yield a highly viscous purple melt. This product was purified by passing through an alumina column and methanol extraction.

25

This material is a rigid glass at room temperature and has a well-defined glass transition temperature at 82°C (see DSC thermogram in figure 1. When heated above 100°C it is a viscous liquid which may be mechanically pressed between flat surfaces into supported or free standing films for optical applications.

Lead Tetrakis (N,N-Bis(3-phenoxy-2-hydroxy-1-propyl)-3-aminophenoxy)phthalocyanine. The lead-substituted phthalocyanine (PbPc(PGE3Ap)<sub>4</sub>) was subsequently prepared from metal-free phthalocyanine by treatment with lead acetylacetonate.

The general synthetic scheme for preparing glassy phthalocyanines as shown in Scheme I involves the K<sub>2</sub>CO<sub>3</sub>-catalyzed nucleophilic nitro displacement of 4-nitrophthalonitrile by 3-aminophenol which yields a 4-(3-aminophenoxy)phthalonitrile precursor which is then converted to the phenyl glycidyl etheramine adduct. This adduct is then cyclotetramerized in the presence of hydroquinone as reducing agent to form the metal-free product, tetrakis (N,N-Bis(3-phenoxy-2-hydroxy-1-propyl)-3-aminophenoxy)phthalocyanine, abbreviated H<sub>2</sub>Pc(PGE3Ap)<sub>4</sub>.

These peripherally substituted phthalocyanine products have several features of irregular symmetry which inhibit crystallization and/or long range molecular order. These

include a mixed geometrical isomer substitution at either of the outer benzo positions of the phthalocyanine structure, a meta as opposed to para substitution of the aminophenoxy group, and a diastereomeric relationship between the two asymmetric carbons in the amine-epoxy adduct structure.

5 Intermolecular hydrogen bonding from the amine-epoxy adduct structure restricts molecular motion, thereby raising the glass transition temperature. The flexible ether linkages positioned at the phthalocyanine macrocycle periphery and within the aliphatic epoxy adduct contribute to a well-  
10 defined glass transition temperature and a lowered viscosity above it.

Other substituted phthalocyanines with various pendant groups (e.g. (cumylphenoxy, butoxy) exhibit birefringence under crossed polarizers. Dark field optical microscope  
15 observations for the phthalocyanines of the present invention showed no detectable birefringence when the phthalocyanine films were cast from solution and thermally cycled above their glass transition temperatures. Differential scanning  
20 calorimetry thermograms for both the lead and metal-free phthalocyanines display well-defined glass transition temperatures at 65°C and 80°C and no melting or other detectable phase transitions (Fig. 1 a, b).

At the molecular level, when a co-facial phthalocyanine dimer or a higher aggregate forms, the  $\pi$ - $\pi^*$  transition (Q-  
25

band) is perturbed. In the metal-free phthalocyanine electronic spectrum, the monomer Q-band is converted to a broadened and blue-shifted transition corresponding to an associated species. Comparative spectra of this phthalocyanine in a dilute  $\text{CHCl}_3$  solution ( $10^{-6}\text{M}$ ) and as a solid-state glassy thin film are shown in Figure 2(a, b). The spectrum of the dilute solution corresponds to that for an isolated phthalocyanine monomer, whereas, the spectrum of the film displays characteristics of significant co-facial association. At temperatures above the glass transition, the solid state Q-band displays a very slight spectroscopic shift in the direction of the monomer, but the spectral lineshape of the associated species predominates. The molecular design of this example successfully promotes a glassy morphology, but does not appear to suppress the strong tendency of the phthalocyanine molecules to associate co-facially. This short range molecular order is not sufficient to cause visually observable scattering or macroscopic birefringence. If a transition from short range order to long range order is considered to be the scattering of visible light or the optical magnification limit for observable birefringence, this would occur at a domain size on the order of 500 nm. Such a domain might accommodate 50 to 500 phthalocyanine molecules. This example ( $\text{H}_2\text{Pc}(\text{PGE3Ap})_4$ ) is isotropic down to this threshold.

Q-bands for  $(\text{PbPc}(\text{PGE3Ap})_4)$  are shown in Figure 2 (c, d) for a dilute solution and for a thin film. These spectra are remarkably similar, predominantly exhibiting a monomer Q-band in both the solution and solid film spectra. The thin film spectrum exhibits a small red-shift with slight peak broadening the appearance of a broad peak under the Q-band. In contrast with spectra observed for the metal-free phthalocyanine, these data indicate that the introduction of a large metal ion such as  $\text{Pb}^{2+}$  which is thought to lie out of the plane of the Pc ring disrupts the short range co-facial oligomer association at the molecular level. As a result, films of this Pc appear isotropic down to a molecular size domain, unlike films of the metal free phthalocyanine which was described above as isotropic down to a domain size of approximately 500 nm.

The nonlinear optical properties of a thin film of  $\text{PbPc}(\text{PGE3Ap})_4$  at 590 nm were measured via nonlinear absorption, picosecond time-resolved degenerate four-wave mixing and broadband transient absorption experiments. These experiments, showed that a major component of the nonlinear optical response at this wavelength arises from optical pumping of the excited electronic state. This is presented in Figure 3 which shows the observed change in optical density as a function of wavelength, measured with a time delayed white light continuum, ~1 nsec after excitation with

a 1.2 psec pulse at 590 nm. An increase in absorbance is seen in the wavelength range 420 nm to >580 nm. This demonstrates that this phthalocyanine material has a strongly absorbing excited state with a lifetime longer than 1 nsec. The absorption coefficient for this excited state exceeds that for the ground state over a substantial portion of the visible region of the spectrum. This makes this phthalocyanine appealing as a potentially useful thin film optical limiter material.

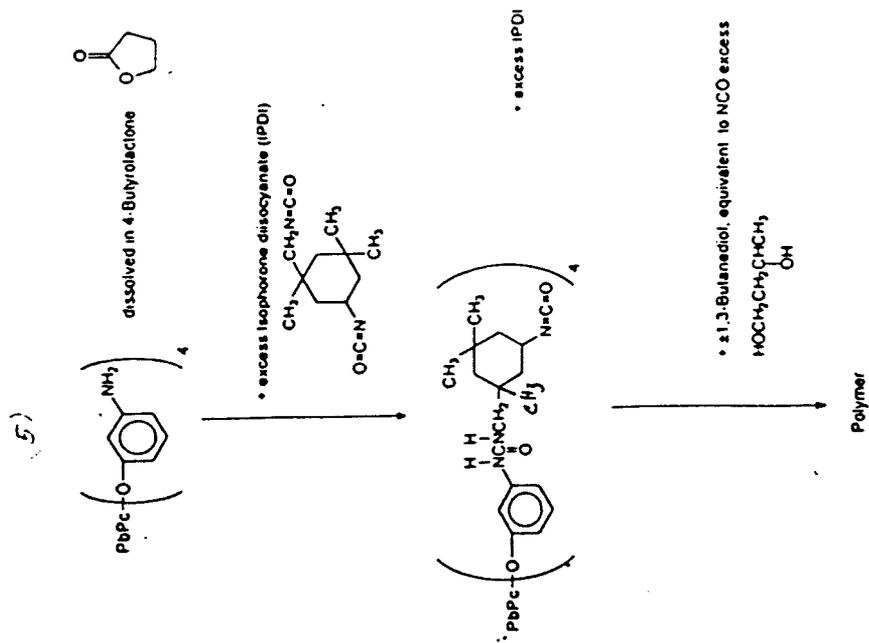
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EXAMPLE 2  
IRREVERSIBLY PROCESSED ORGANIC DYE

The chemical synthesis of an irreversibly processed organic dye thermoset glass, is presented in Scheme II, A, B, C. Procedures for the synthesis of those compounds not commercially available are described below.

15  
All reagents and solvents were of reagent grade quality, purchased commercially and used without further purification unless otherwise noted. Spectroscopic data were obtained from the following instruments: IR/Perkin-Elmer Model 1800 FTIR, IR/Nicolet 750 Magna-IR (IR data was collected either from thin films/NaCl supported or KBr pellets), UV-VIS/Cary 2390 spectrophotometer and <sup>1</sup>H and <sup>13</sup>C NMR/Bruker AC-300 spectrometer at ambient temperature. Thermal analyses (DSC and TGA) were conducted with a DuPont 2100 Thermal Analyzer interfaced to a DuPont 910 DSC and a 950 TGA module.



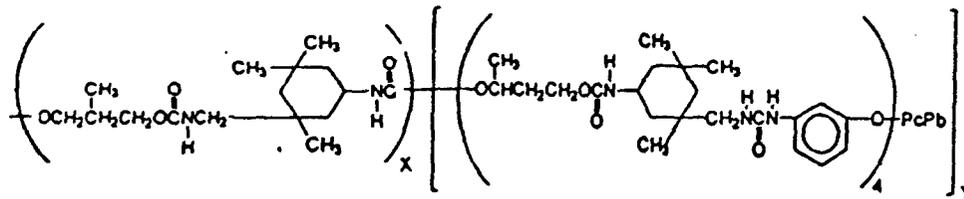
# Synthesis of a Urethane/Pb Phthalocyanine Copolymer



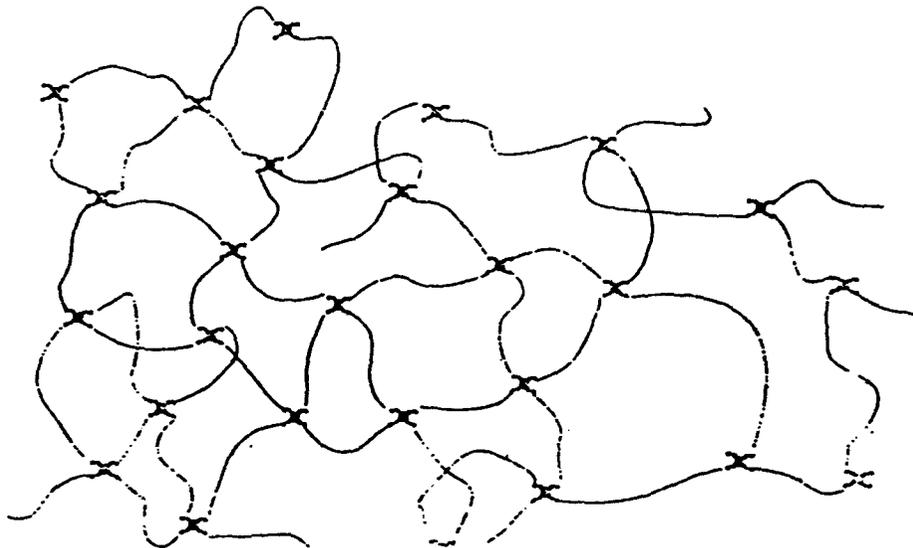
SCHEME II-B

# PbF/Urethane/Butanediol Copolymer Structure

## Phthalocyanine Unit



## Macro Structure



SCHEME II-C

4-(3-Aminophenoxy)phthalonitrile (1). DMSO (50 mL, 4-nitrophthalonitrile (10.8 g, 62 mmol), and *o*-aminophenol (7.1 g, 65 mmol) are stirred under N<sub>2</sub> until a solution is formed. Stirring is continued while anhydrous potassium carbonate (14.8 g, 107 mmol) is added in 1-g increments over 6 h, and the resulting mixture is stirred overnight at room temperature. The reaction mixture is filtered, and the filtrate is added dropwise to 700 mL of water to reprecipitate 14.1 g of crude product. The product is recrystallized from hot methanol yielding 9.1 g (39 mmol, 63%) of a golden-yellow microcrystalline solid: m.p. 175.5-176.5°C; the IR spectrum is shown in Figure 4a; <sup>1</sup>H NMR (300 MHz, 0.056 M, DMSO-*d*<sub>6</sub>) is given in Figure 5a; <sup>13</sup>C NMR (300 MHz, 0.056 M, DMSO-*d*<sub>6</sub>);  $\delta$  = 161.43, 154.60, 151.01, 136.22, 130.68, 122.45, 121.72, 116.53, 115.94, 115.43, 111.36, 107.62, 106.63 and 104.84 ppm.

