

Synthesis and Characterization of Melt-Polymerizable Aminophthalocyanine Monomers

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SYNOPSIS

The strategy, synthesis, and characterization of a soluble amine-functionalized phthalocyanine monomer and two examples of its polymerization into optically transparent glasses are reported. A simple, fast, and versatile method for incorporating metal ions into the metal-free phthalocyanine is demonstrated. Measurements of the nonlinear optical properties associated with a lead-substituted phthalocyanine/urethane copolymer are also reported. © 1995 John Wiley & Sons, Inc.[†]

INTRODUCTION

Peripherally functionalized phthalocyanine monomers which may be polymerized to yield optically transparent films and panels are a special challenge in synthetic polymer chemistry. Very few examples of this class of monomer are known,¹⁻⁴ and characterization of these monomers has not been rigorous. This occurs because in many cases the functionalized phthalocyanine monomers lack sufficient solubility for normal purification operations and characterization methods. In this article we present the strategy, synthesis, and characterization of a soluble amine functionalized phthalocyanine monomer and two examples of its polymerization into optically transparent glasses. Nonlinear optical measurements of a lead-derivatized polyphthalocyanine film are also reported. 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.⁵⁻⁷

EXPERIMENTAL

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, FTIR/Nicolet 750 Magna-IR (infrared [IR] data were collected either from thin films/NaCl supported or KBr pellets), UV-VIS/Cary 2390 spectrophotometer, and ¹H- and ¹³C-NMR (nuclear magnetic resonance)/Bruker AC-300 spectrometer at ambient temperature. Thermal analyses (differential scanning calorimetry [DSC] and thermogravimetric analysis [TGA]) were conducted with a DuPont 2100 Thermal Analyzer interfaced to a DuPont 910 DSC and a 950 TGA module.

4-(3-Aminophenoxy)phthalonitrile (1)

Dimethyl sulfoxide (DMSO; 50 mL), 4-nitrophthalonitrile (10.8 g, 62 mmol), and *o*-aminophenol (7.1 g, 65 mmol) are stirred under N₂ 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

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golden-yellow microcrystalline solid: mp 175.5–176.5°C; the IR spectrum is shown in Figure 1(a); $^1\text{H-NMR}$ (300 MHz, 0.056 *M*, $\text{DMSO-}d_6$) is given in Figure 2(a); $^{13}\text{C-NMR}$ (300 MHz, 0.056 *M*, $\text{DMSO-}d_6$): δ = 161.34, 154.60, 151.10, 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**) (11.5 g, 49 mmol) and phthalic anhydride (7.4 g, 50 mmol) is refluxed under N_2 for 4 h. 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: mp 160–162°C; the IR spectrum is shown in Figure 1(b); $^1\text{H-NMR}$ (300 MHz, 0.049 *M*, $\text{DMSO-}d_6$) is given in Figure 2(b); $^{13}\text{C-NMR}$ (300 MHz, 0.049 *M*, $\text{DMSO-}d_6$): δ = 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.

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 tetrahydrofuran (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. UV/VIS: λ_{max} (slightly soluble in DMSO) 702, 666, 641, and 607 nm; the IR spectrum is shown in Figure 1(c); lack of solubility precluded NMR characterization.

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 min 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, 61%) that did not melt below 325°C. The IR spectrum is shown in Figure 3(a); UV/VIS (Fig. 4a): λ_{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*, $\text{THF-}d_4$) is given in Figure 5(a); $^{13}\text{C-NMR}$ (300 MHz, $\text{DMSO-}d$): δ = 157.63, 150.89, 145.95, 135.86, 130.54, 122.94, 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 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 (0.14 mmol, 70%) of a green microcrystalline product which did not melt below 325°C. The lead ion in this peripherally substituted phthalocyanine is labile and does not survive chromatographing on alumina or silica. The IR spectrum is shown in Figure 3(b); UV/VIS (Fig. 4b): λ_{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, $\text{THF-}d_4$) is given in Figure 5(b).

