

Aggregation of Lead Phthalocyanine in Blends with Polycarbonate

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ABSTRACT: The blends of a nonlinear optical dye with polycarbonate are described and comparisons are made with solutions of the dye in chloroform. Absorption spectra of blends with up to 1 wt % lead tetracumylphenoxy phthalocyanine showed the dye to be primarily in the monomer form. The monomer absorption spectrum and the measured extinction coefficient replicated those in chloroform solution. As the dye concentration increased to 20 wt %, the monomer intensity decreased and new spectral features characteristic of the dimer appeared. The spectra were resolved into contributions of monomer and dimer, and the concentration effect was analyzed according to the monomer/dimer equilibrium. Much higher monomer concentra-

tions were achieved in polycarbonate blends compared to chloroform solutions. It was concluded that when the blends were quenched from the melt, the equilibrium established at the melt temperature was preserved in the solid state glass. Quenching the blend from different melt temperatures confirmed this interpretation. Extrapolation of the temperature dependent equilibrium constant to 25°C yielded a value close to that reported for chloroform solution at 25°C. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 464–469, 2007

Key words: phthalocyanines; aggregation; polycarbonate; NLO; dyes

INTRODUCTION

Phthalocyanines are conjugated aromatic macrocycles with rich absorption spectra in the visible and ultraviolet regions. They are useful as dyes and coloring agents.¹ They are also one of the best classes of nonlinear compounds for optical limiting applications.² However, owing to the extended π system, phthalocyanines exhibit a tendency to aggregate in solution to form the dimer and higher oligomeric species,³ a characteristic that may negatively impact their nonlinear optical properties.

Peripheral substitution is used to enhance the solubility of phthalocyanine compounds in aqueous and organic media and to alter the aggregation behavior.^{4,5} Aggregation is usually measured by repetitive scans of the visible spectrum as the concentration is systematically varied. As a rule, only the dimer is considered. The initial aggregating tendency is described by the monomer/dimer equilibrium constant.

Phthalocyanines with peripheral cumylphenoxy substituents have good nonlinear optical properties, excellent solubility, and relatively low monomer/dimer equilibrium constants; however, they do not form transparent films in the solid state.⁶ The possibility exists for expanding the solid state applications of phthalocyanine compounds by dispersing them in a transparent polymeric matrix.

Achieving dispersion as the monomeric form, with conservation of the electronic structure, is an important consideration in choosing a polymer for phthalocyanine blends. When lead tetracumylphenoxy phthalocyanine (PbPc(β -CP)₄) was blended with some aromatic polyesters, poly(ethylene terephthalate), and poly(ethylene naphthalate), the central lead atom was replaced with a proton to give the less efficient lead-free form.⁷ However, the lead-containing form persisted with a high fraction of monomer in blends with polycarbonate (PC), poly(methyl methacrylate) (PMMA), and a styrene-acrylonitrile copolymer (SAN). The present study was undertaken to characterize the monomer/dimer equilibrium of PbPc(β -CP)₄ in PC blends. To our knowledge, this is the first systematic investigation of the solubility and aggregation of lead phthalocyanine in a high molecular weight polymer.

EXPERIMENTAL

Lead tetracumylphenoxy phthalocyanine (PbPc(β -CP)₄) was obtained in powder form from Sigma Aldrich

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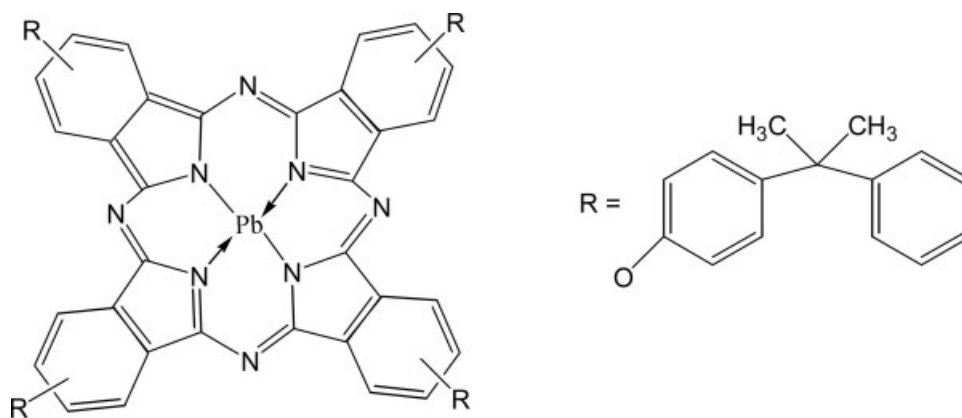


Figure 1 Chemical structure of lead tetracumylphenoxy phthalocyanine ($\text{PbPc}(\beta\text{-CP})_4$).