4-(3-Phthalimidophenoxy)phthalonitrile (2). A DMF (30 mL) solution of 4-(3-aminophenoxy)phthalonitrile (1) (11.5g, 49 mmol), and phthalic anhydride (7.4 g, 50 mmol) is refluxed under N<sub>2</sub> for 4h. The solvent is removed by distillation under vacuum at 90°C. The resulting yellow/brown solid is crushed and then recrystallized from hot methanol, yielding 12.0 g (33 mmol, 67%) of a creamy colorless powder; m.p. 160-162°C; the IR spectrum is shown in Figure 4b; <sup>1</sup>H NMR (300

MHz, 0.049 M, DMSO- $d_6$ ) is given in Figure 5b;  $^{13}\text{C}$  NMR (300 MHz, 0.049 M, DMSO- $d_6$ ;  $\delta$  = 166.66, 160.34, 153.94, 136.40, 134.81, 133.63, 131.46, 130.72, 124.31, 123.50, 123.23, 122.52, 119.45, 118.83, 115.82, 115.34 and 108.74 ppm.

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10  
15  
Tetrakis (3-phthalimidophenoxy)phthalocyanine (3). A mixture of 4-(3-phthalimidophenoxy)phthalonitrile (2) (0.2 g, 0.54 mmol) and hydroquinone (20 mg, 0.018 mmol) is reacted in a sealed vial at 180°C for 18 h. The solid product is crushed and washed sequentially with THF, acetone, methanol and diethyl ether to yield 0.2 g (0.1 mmol, 89%) of a purplish/green microcrystalline solid which did not melt below 325°C;  $\lambda_{\text{max}}$  (slightly soluble in DMSO) 702, 666, 641, and 607 nm; the IR is shown in Figure 4c; lack of solubility precluded NMR characterization of the product.

20  
Tetrakis (3-aminophenoxy)phthalocyanine (4). Tetrakis (3-phthalimidophenoxy)phthalocyanine (110 mg, 0.07 mmol) is mixed with 5 mL of THF. Hydrazine (2.0 g, 64 mmol) is added and the mixture is stirred at room temperature for 30 minutes, and then added dropwise to 500 mL of rapidly stirred methanol. The green precipitate is collected, washed with methanol and diethyl ether and allowed to dry in air. The product is a green, microcrystalline solid (40 mg, 0.04 mmol, 60%) that did not melt below 325°C. The IR spectrum is shown

in Figure 6a; UV/VIS (Figure 7a);  $\lambda_{\max}$ (THF) ( $\epsilon \times 10^{-4} \text{M}^{-1}\text{-cm}^{-1}$ ) 711(9.6), 643 (2.1) and 361 nm (3.3);  $^1\text{H}$  NMR spectrum (300 MHz, 0.030 M, THF- $d_4$ ) is given in Figure 8a;  $^{13}\text{C}$  NMR (300 MHz, DMSO- $d$ );  $\delta = 157.63, 150.89, 145.95, 135.866, 130.54, 122.94,$   
5 120.20, 110.56, 107.08 and 105.40 ppm. The saturation solubility in THF is 3.3% (w/w).

Lead tetrakis-(3-aminophenoxy)phthalocyanine (5). To a solution of 0.3 g (0.8 mmol) of lead acetylacetonate in 5 mL of warm dimethyl sulfoxide, 0.2 g (0.2 mmol) of tetrakis (3-aminophenoxy)phthalocyanine (4) is added with stirring. The  
10 reaction mixture is stirred for 5 min. and then added to rapidly-stirred water (0.5 L) and the precipitate is collected, washed in turn with water, methanol and diethyl ether, and dried under vacuum overnight, yielding 0.18 g  
15 (0.14 mmol, 70%) of a green microcrystalline product which did not melt below 325°C. The IR spectrum is shown in Figure 6b; UV/VIS (Figure 7b);  $\lambda_{\max}$ (THF) ( $\epsilon \times 10^{-4} \text{M}^{-1}\text{-cm}^{-1}$ ) 711 (9.6), 643 (2.1), and 361 nm (3.3);  $^1\text{H}$  NMR (300 MHz, THF- $d_4$ ) is given in Figure 8b.

20 Copolymers of 5 and isophorone diisocyanate. Lead tetrakis (3-aminophenoxy)phthalocyanine (5) is dissolved in  $\gamma$ -butyrolactone and reacted with an excess of isophorone diisocyanate at room temperature for 16 h. Then 1,3 butanediol is added and the mixture is heated for 72 h at

40°C to yield a urethane polymer containing lead phthalocyanine groups in the backbone (~5.9% by weight). For a thin film of the solvent free copolymer, the UV/VIS spectrum is presented in Figure 7c. DSC data are shown in Figure 9.

Two issues are important in the strategy of synthesizing amine functionalized phthalocyanine monomers. First is the selection of an amine bearing pendant group that is of the proper size and symmetry to induce solvent and comonomer solubility. Second is whether the amine functionality should be incorporated before or after the phthalocyanine forming reaction.

One selected pendent group was the aminophenoxy structure for the purpose of subsequent phthalocyanine solubilization and to take advantage of a facile nuclear aromatic nitro displacement reaction. The 4-(3-aminophenoxy) phthalonitrile is obtained in good yield. However, at elevated temperatures, the amino group reacts with the phthalonitrile to yield a non-phthalocyanine structure. This is observed in the differential scanning calorimetry (DSC) thermogram of 4-(3-aminophenoxy)phthalonitrile in Figure 10 where melting occurs at 174°C and the side reaction exotherm at 262°C. The product of this side reaction is an insoluble mass with an infrared spectrum indicating that the amine hydrogen and nitrile groups are consumed, but that metal-free

phthalocyanine (diagnostic bands at 3290 and 1010  $\text{cm}^{-1}$ ) is not formed.

To prevent an amine-phthalonitrile reaction, the amine groups are blocked by conversion to the phthalimide (2) by reaction with phthalic anhydride. This is clearly demonstrated by the disappearance of the N-H stretch in the IR (3365 and 3449  $\text{cm}^{-1}$ ) and the appearance of the carbonyl stretch at 1723  $\text{cm}^{-1}$  (Figure 4b). The  $^1\text{H}$  NMR data also show this conversion via the disappearance of the free amine signal at  $\delta = 5.4$  (Figure 5b). The amine-blocked phthalonitrile (2) is then readily converted to the phthalocyanine (3) by a redox reaction with hydroquinone. The IR spectrum is consistent with this transformation as the nitrile stretch at 2236  $\text{cm}^{-1}$  is replaced by the phthalocyanine bands at 3290 and 1010  $\text{cm}^{-1}$  (Figure 4c). The limited solubility of this compound (probably arising from the rigid phthalimide peripheral groups) did not allow for sufficient solubility to obtain an NMR spectrum. In the final step, the phthalimide blocking group is removed by reaction with hydrazine to regenerate the amine (4). The IR spectrum displays a complex band structure  $\sim 3300 \text{ cm}^{-1}$  corresponding to the peripheral amine and phthalocyanine cavity N-H stretches, as well as the disappearance of the carbonyl band at 1723  $\text{cm}^{-1}$  (Figure 6a). The  $^1\text{H}$  NMR (Figure 7a) is also consistent with (4) as the reaction product, the

phthalocyanine cavity N-H band being clearly visible at  $\delta =$   
-4.8 ppm as is the peripheral group amine signal at  $\delta = 4.8$   
ppm. The proposed structure of (4) should result in a ratio  
of 1:4:14 for the integrated NMR intensities for the central  
ring protons; free amine protons; aryl protons. The measured  
5 ratio is 1:4:16.

In addition to forming soluble intermediates (except for  
the imidophthalocyanine) this synthesis differs from many  
phthalocyanine forming schemes in that it does not employ  
10 metal salts which may complex and contaminate the final  
phthalocyanine product. In our synthesis route, the metal-  
free tetrakis (3-aminophenoxy)phthalocyanine (4) is converted  
to the lead analog (5) by a simple one-step exchange reaction  
in good yield (~70%) using the metal acetylacetonate. This  
15 conversion route has been successfully used with a number of  
different phthalocyanine and naphthalocyanine systems. It is  
interesting to note that incorporation of the lead atom into  
the cavity of the phthalocyanine system resulted in a  
significant improvement in the resolution of the aromatic  
20 proton region of the NMR with shifts of ~1ppm to several  
bands (Figure 8a and 8b). Apparently, the lead ion acts as  
an NMR shift reagent, affecting the ring current associated  
with the phthalocyanine macrocycle.

By reacting lead phthalocyanine (5) with 1,3 butanediol  
25 and isophorone diisocyanate in  $\gamma$ -butyrolactone, a

polyurethane copolymer is formed. Polymers formed from 5 and isophorone diisocyanate alone are intractable while inclusion of the 1,3 butanediol incorporates urethane linkages in the backbone, increasing the flexibility of the polymer. The lead phthalocyanine copolymer formed in this fashion is a transparent glassy solid (soluble in  $\gamma$ -butyrolactone) that can be processed into thin films (on the order of 15-30 microns at 150°C. The DSC trace (Figure 9) is indicative of a relatively non-crystalline polymer. TGA data shows that thermal degradation (under N<sub>2</sub>) does not occur until about 180°C and is complete by 525°C with approximately 5% char yield.

It is particularly interesting to note that the Q band ( $\pi$ - $\pi^*$  transition) of the lead phthalocyanine (5) is not appreciably broadened or blue-shifted when the phthalocyanine entity is incorporated into the urethane-phthalocyanine copolymer (Figure 7). A small amount of inhomogeneous broadening is expected as the phthalocyanine molecules within the copolymer undoubtedly find themselves in slightly different environments. We interpret the UV/VIS data to indicate that there is no significant aggregation or association of phthalocyanine molecules in the polymer, i.e., they are isolated chromophores.

Optical measurements of a urethane copolymer film containing 5.9% (w/w) of lead phthalocyanine (5) indicated

that its nonlinear optical properties are similar to those of the analogous lead-substituted phthalocyanine  $PbPc(CP)_4$ , tetrakis(cumylphenoxy)phthalocyanine), in solution. There is a strong excited state absorption in the 450-600 nm region which persists with little or no change for longer than 10 nsec and is larger than that of the ground state, except near the intense ground state Q-band absorption. Tetrakis (cumylphenoxy)phthalocyanine in  $CHCl_3$  shows a similar broad-band transient absorption with a pulse-width limited rise time  $\sim 2$  psec) and  $>1$  nsec decay time. Clearly, changes in the peripheral substitution and the incorporation of the phthalocyanine into a copolymer (at this concentration) do not appear to alter the basic character of the nonlinear response in these lead-substituted phthalocyanines.

Transient absorption and degenerate four-wave mixing measurements on a thin film Pb-phthalocyanine-urethane-butenediol copolymer show that this material has a strong excited state absorption in the visible and near-IR. Degenerate four wave mixing (DFWM) measurements at 590 nm show both an instantaneous response ( $\tau < 1$  ps) and a long lived response from an excited state with a rise time of less than 1 ps, and a decay time of  $>10$  ns. These non-linear optical properties indicate that the lead phthalocyanine-urethane-butenediol system has potential for use in optical limiting devices.