Copolymers of 4- and Bisphenol A Diglycidyl Ether (DGEBA)

To obtain miscibility, a subequivalence of **4** was added to an excess of DGEBA 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 (Jeffamine D230, equiv wt 60), and the thermoset was cured at 80°C/9 h, 125°C/8 h, and 180°C/1 h. 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 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.

Copolymers of 5 and Isophorone Diisocyanate

Lead tetrakis(3-aminophenoxy)phthalocyanine (**5**) is dissolved in γ -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

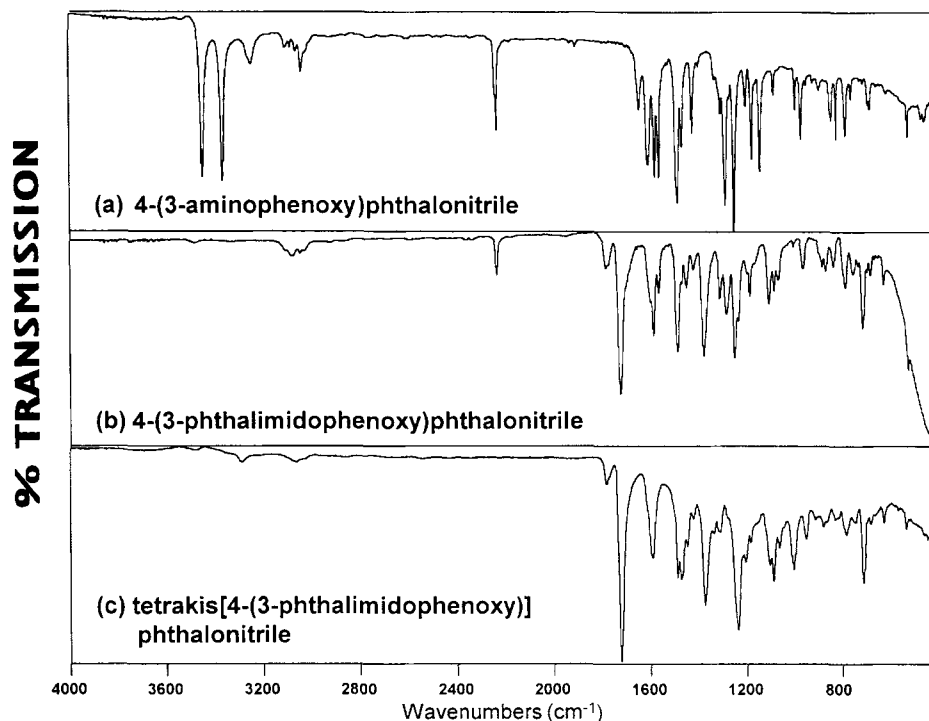


Figure 1 IR spectra of (a) 4-(3-aminophenoxy)phthalonitrile (1); (b) 4-(3-phthalimidophenoxy)phthalonitrile (2); (c) tetrakis(3-phthalimidophenoxy)phthalocyanine (3).

the backbone ($\sim 5.9\%$ by weight). The UV/VIS spectrum of a thin film of the solvent-free copolymer is presented in Figure 4(c). DSC data are shown in Figure 6.

RESULTS AND DISCUSSION

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. Previously reported amine-substituted phthalocyanine monomers have involved phthalocyanine formation from nitro-substituted phthalonitriles followed by reduction to the amine-substituted phthalocyanine.^{2,3} Achar et al.² substituted a simple amino group at the four benzo rings of the phthalocyanine structure. This group is small in size and does little to promote solubility. In our hands, the reduction of the nearly insoluble tetranitro-phthalocyanine 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.³ substituted four aminophenoxy groups at the phthalocyanine periphery by reducing the nitrophenoxy analog with SnCl_2 . Very little with regard to solubility and rigorous characterization was reported. This aminophthalocyanine is closely related to that of our study, but we wished to avoid the use of metallic reagents and followed a route not involving the reduction of nitro groups.