(St. Louis, MO). Its chemical structure is shown in Figure 1. Polycarbonate (Calibre 200-14) was provided as pellets by the Dow Chemical Company, Midland, MI. The dye powder was mixed with polycarbonate by solution blending in chloroform to a target concentration of 20 wt %. Chloroform was evaporated by drying under vacuum at 60°C for 6 h. The dry blend was further mixed by passing it through the DACA (Santa Barbara, CA) mini twin screw extruder at 270°C. The residence time in the extruder was 3 min. The extrudate strand was quenched in dry ice and pelletized. The 20 wt % master blend was diluted by dry blending with polycarbonate pellets and mixing in the DACA mini twin screw extruder at 270°C. Blends with target concentrations of 0.01, 0.05, 0.1, 0.5, 1, 2, 4, 8, 10, 12, and 16 wt % were made by this method.

The blend concentration was confirmed by UV-VIS absorbance spectroscopy using a Perkin-Elmer (Boston, MA) Lambda 9000 spectrometer. Dilute chloroform solutions ($<10^{-5}\text{ M}$ in $\text{PbPc}(\beta\text{-CP})_4$) were prepared and UV-VIS measurements were carried out in 1 cm cuvettes. The reference contained an equivalent concentration of PC in chloroform. The extinction

coefficient of $\text{PbPc}(\beta\text{-CP})_4$ at 724 nm was determined from standard solutions to be 1.28×10^5 liters/mol cm. The target concentration and the measured concentration of each blend are given in Table I.

Thin films of the blends were prepared for UV-VIS spectroscopy measurements. To avoid signal saturation, the target film thickness was 25 μm for blend concentrations up to 8 wt % and 12 μm for more concentrated blends. The blends were taken to 270°C in the Rheometrics DSC (Piscataway, NJ), held for 5 min and quenched in dry ice. In addition, films of 1 and 2 wt % $\text{PbPc}(\beta\text{-CP})_4$ blends were quenched from different melt temperatures between 180 and 270°C following the same procedure. The film thickness was measured with a micrometer. Although polycarbonate is very transparent in the spectral region of interest, polycarbonate films prepared under identical conditions as the blends were used as the reference. The extinction was taken as $\varepsilon(\lambda) = A(\lambda)/cl$ where $A(\lambda)$ is the absorbance, c is the concentration, and l is the film thickness. The average of three measurements is reported.

A density gradient column was constructed from a solution of calcium nitrate and water in accordance with ASTM D Standard 1505 Method B. The column

TABLE I
Monomer Fraction and Dimer Formation Constant of $\text{PbPC}(\beta\text{-CP})_4$
in Polycarbonate Blends

$\text{PbPC}(\beta\text{-CP})_4$ (wt %)	Density (g/cm^3)	C_o at 270°C (mol/L)	f_m	K_{eq} (L/mol)
0.01	1.1930	6.80×10^{-5}	1.0	–
0.05	1.1934	3.40×10^{-4}	0.99 ± 0.01	15.0
0.10	1.1938	6.81×10^{-4}	0.98 ± 0.02	15.3
0.50	1.1948	3.41×10^{-3}	0.95 ± 0.02	8.17
0.94	1.1958	6.41×10^{-3}	0.90 ± 0.01	9.65
1.85	1.1975	1.26×10^{-2}	0.80 ± 0.01	12.4
3.85	1.2001	2.63×10^{-2}	0.64 ± 0.01	16.7
7.76	1.2054	5.33×10^{-2}	0.54 ± 0.01	14.8
9.73	1.2083	6.70×10^{-2}	0.46 ± 0.01	19.1
11.6	1.2105	7.99×10^{-2}	0.42 ± 0.01	20.6
15.5	1.2208	1.08×10^{-1}	0.36 ± 0.01	22.9
19.5	1.2265	1.35×10^{-1}	0.31 ± 0.01	26.5

was calibrated with glass floats of known density. Small pieces of compression molded films (*ca.* 25 mm²) were placed in the column and allowed to equilibrate for 30 min before measurements were taken. Averages of four measurements are reported.

RESULTS AND DISCUSSION

The absorbance spectrum of PbPc(β -CP)₄ monomer shown in Figure 2(a) is dominated by the narrow Q-band (724 nm) with a smaller vibronic side band (650 nm). Correspondence between the monomer spectrum in dilute chloroform solution and the spectrum of PbPc(β -CP)₄ in the blend of lowest concentration (0.01 wt %) confirmed that PbPc(β -CP)₄ was dispersed as monomer in the PC blend, Figure 2(a). The corresponding extinction coefficient of the monomer in PC was 1.30×10^5 liters/mol cm, essentially the same as the extinction coefficient in chloroform.