## EXPERIMENTAL

The experimental apparatus consists of a dye laser that is synchronously pumped by a CW mode-locked, doubled Nd/Yag laser. The output of the dye laser is regeneratively amplified to provide 1.2 ps pulses with energies up to 1 mJ. Nonlinear transmission experiments are performed by directing the output of the laser through the sample and measuring the transmitted intensity as a function of incident intensity. Transient absorption measurements are made by splitting the laser output into two beams. The first, or pump beam, is sent through an optical delay line and is used to excite a portion of the sample; the unexcited portion of the sample serves as the reference. The second beam is focussed into a water cell to provide a broad band, ps, continuum. The continuum is filtered, recollimated, and directed onto the sample and the reference. The variable delay in the pump beam assures control of the relative arrival times of the excitation and probe beams. The transmitted light from both sample and reference is focussed onto the slits of a monochromator and the output imaged onto a CCD array. The change in optical density due to the formation of the excited state is calculated from the ratio of sample to reference signal after subtraction of the background signals. The polarization vector of the excitation beam is fixed at  $54.7^\circ$

relative to the polarization vector of the continuum to  
remove any effects due to orientational relaxation.

For the degenerate four-wave mixing experiments, the  
output of the laser is split into three beams which are  
5 overlapped in the sample in the phase conjugate geometry.  
The phase conjugate signal intensity is measure as a function  
of the incident intensity and is fit to a cubic dependence.  
The resulting cubic coefficient is always measured relative  
to that observed from CS<sub>2</sub> in the same apparatus. The time  
10 dependence of the phase conjugate signal is measured by  
delaying the arrival of the back pump beam. The polarization  
dependencies are measured by rotating  $\lambda/2$  wave plate in the  
probe beam.

## 15 RESULTS

The linear absorption spectrum of a thin film, nominally  
25  $\mu\text{m}$  thick, of the Pb phthalocyanine (Pc)-butanediol-  
urethane copolymer(5.9% by weight Pc) is shown in Fig. 11.  
The absorption spectrum is typical of a phthalocyanine. It  
20 has a strong  $\pi-\pi^*$  transition, called the Q band, peaked near  
710 nm, with a vibronic shoulder near 650 nm. There is a  
window of low absorption from about 430 nm to 610 nm. The  
first absorption peak in the UV occurs at about 370 nm. The  
position of the absorption maxima in the polymer are similar  
25 to those observed in solutions of Pb tetrakis(cumylphenoxy)

phthalocyanine (PbPc(CP)<sub>4</sub>) in CHCl<sub>3</sub>. The absorption bands in this polymer spectrum are somewhat broader than those observed for solutions.

5 Transient absorption spectra of this copolymer were measured using an ~45 μm thick film. The excitation wavelength of 675 nm, is close to resonance with the Q band. The observed change in absorbance (ΔO.D.) is shown as a function of wavelength at 40 ps and 1 ns after the excitation pulse in Fig. 12. An increase in absorbance upon excitation is observed between 430 nm and 610 nm and is due to a strong  
10 excited state absorption. The spectra do not evolve significantly between 40 ps and 1 ns, which shows that excited state responsible for this absorption has a life time substantially longer than 1 ns.

15 The excited state absorption cross sections  $\sigma_{ex}$ , can be found from the data in Figs. 11 and 12, if the excited state number density,  $N_{ex}$ , is known. At 590 nm, an approximate value of  $\sigma_{ex} \sim 2.5 \times 10^{-17} \text{ cm}^2$  was derived from this data. The estimated  $\sigma_{ex}$  was found to be constant to within a factor of  
20 2 from 230 nm to 620 nm. This can be seen qualitatively from Fig. 12, where the shape of the observed ΔO.D. follows the inverse of the ground state absorbance given in Fig. 11. The excited state responsible for this absorption has a lifetime substantially longer than 1 ns.

The nonlinear transmission of the ~45  $\mu\text{m}$  film, measured at 590.5  $\mu\text{m}$  using the same laser system, is shown in Figure 13. The copolymer is a reverse saturable absorber at this wavelength, i.e., the nonlinear coefficient,  $\alpha_{nl}$ ,<sup>7</sup> is positive in the equation:

$$\alpha(I) = \alpha_0 + \alpha_{nl} I \quad (1)$$

here  $\alpha(I)$  is the observed absorption coefficient,  $\alpha_0$  is the low intensity value. The empirical  $\alpha_{nl} = 34 \text{ cm/GW}$  for the 1.2 ps pulses was derived from the data in Fig. 13. using the equations given by Van Stryland et al. A similar experiment using 35 ps pulses at 1064 nm showed that the polymer was also a reverse saturable absorber at this wavelength with  $\alpha_{nl} = 0.9 \text{ cm/GW}$ .

Degenerate four-wave mixing (DGWM) experiments were performed at 590.5 nm on the same film. The observed phase conjugate intensity was found to follow the expected cubic dependence on the laser intensity at low intensities. The data reduction methods have been described elsewhere. In brief, the signal, S, is fit via least squares analysis yielding a coefficient for the cubic component of the phase conjugate intensity as a function of the incident laser intensity. It will be seen below that the copolymer clearly shows contributions to the signal from processes with

lifetimes longer than the laser pulse width. This means that the nonlinear response has not attained steady state and is more properly described by an envelope response function rather than as  $X^{(3)}$ . Accordingly, in Table 1, the magnitude of the nonlinear response is given as a  $X_{\text{eff}}^{(3)}$ . The significance of this quantity will be discussed below.

The DFWM signal was measured as a function of the delay time of the back pump beam. The results for all the beams polarized parallel to each other,  $S_{\text{xxxx}}$ , are shown in Figure 14 and on an expanded timescale in Fig. 15. The time dependence of the signal has at least two components. There is a fast component which follows the laser pulse (see Fig. 15) and a second component with a long decay time. The latter signal is due to an optically pumped excited state, and is consistent with the long lived absorption observed in the transient absorption experiment (Fig. 12). Analysis of the DFWM data shows that the excited state appears in a time short compared to the laser pulse and decays less than 10% in 1200 ps. Thus the rise time is less than 1 ps and the lifetime of the excited state is thus at least 10 ns. The fast component in Fig. 15 could be due to an instantaneous electronic  $X^{(3)}$ . Alternately, it could be due to a higher excited state which relaxes within the laser pulse width to the long lived state.

DFWM experiments were also performed with the probe and signal beams polarized orthogonal to the two pump beams, i.e., the  $xyyx$  polarization. The ratio of the signal in this polarization,  $S_{xyyx}$ , To  $S_{xxxx}$  was 0.015 at zero time delay. The ratio does not change significantly for delays up to 1 ns. The observed ratio is close to the value of 0.0156 ( $=.125^2$ ) expected for the four-wave mixing signal from optically pumping a transition for which the upper state is degenerate. This is the case for 590.5 nm excitation of the Q-band in PbPc.

The temporal dependence of the  $S_{xyyx}$  was similar to that of  $S_{xxxx}$ ; it showed no significant decay for times up to 1 ns. Both the upper state lifetime and the orientational correlation time of the phthalocyanine moiety in the polymer is  $> 10$  ns. The implication is that the phthalocyanine moieties do not reorient in the solid on this time scale. Furthermore, since energy migration between randomly oriented phthalocyanine sites via a Forster mechanism would also result in a loss of orientational order, any such energy migration must be on the nanosecond time scale or slower.

When excited at higher fluences, the temporal response of the DFWM signal,  $S_{xxxx}$ , shows a minimum near 550 ps and a small rise at times  $> 600$  ps. The appearance of this minimum is fluence dependent, consistent with an acoustic signal where the sample  $n_2$  is of opposite signal to that of the

acoustic signal. The sign of an acoustic  $n_2$  signal is negative, therefore, the sample  $n_2$  and  $\text{Re}X_{\text{eff}}^{(3)}$  should be positive. The magnitude of the acoustic response observed for the copolymer is less than is observed for comparable solutions  $\text{PbPc}(\text{CP})_4$ , consistent with smaller thermal expansivities and larger heat capacities for polymers relative to common solvents.

Both the DFWM data at 590.5 nm and the transient absorption experiments pumped at 675 nm show evidence of a long lived excited state. Since both 590 nm and 675 nm are within the Q-band absorption, it is likely that same excited state is populated in both experiments. Transient absorption shows that this material is a reverse saturable absorber between 430 and 610 nm. The excited state absorbs more strongly than the ground state throughout this spectral region. This observation was confirmed at 590.5 nm where the measured nonlinear coefficient,  $\alpha_{\text{nl}}$ , is positive.

The coefficient of nonlinear absorption measured at 590 nm in the non-linear transmission (NLT) experiment is equivalent to  $t=0$  ps delay. It can also be derived across the visible range at 40 and 1200 ps after excitation from the transient absorption experiments. The two values are not necessarily the same since the former can have contributions from either a direct two-photon transition or a sequential two-photon absorption. An upper limit to the difference

between the absorption cross sections of the ground and excited states can be estimated from the  $\alpha_{nl}$  observed in the NLT experiment if one assumes that only sequential processes occur. The effective absorption coefficient,  $\alpha(I)$ , in an optically pumped four level system was given by Hercher as

$$\alpha(I) = b_0 + \left( \frac{a_0 - b_0}{1 + \frac{I}{I_s}} \right) * \left( 1 + \frac{I}{I_s} \exp \left( - \left( 1 + \frac{I}{I_s} \right) \left( \frac{I}{\tau} \right) \right) \right) \quad (2)$$

where  $a_0 = N_0 \sigma_g$ , and is identical to  $\alpha_0$  defined above and  $b_0 = N_0 \sigma_{ex}$ ,  $N_0$  is the number density of the absorber,  $I$  is the incident intensity,  $I_s$  is the saturation intensity of the transition,  $\tau$  is the excited state lifetime, and  $t$  is the duration of the irradiation. For  $I \ll I_s$  and  $t \ll \tau$  equation 2 can be approximated by

$$\alpha(I) = \alpha_0 + \frac{(\sigma_{ex} - \sigma_g)}{h\nu} \alpha_0 I t \quad (3)$$

In this limit,  $\alpha$  is fluence dependent. The coefficient of  $I$  in the second term of equation 3 can be identified with  $\alpha_{nl}$

as defined in equation 1, i.e.

$$\alpha_{nl}(t) = \frac{(\sigma_{ex} - \sigma_g)}{h\nu} \alpha_0 t \quad (4)$$

5

$\alpha_{nl}$  is a function of the irradiation time,  $t$ . From the observed  $\alpha_{nl}$  at 590.5 nm, the derived  $(\sigma_{ex} - \sigma_g) \leq -4 \times 10^{-17} \text{ cm}^2$ . This gives an upper limit for  $\sigma_{ex}$  which is a little larger than the estimate from the transient absorption experiment where there is a 40 ps delay between the pump and probe.

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The DFWM signal for this material contains contributions from processes with relaxation times longer than the laser pulse. The nonlinear response is thus in the transient regime and probably results from mechanisms slower than the material dephasing times. The observed signal is primarily due to the excited state and acoustic gratings formed by the interaction of the material with the interfering beams. The diffraction efficiency of these gratings is determined by the nonlinear refractive index,  $n_{nl}$ , and nonlinear absorption,  $\alpha_{nl}$ , of the material. It is convenient to express these quantities as the real and imaginary parts of the change in the optical susceptibility. The term, "effective  $\chi^{(3)}$ ", has been used for the latter quantity and this is the quantity reported in Table 1. The effective  $\chi^{(3)}$  is the induced  $(\partial\chi/\partial E^2)_{E=0}$  for the laser pulses used. It is equivalent to

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the usual  $\chi^{(3)}$  in the limit that the pulse width is long compared molecular processes involved. For laser pulses shorter than the lifetime of the upper state,  $\chi^{(3)}_{\text{eff}}$  will depend on the pulse width. Similarly, equation 4 shows that  $\alpha_{\text{nl}}$  depends on the laser pulse width and  $n_{\text{nl}}$  should have a similar dependence.

The nonlinear refractive index,  $n_{\text{nl}}$ , is given in Table 1 is derived from the measured  $\chi^{(3)}_{\text{eff}}$  and the measured  $\alpha_{\text{nl}}$ . It can be shown that  $\chi^{(3)}_{\text{eff}}$  is predominantly real. Thus in the DFWM experiment, the signal is due predominately to the refractive grating rather than the absorptive contribution. The implication is that there is a relatively large change in the refractive index between the ground and excited states of the phthalocyanine in this copolymer at 590 nm.