The scheme we followed is illustrated in Chart I. As a pendant group, we selected the 3-aminophenoxy structure for the purpose of subsequent phthalocyanine solubilization and to take advantage of a facile nuclear aromatic nitro displacement reaction.⁸ The 4-(3-aminophenoxy)phthalonitrile is obtained in good yield, and we had hoped to proceed directly to the phthalocyanine-forming reaction. However, at elevated temperatures, the amino group reacts with the phthalonitrile to yield a nonphthalocyanine structure. This is observed in the DSC thermogram of 4-(3-aminophenoxy)phthalonitrile in Figure 7, where melting occurs at 175°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

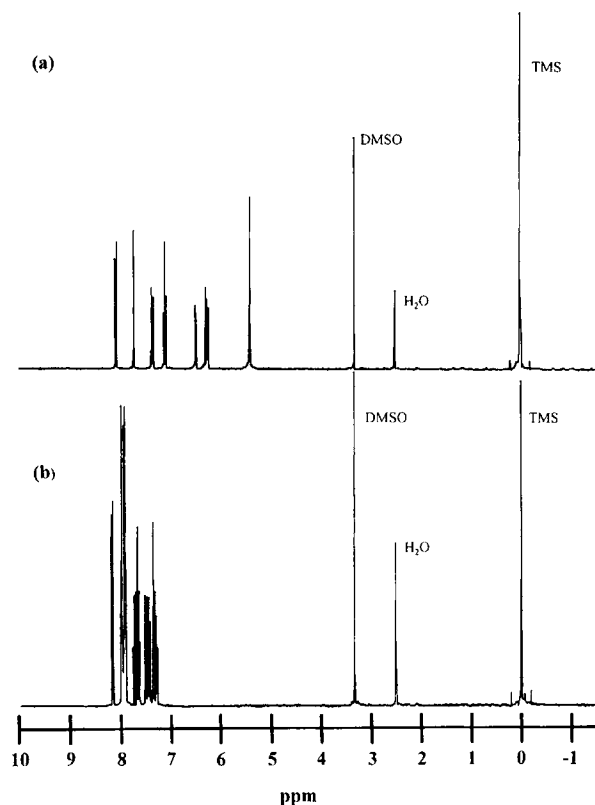


Figure 2 $^1\text{H-NMR}$ spectra of (a) 4-(3-aminophenoxy)phthalonitrile (1), 0.056M, $\text{DMSO-}d_6$; (b) 4-(3-phthalimidophenoxy)phthalonitrile (2), 0.054M, $\text{DMSO-}d_6$.

(diagnostic bands⁹ at 3290 and 1010 cm^{-1}) is not formed. The addition of a primary amine to phthalonitrile has been reported to yield a 1,3-bis(arylimino)isoindoline.¹⁰ This structure is consistent with, but an oversimplification of, 4-(3-aminophenoxy)phthalonitrile self-condensation.¹¹

To prevent this 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 cm^{-1}) and the appearance of the carbonyl stretch at 1723 cm^{-1} (Fig. 1b). The $^1\text{H-NMR}$ data also show this conversion via the disappearance of the free amine signal at $\delta = 5.4$ (Fig. 2b). The amine-blocked phthalonitrile (2) is then readily converted to the phthalocyanine (3) by a redox reaction with hydroquinone.⁹ The IR spectrum is consistent with this transformation as the nitrile stretch at 2236 cm^{-1} is replaced by the phthalocyanine bands at 3290 and 1010 cm^{-1} (Fig. 1c). 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).¹² 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 cm^{-1} (Fig. 3a). The $^1\text{H-NMR}$ (Fig. 5a) is also consistent with (4) as the reaction product, and the phthalocyanine cavity N—H band is clearly visible at $\delta = -4.8\text{ ppm}$, as is the peripheral group amine signal at $\delta = 4.8\text{ ppm}$. 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 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 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 ($\sim 70\%$) using the metal acetylacetonate. We have successfully used this conversion route 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 proton region of the NMR (Fig. 5). Apparently, the lead ion affects the ring current associated with the phthalocyanine macrocycle and thereby acts as an NMR shift reagent.

The tetraaminophthalocyanine monomer 4 was not sufficiently soluble in the DGEBA resin to form a stoichiometric uniphase melt. Compatibility was achieved by dispersing and prereacting a subequivalent amount of 4 in an excess of DGEBA sufficient to avoid crosslinking. Jeffamine 230 was then added to the phthalocyanine amine-epoxy prepolymer to achieve an amine-epoxy equivalence, and this final melt was cured to a green transparent thermoset. A series of epoxy-amine polymers were prepared using incremental amounts of 4. As the phthalocyanine amine equivalence percent progresses from 0 to 5.1 to 10.5 to 14.2, the glass transition temperature (T_g) remains at 60 to 70°C . However, at a phthalocyanine amine equivalence percent of 24.9, the T_g drops to 37°C , and the cure exotherm drops by a factor of 2. This indicates an incomplete curing reaction. While not visible to the eye, it is possible that a phase separation occurred or that the octafunctional phthalocyanine amine monomer has become isolated

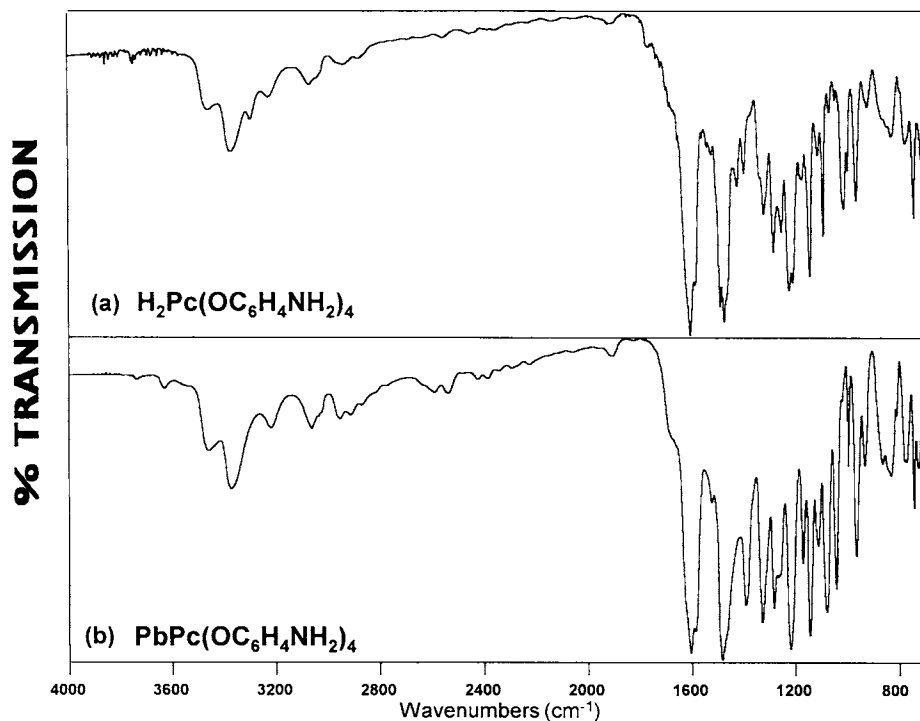


Figure 3 IR spectra of (a) tetrakis(3-aminophenoxy)phthalocyanine (4) and (b) lead tetrakis(3-aminophenoxy)phthalocyanine.

in the network before complete reaction was achieved. Sterically, this phthalocyanine amine can accommodate eight epoxy-derived linkages, as recently demonstrated by a model compound.¹¹ The DSC observations appear to indicate that a threshold composition between 15 and 25 amine equivalence percent exists above which full cure is not achieved for reasons of either incompatibility or functional group isolation.