Table 1

Summary of Optical Properties for PbPc/Urethane Thin film

	590 nm	1064 nm
$\alpha_0$	300 cm <sup>-1</sup>	4.8 cm <sup>-1</sup>
$\alpha_{nl}(1.2 \text{ ps})$	34 cm/GW	0.9 cm/GW
$n_{nl}(1.2 \text{ ps})$	1.1x10 <sup>-3</sup> cm <sup>2</sup> /GW	
$\alpha_{nl}/\alpha_0$	13x10 <sup>-2</sup> cm <sup>2</sup> /GW	18x10 <sup>-2</sup> cm <sup>2</sup> /GW
$(\chi^{(3)}_{xxx})_{eff}(1.2 \text{ ps})$	1.8x10 <sup>-11</sup> esu	
$(\chi^{(3)}_{xyyz})_{eff}(1.2 \text{ ps})$	2.3x10 <sup>-12</sup> esu	
$(S_{xyyz}/S_{xxxx})^{1/2}$	0.126	

Transient absorption measurements on a thin film of Pb phthalocyanine-urethane-butanediol copolymer that is 5.9% by weight phthalocyanine show that optical pumping of the first  $\pi$ - $\pi^*$  transition (the Q band) of the phthalocyanine gives a strong excited state absorption in the visible and near-IR. The excited state absorption cross section,  $\sigma_{ex}$ , is relatively constant and exceeds  $\sigma_g$  from 430 to 610 nm.  $\sigma_{ex}$  also exceeds  $\sigma_g$  at 1064 nm.

DFWM measurements at 590 nm show that the excited state has rise time of less than 1 ps, and a decay time of >10 ns.

The material's broad excited state absorption which arises quickly and decays slowly makes it a useful reverse saturable absorber over a good fraction of the visible spectrum. The nature of the excited state is not known. Reasonable candidates include the triplet state of the phthalocyanine moiety or a state characteristic of a phthalocyanine aggregate.

This study demonstrates that the thin films of a phthalocyanine-urethane-butanediol copolymer with the phthalocyanine moieties incorporated into the backbone exhibit strong reverse saturable absorption in the visible. The strong reverse saturable absorption is accompanied by a large change in the refractive index. These effects make this material an especially promising candidate for optical limiting devices.

### EXAMPLE 3

The chemical synthesis of another irreversibly processed organic dye thermoset glass is presented in Scheme III. The procedure for the synthesis of these compounds not commercially available and not already described are presented below.

Copolymers of 4 and bisphenol and diglycidyl ether (DGEBA). In order to obtain miscibility, a subequivalence of 4 was added to an excess of DGBA with a small amount of THF

to promote initial solubility. A uniphase blue viscous medium was produced after gentle heating and removal of the solvent under vacuum. The amine content was brought to equivalence by addition of a compatible amine such as

5 Jeffamine™ D-230 polyoxypropylenediamine, supplied by Texaco Chemical Company, eq. wt. 60, and the thermoset was cured at 80°C/9hr, 125°C/8hr and 180°C/1hr. In this manner, four samples with amine equivalence percents of 5.1, 10.5, 14.2 and 24.9% derived from 4 were prepared. These samples were

10 green transparent solids. An attempt to increase the amine equivalence percent of 4 to 100% was unsuccessful. It resulted in phase separation after removal of the THF and incomplete cure after heating.

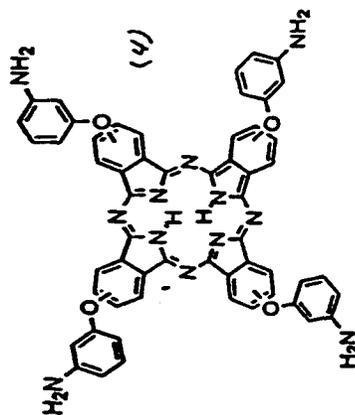
## ABSTRACT

A new class of materials; optically clear, non-birefringent phthalocyanine glasses and their thin film nonlinear optical properties are described. This synthetic approach consists of introducing functionality at the phthalocyanine ring periphery with a design for hydrogen bonding, stereochemical interaction, and irregular symmetry to promote glass formation by inhibiting molecular organization. Additionally, the peripheral functionality depresses the glass transition temperature to a practical processing range. The thin film nonlinear optical properties of these materials exhibit excited state absorption characteristics which give rise to a nonlinear optical response potentially useful for optical limiting. Herein, the design, synthesis and physical properties of metal-free and lead tetrakis (N,N-Bis(3-phenoxy-2-hydroxy-1-propyl)-3-aminophenoxy)phthalocyanines are disclosed. Nonlinear optical properties of the lead phthalocyanine are also presented and discussed. These phthalocyanine materials are melt-processable and form optically isotropic, non-birefringent organic glasses.

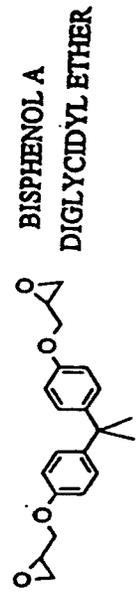
Furthermore, the strategy, synthesis and characterization of a soluble amine functionalized phthalocyanine monomer and two examples of its polymerization

5 into optically transparent glasses are presented and nonlinear optical properties of a lead derivatized polyphthalocyanine film are discussed. The combination of enhanced third-order nonlinear optical properties derived from the phthalocyanine structure with the processing and transparency properties of polymerized glasses offers a promising material for use in optical devices.

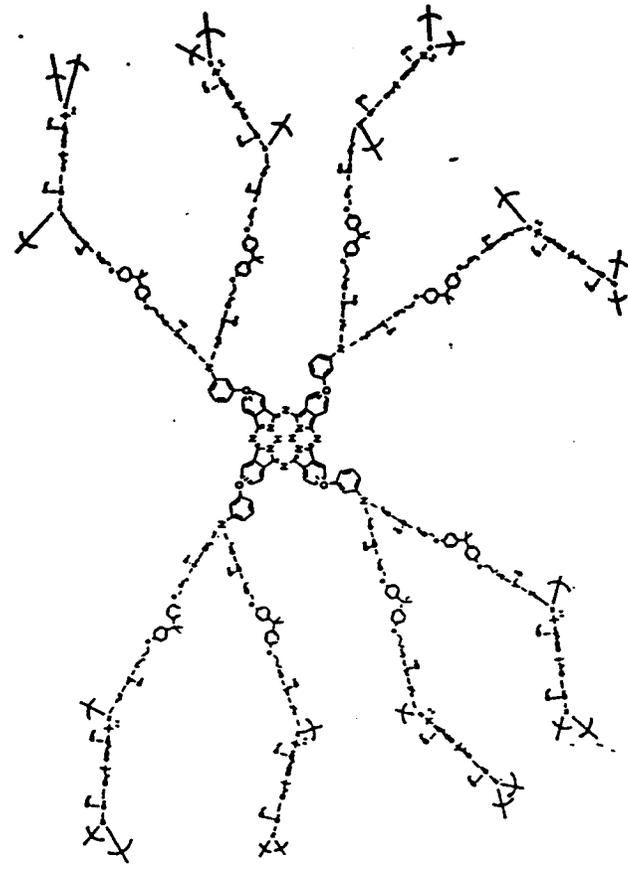
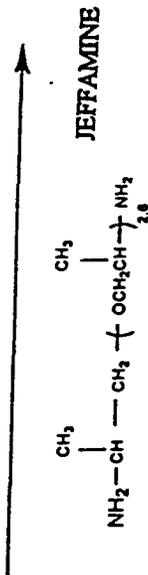
**THERMOSET SYNTHESIS SCHEME**