By reacting lead phthalocyanine (5) with 1,3-butanediol and isophorone diisocyanate in γ -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 γ -butyrolactone) that can be processed into thin films (on the order of 15–20 μm) at 150°C. The DSC trace (Fig. 6) is indicative of a relatively noncrystalline polymer. TGA data show that thermal degradation (under N_2) 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 (π - π^* transition) of the lead phthalocyanine

(5) is not appreciably broadened or blue-shifted when the phthalocyanine entity is incorporated into the urethane-phthalocyanine copolymer (Fig. 4). A small amount of inhomogeneous broadening is expected as the phthalocyanine molecules within the copolymer undoubtedly are 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 $\text{PbPc}(\text{CP})_4$ [6, tetrakis(cumylphenoxy)phthalocyanine] in solution, which has been shown to be an effective optical limiter material.⁵⁻⁷ Such materials allow most of the light to be transmitted at low-light fluences but decrease the transmittance as the fluence level increases. To be an effective optical limiter, where nonlinear absorption is the dominant mechanism, the material must possess a long-lived excited state with an absorption cross section that is greater than that of the ground state over a particular wavelength region. In addition, the material must have a low threshold to begin limiting as well as a large operating range of fluences

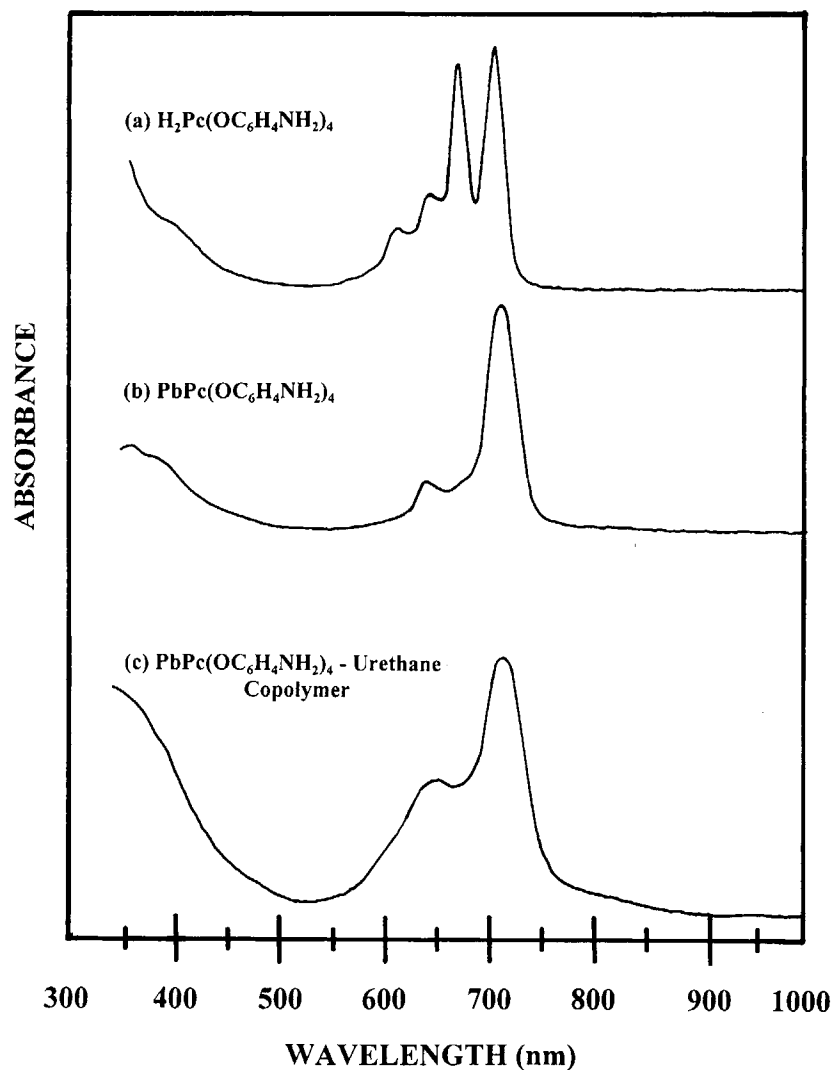


Figure 4 UV/VIS spectra of (a) tetrakis(3-aminophenoxy)phthalocyanine (THF); (b) lead tetrakis(3-aminophenoxy)phthalocyanine (THF); and (c) thin film of the polyurethane/lead tetrakis(3-aminophenoxy)phthalocyanine copolymer (5.9% phthalocyanine by weight).

against which it can limit. For the urethane/lead phthalocyanine (**5**) copolymer, there is a strong excited-state absorption in the 450–600 nm region which arises in less than 1 ps, persists with little or no change for longer than 10 ns, and is larger than that of the ground state, except near the intense ground state Q-band absorption.⁷ Phthalocyanine (**6**) in CHCl_3 shows a similar broad-band transient absorption with a pulse-width limited rise time (~ 2 ps) and > 1 ns decay time.⁵ 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. A detailed discussion of the non-

linear optical properties of this urethane/lead phthalocyanine (**5**) copolymer system and its potential for use in optical limiting devices has been reported.⁷

SUMMARY

The synthesis of metal-free tetrakis(3-aminophenoxy)phthalocyanine (**4**), a soluble amine-substituted phthalocyanine, is reported. In this scheme, phthalic anhydride is reacted with 4-(3-aminophenoxy)phthalonitrile (**1**) to inhibit the amine group from reacting with nitrile groups during the formation of the phthalocyanine macrocycle.

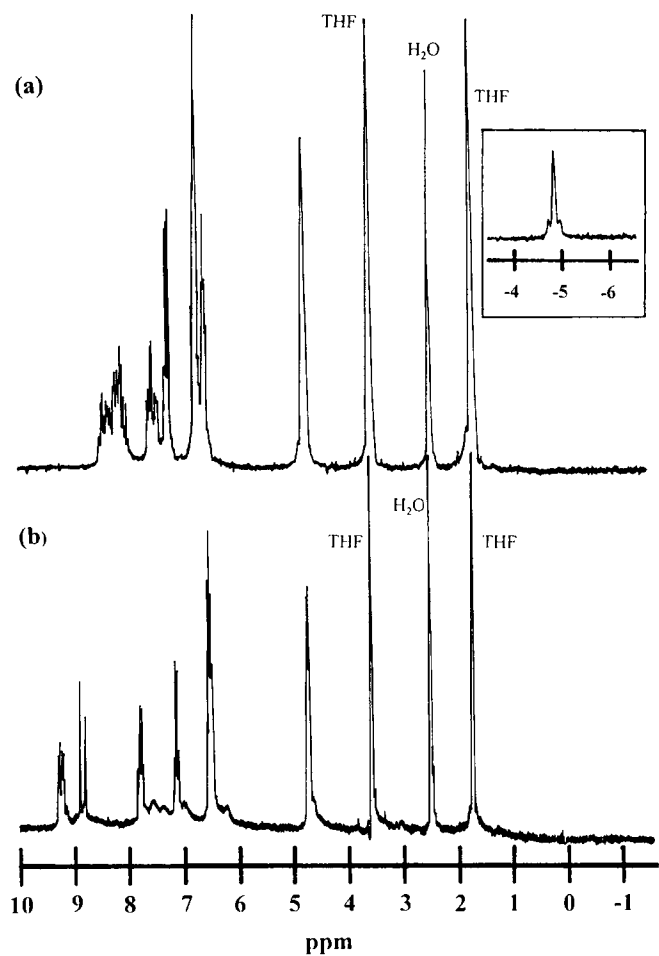


Figure 5 $^1\text{H-NMR}$ spectra of (a) tetrakis(3-aminophenoxy)phthalocyanine (0.03M, THF- d_4) and (b) lead tetrakis(3-aminophenoxy)phthalocyanine (0.01M, THF- d_4).