**TETRAKIS(3-AMINOPHENOXY)  
PHthalOCYANINE**



**BISPHENOL A  
DIGLYCIDYL ETHER**



**TETRAKIS(3-AMINOPHENOXY) PHthalOCYANINE - BISPHENOL A  
DIGLYCIDYL ETHER - JEFFAMINE EPOXY THERMOSET**

**SCHEME III**

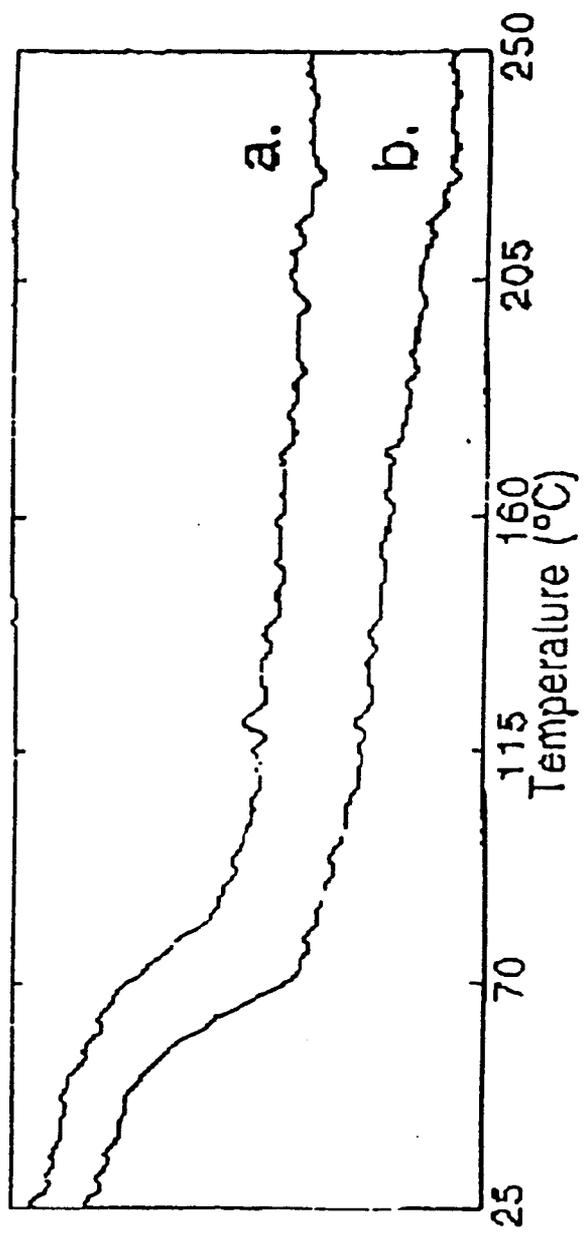


FIGURE 1

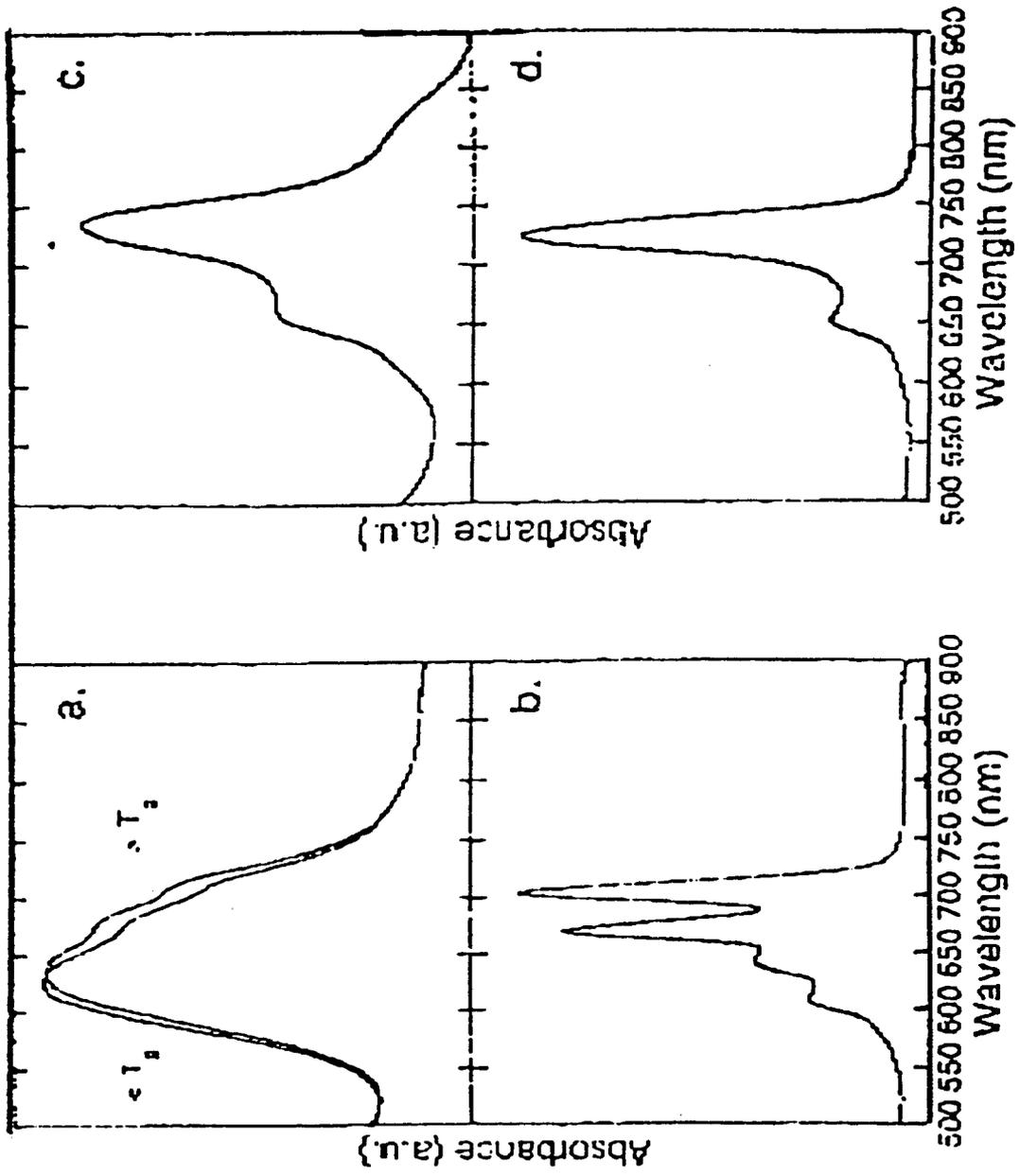


FIGURE 2

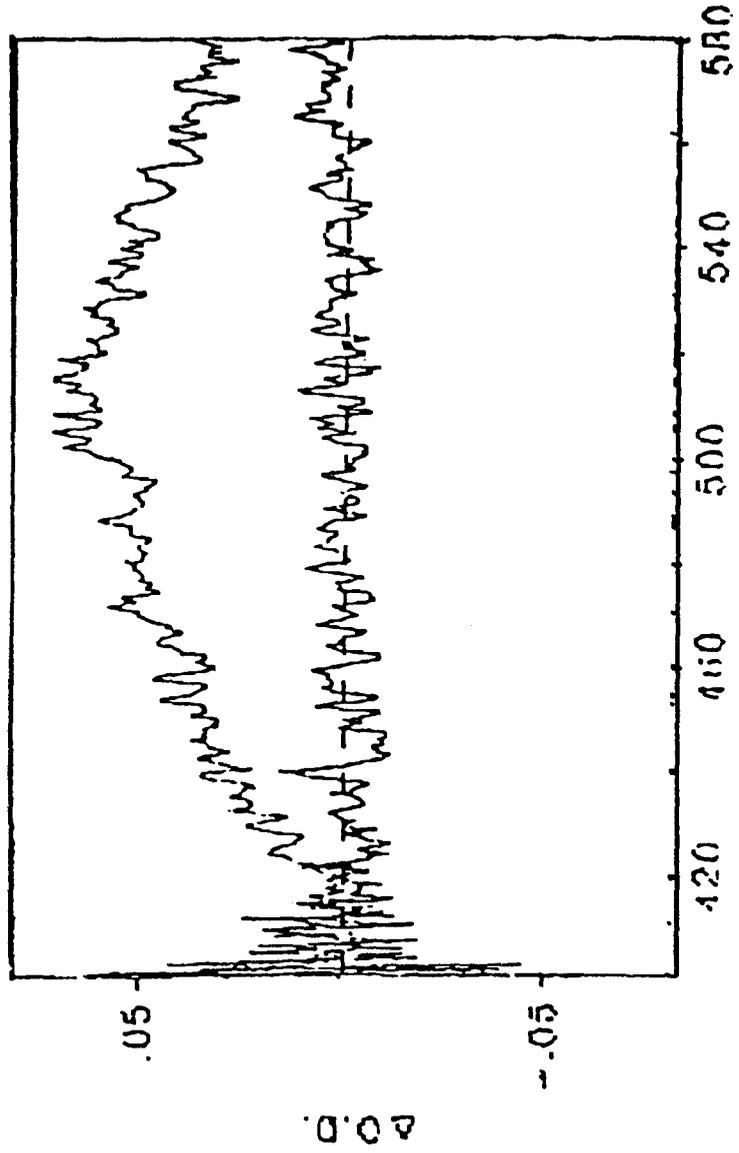


FIGURE 3



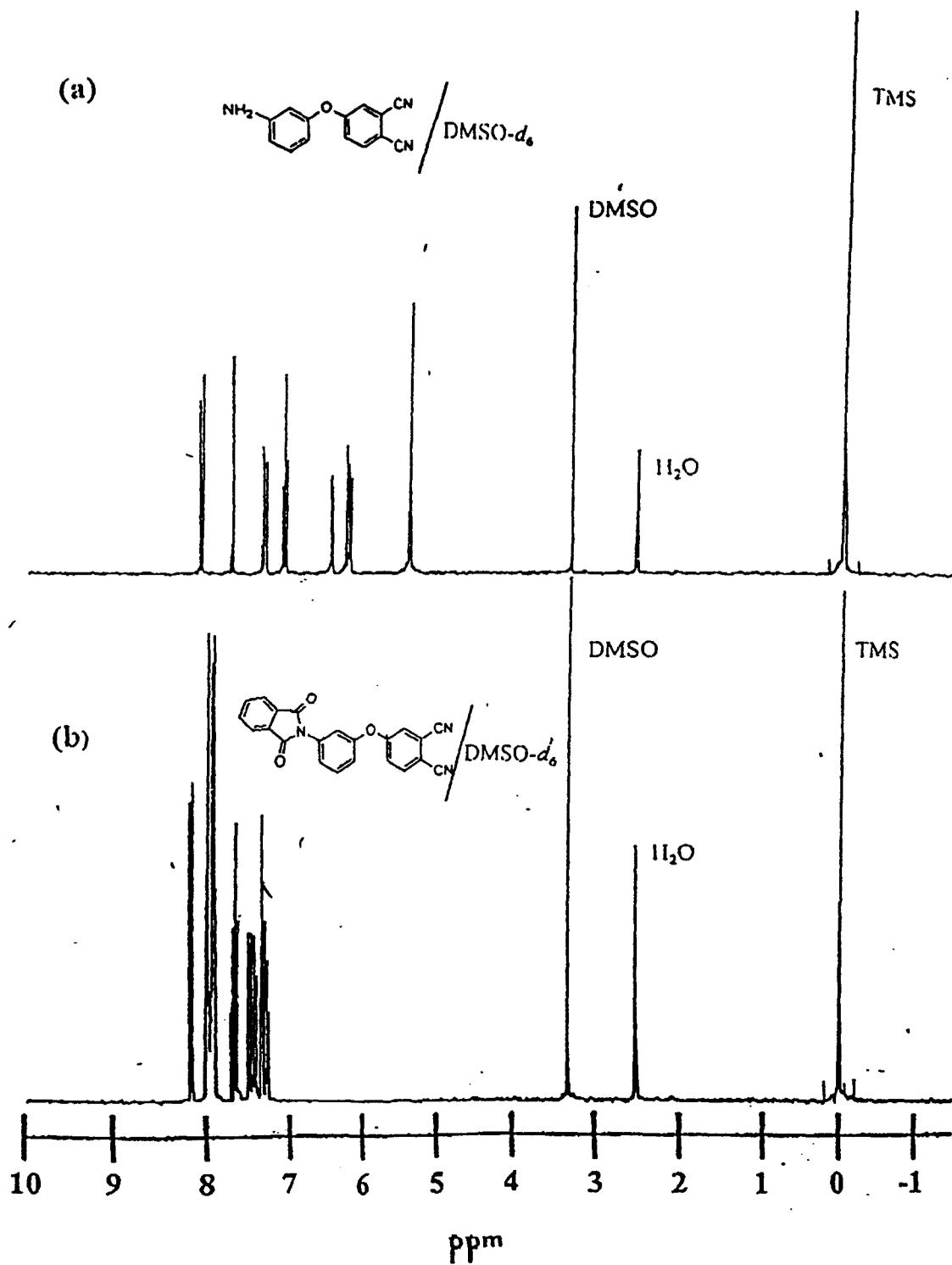
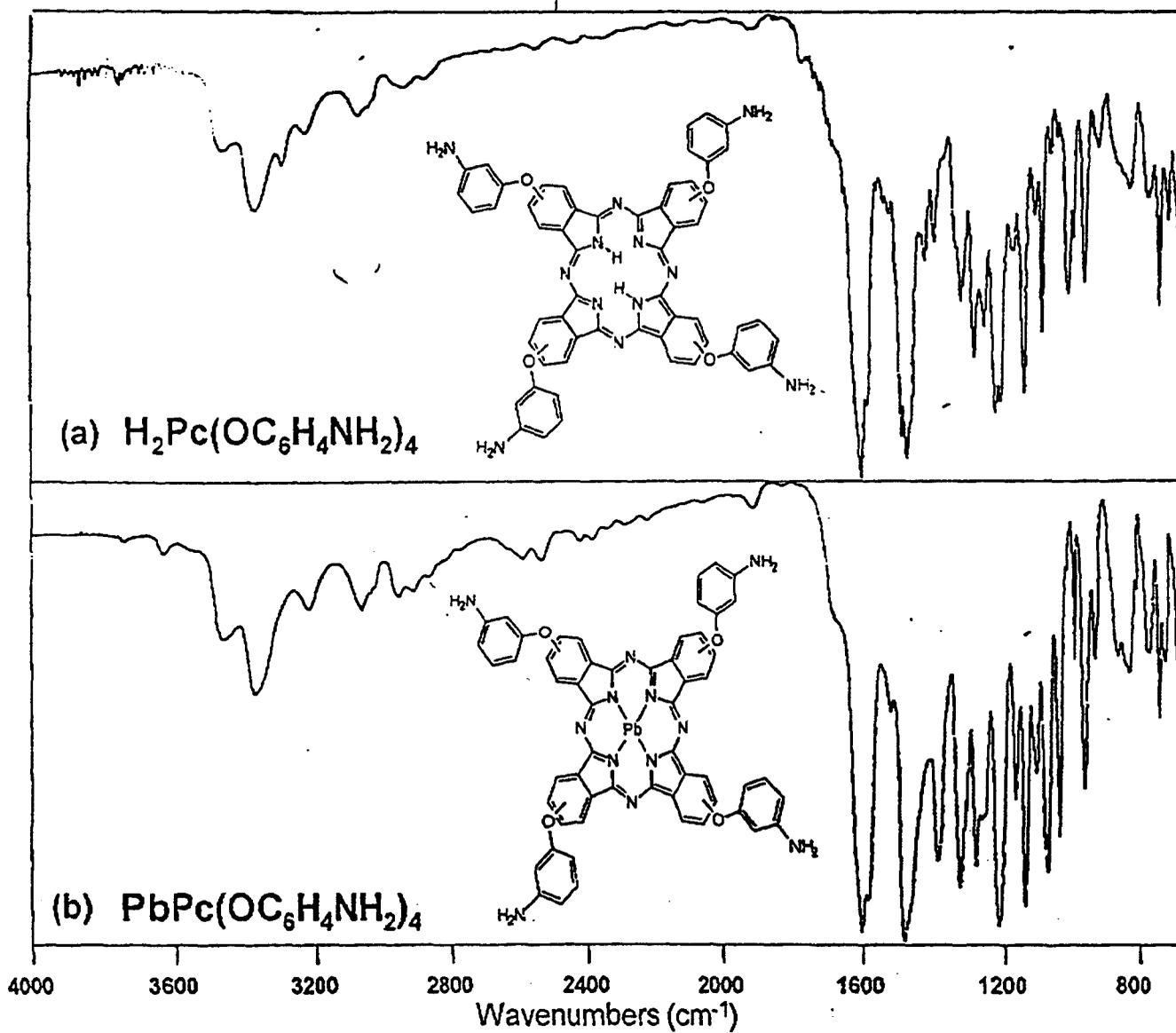