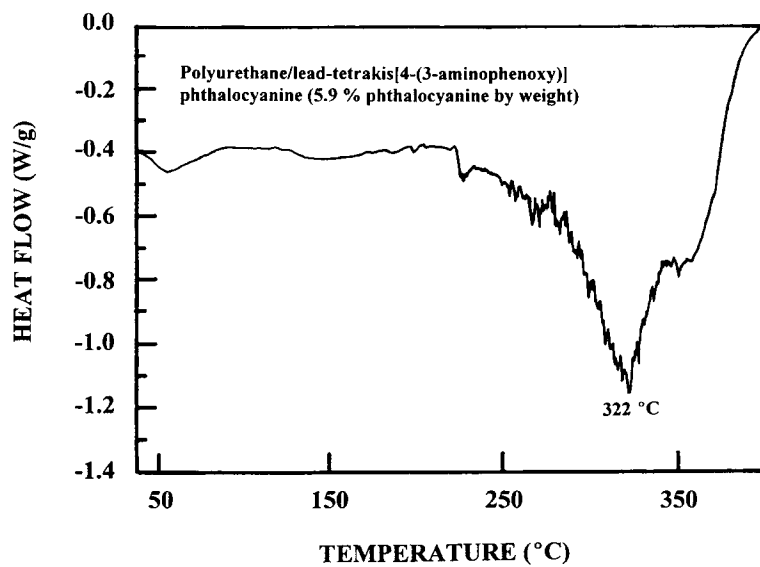


Figure 6 Differential scanning calorimeter trace of the polyurethane/lead tetrakis(3-aminophenoxy) phthalocyanine copolymer (5.9% phthalocyanine by weight).