FIGURE 5

**% TRANSMISSION**



**FIGURE 6**

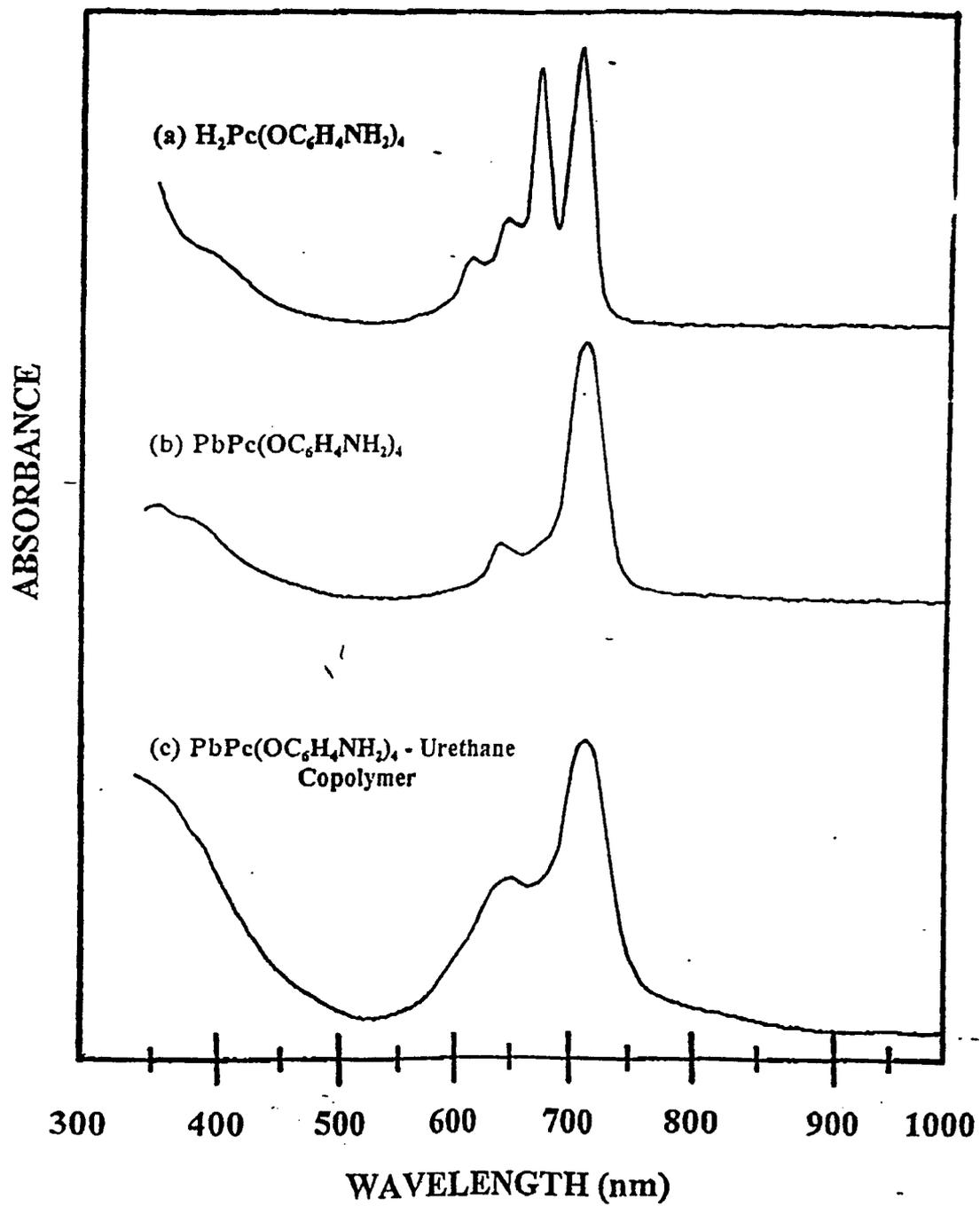


FIGURE 7

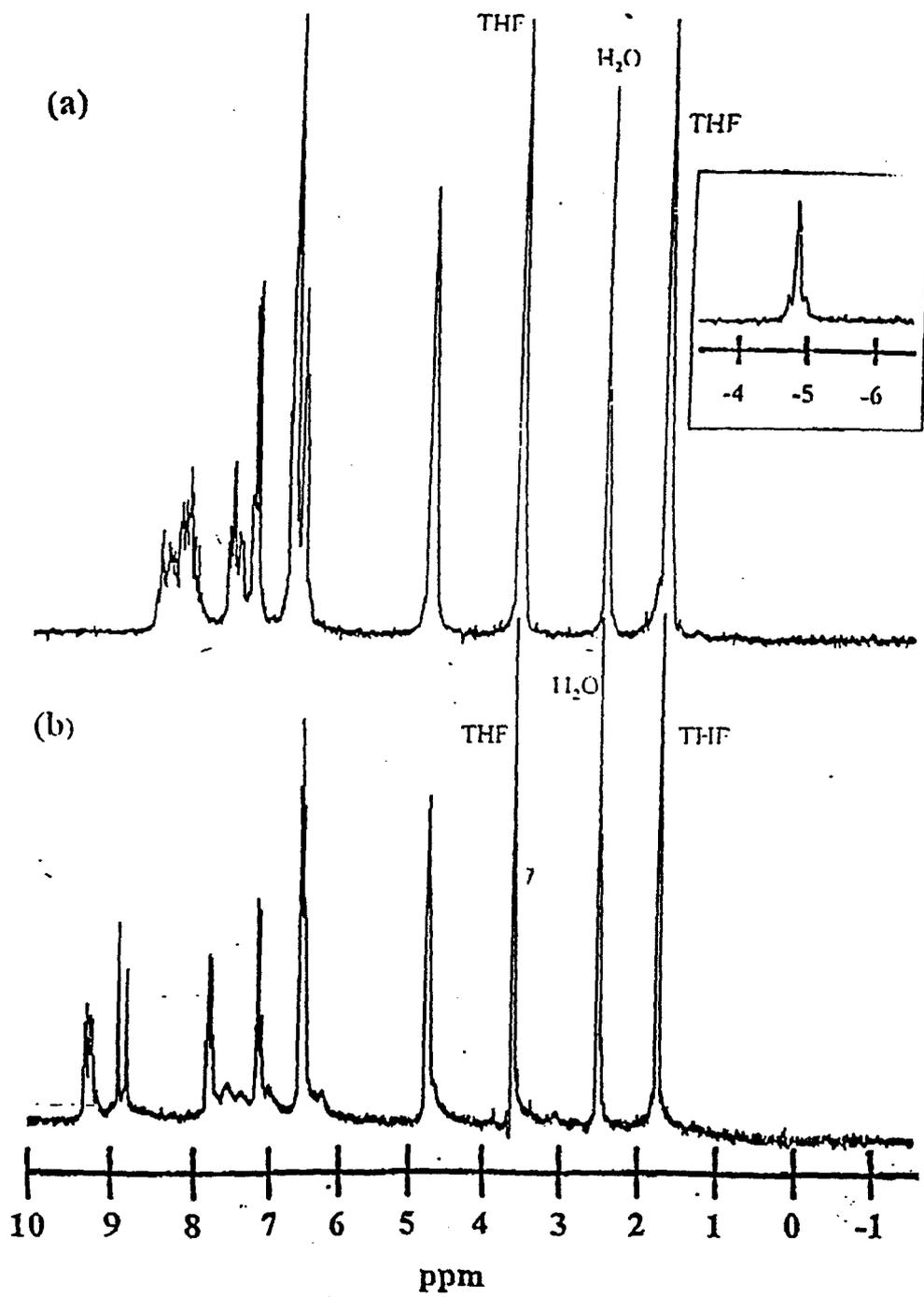


FIGURE 8

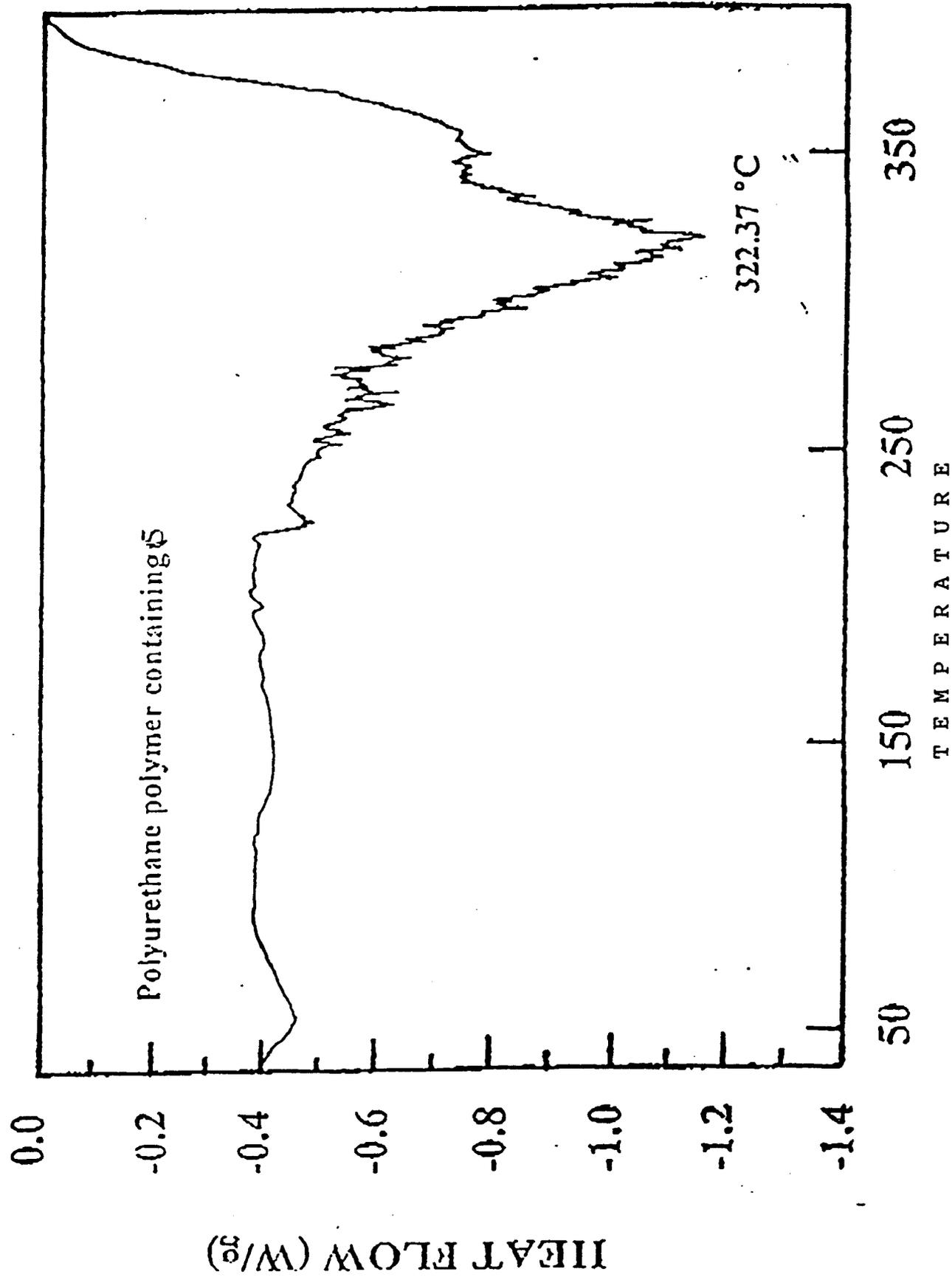
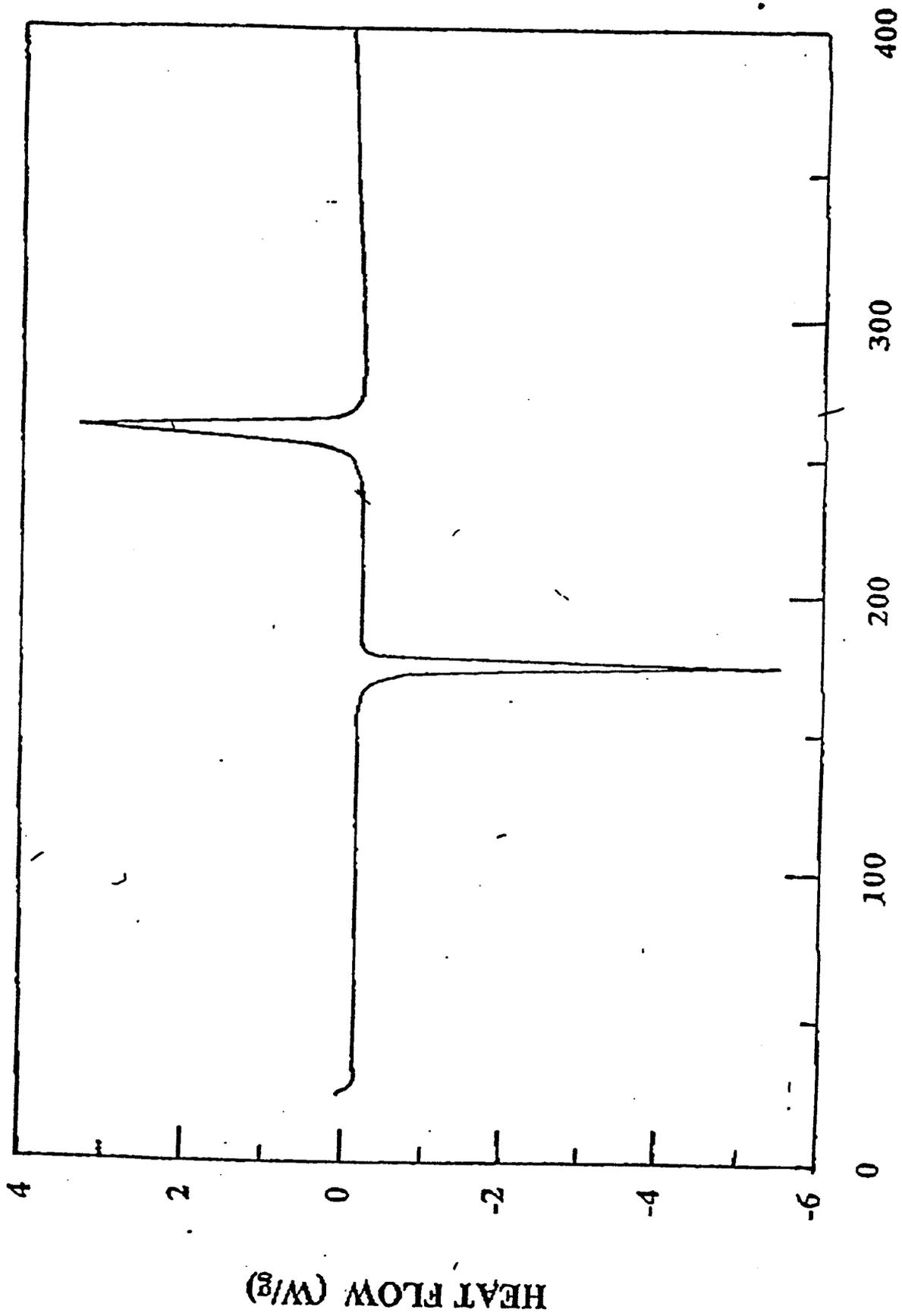


FIGURE 9



TEMPERATURE (°C)

FIGURE 10

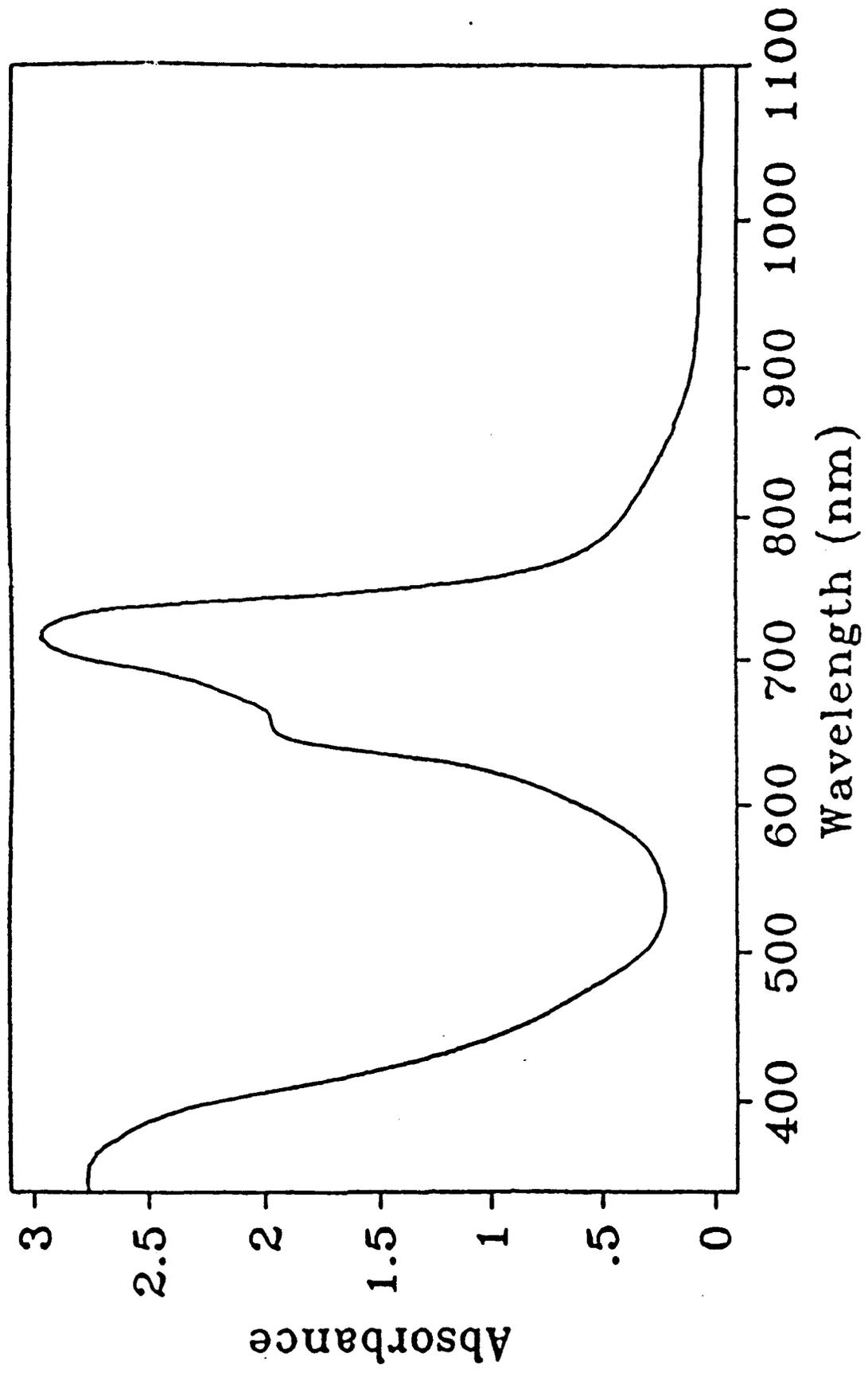


FIGURE 11

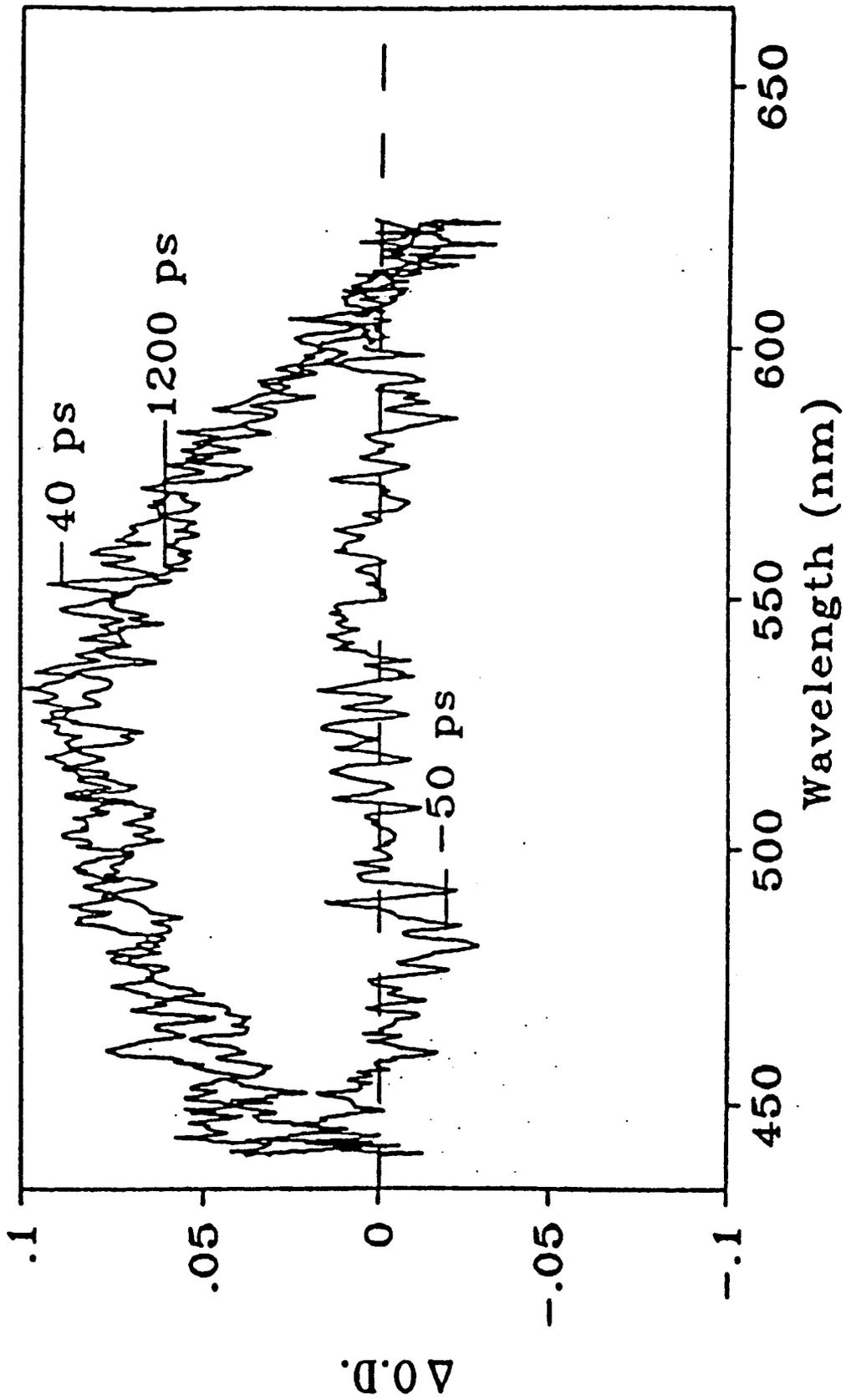


FIGURE 12