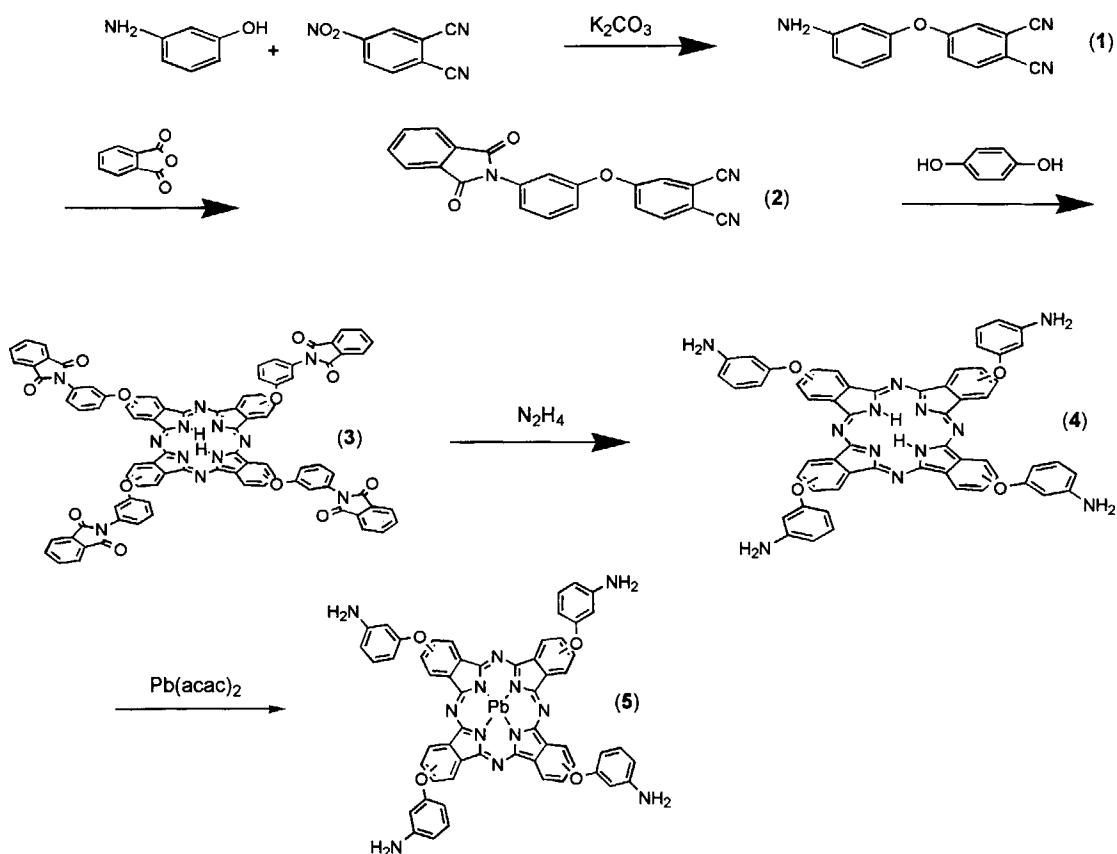


Chart 1.

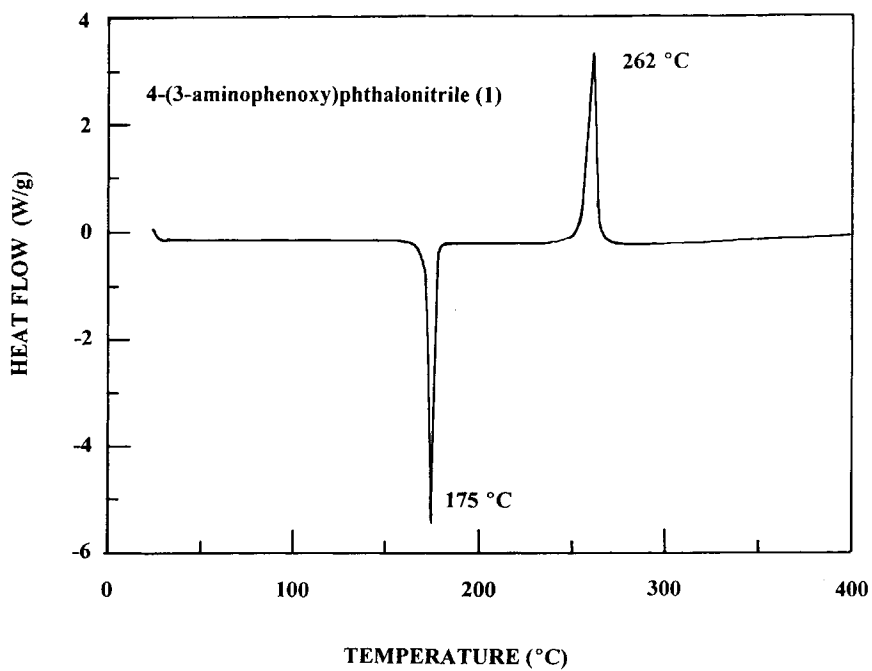


Figure 7 Differential scanning calorimeter trace of 4-(3-aminophenoxy)phthalonitrile detailing the melting point at 175°C and the subsequent self-reaction at 262°C.

Hydrazine is used to convert the resulting tetrakis(3-phthalimidophenoxy)phthalocyanine (**3**) to tetrakis(3-aminophenoxy) phthalocyanine (**4**), which is well characterized by IR, NMR, and UV/VIS spectroscopy. A simple, fast, and versatile method for incorporating metal ions into the metal-free phthalocyanine is also demonstrated.

The preparation of epoxy and polyurethane polymers based on metal-free and lead tetrakis(3-aminophenoxy)phthalocyanine, respectively, is discussed. The nonlinear optical response of lead-substituted phthalocyanines does not appear to be affected by changes in the peripheral substitution or incorporation into a urethane copolymer.

This work was supported in part by the ONR Laser Hardened Materials Project.

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Received August 29, 1994

Accepted January 17, 1995