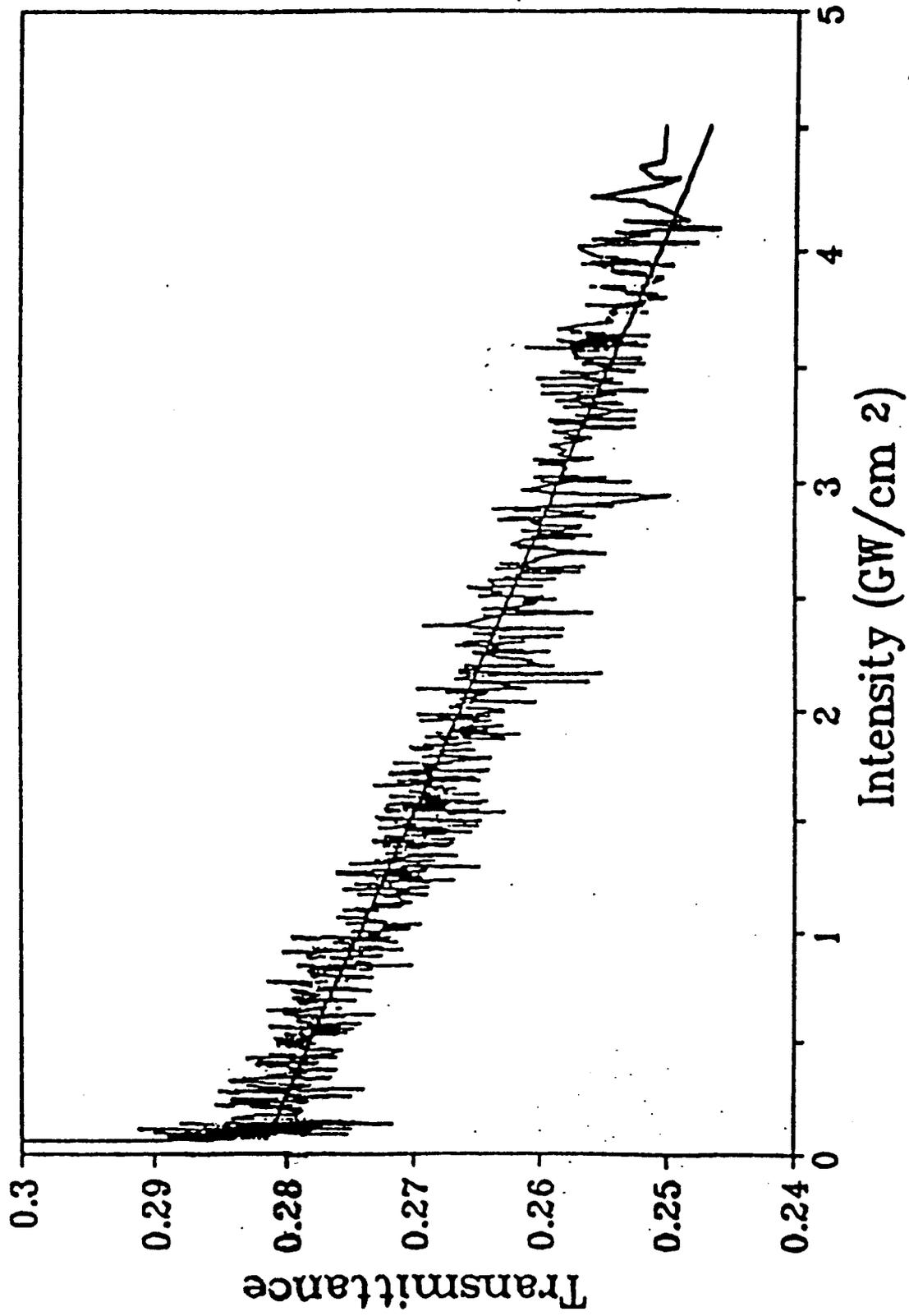


FIGURE 13

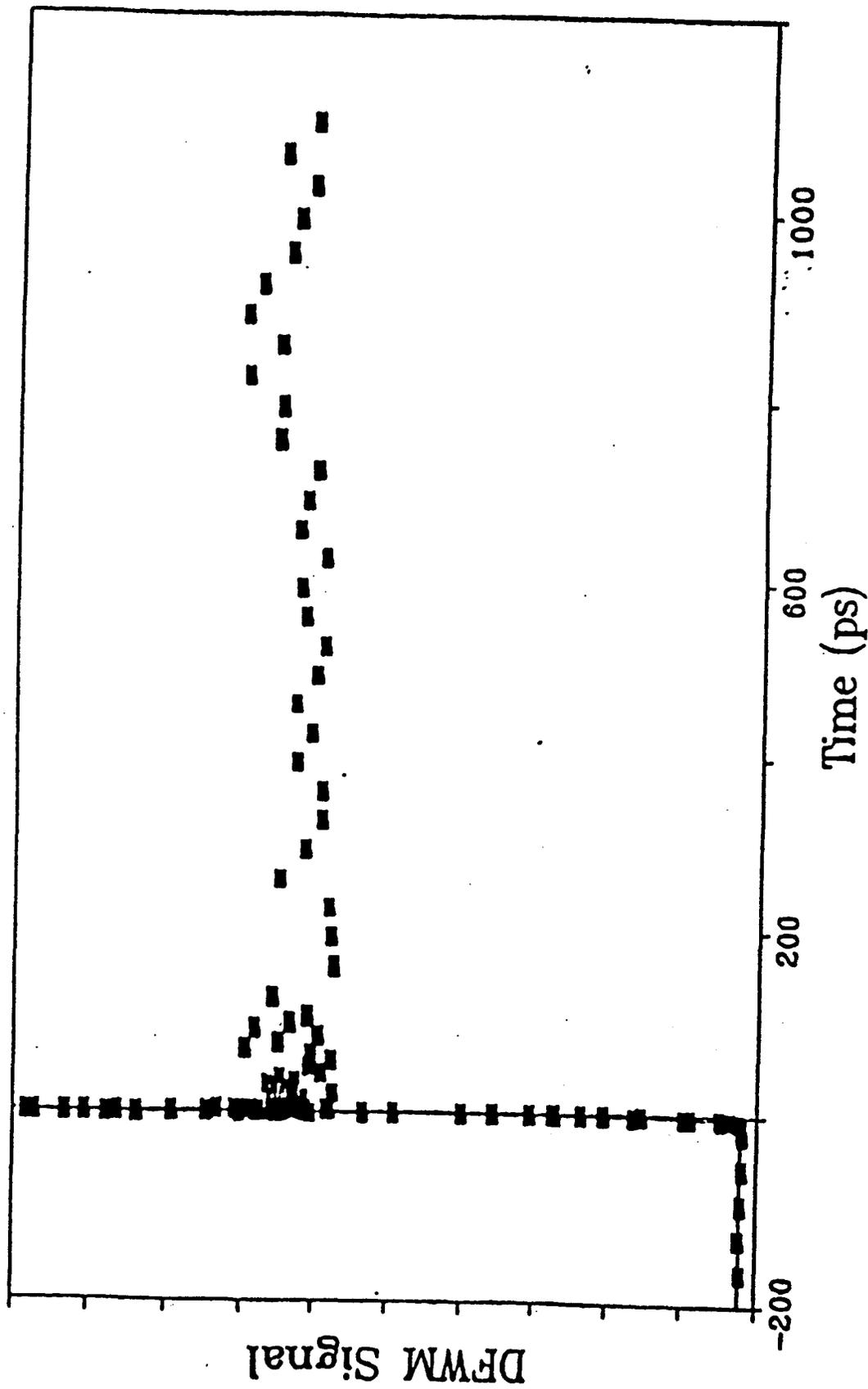


FIGURE 14

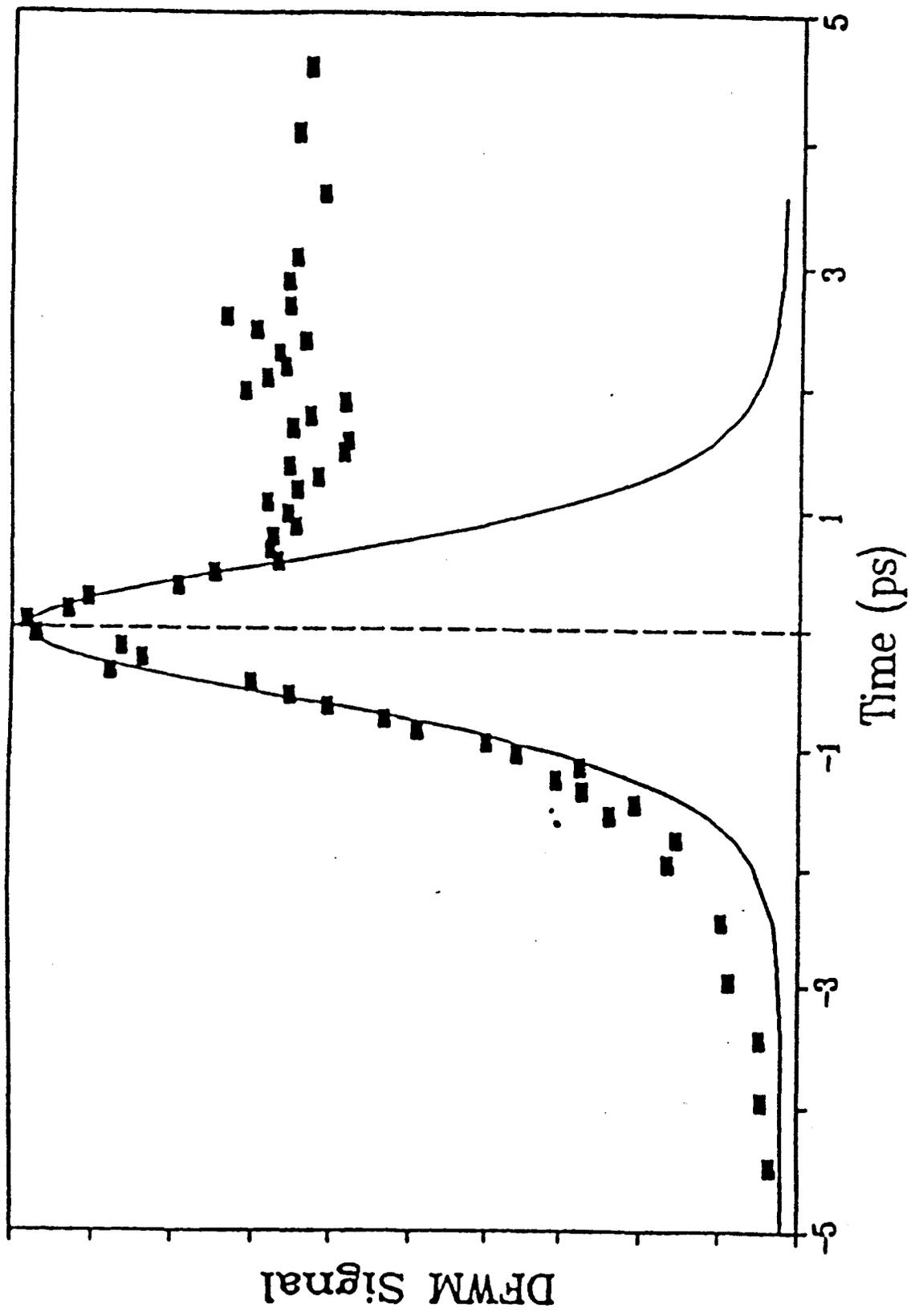


FIGURE 15