The observed spectra for PC blends of different PbPc(β -CP)₄ concentrations are shown in Figure 2(b). As the blend became more concentrated, the 650 and 724 nm bands diminished in intensity and a broader band at ~ 800 nm emerged and increased in intensity. Within this concentration range, the appearance of two isosbestic points at 640 nm and 746 nm indicated two-component equilibrium with overlapping absorption bands. The spectral changes were characteristic of PbPc(β -CP)₄ dimer formation, in chloroform solutions of systematically increasing concentration, as described previously.³ Essentially, PC served as a solvent in which PbPc(β -CP)₄ aggregated to form dimer through a monomer-dimer equilibrium. However, compared to chloroform solutions, much higher concentrations of PbPc(β -CP)₄ were required to produce the series of curves in Figure 2(b). The equilibrium was shifted as it would be in chloroform solutions at elevated temperature. Evidently, when the PC blends were quenched, the equilibrium established at the melt temperature was preserved in the solid state. Thus, it was possible to obtain considerably higher monomer concentrations in PC than in chloroform.

To obtain the dimer spectrum, the monomer spectrum $\epsilon_1(\lambda)$ was subtracted from the spectrum of the blend with the highest dimer content (20 wt %) until the difference spectrum closely resembled the dimer spectrum reported previously for the PbPc(β -CP)₄ in chloroform.³ The dimer spectrum was taken as

$$\epsilon_2(\lambda) = \frac{\epsilon(\lambda)_{20} - f_{m,20} \epsilon_1(\lambda)}{1 - f_{m,20}} \quad (1)$$

where $\epsilon(\lambda)_{20}$ is the spectrum of the 20 wt % blend and $f_{m,20}$ is the fraction of the monomer spectrum that was subtracted. The monomer and dimer spectra are compared in Figure 2(c).

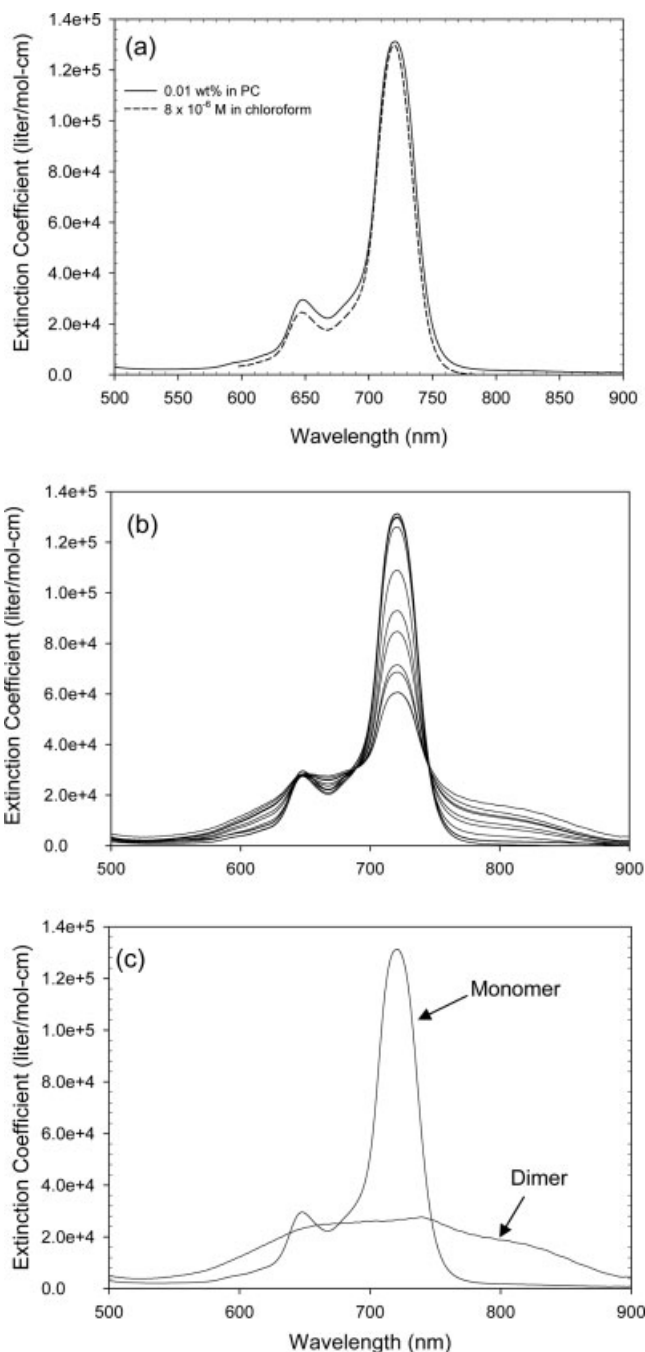


Figure 2 UV-VIS spectra of PbPc(β -CP)₄: (a) the monomer spectrum in 8×10^{-6} M chloroform solution and in 0.01 wt % PC blend; (b) the concentration dependence of the spectrum in PC blends; and (c) the monomer and calculated dimer spectra in PC.

The other spectra were deconvoluted into the monomer and dimer contributions according to

$$\epsilon(\lambda) = f_m \epsilon_1(\lambda) + (1 - f_m) \epsilon_2(\lambda) \quad (2)$$

where $\epsilon(\lambda)$ is the measured spectrum and f_m is the fraction of monomer in the blend. Some typical examples in Figure 3 compare the measured spectra

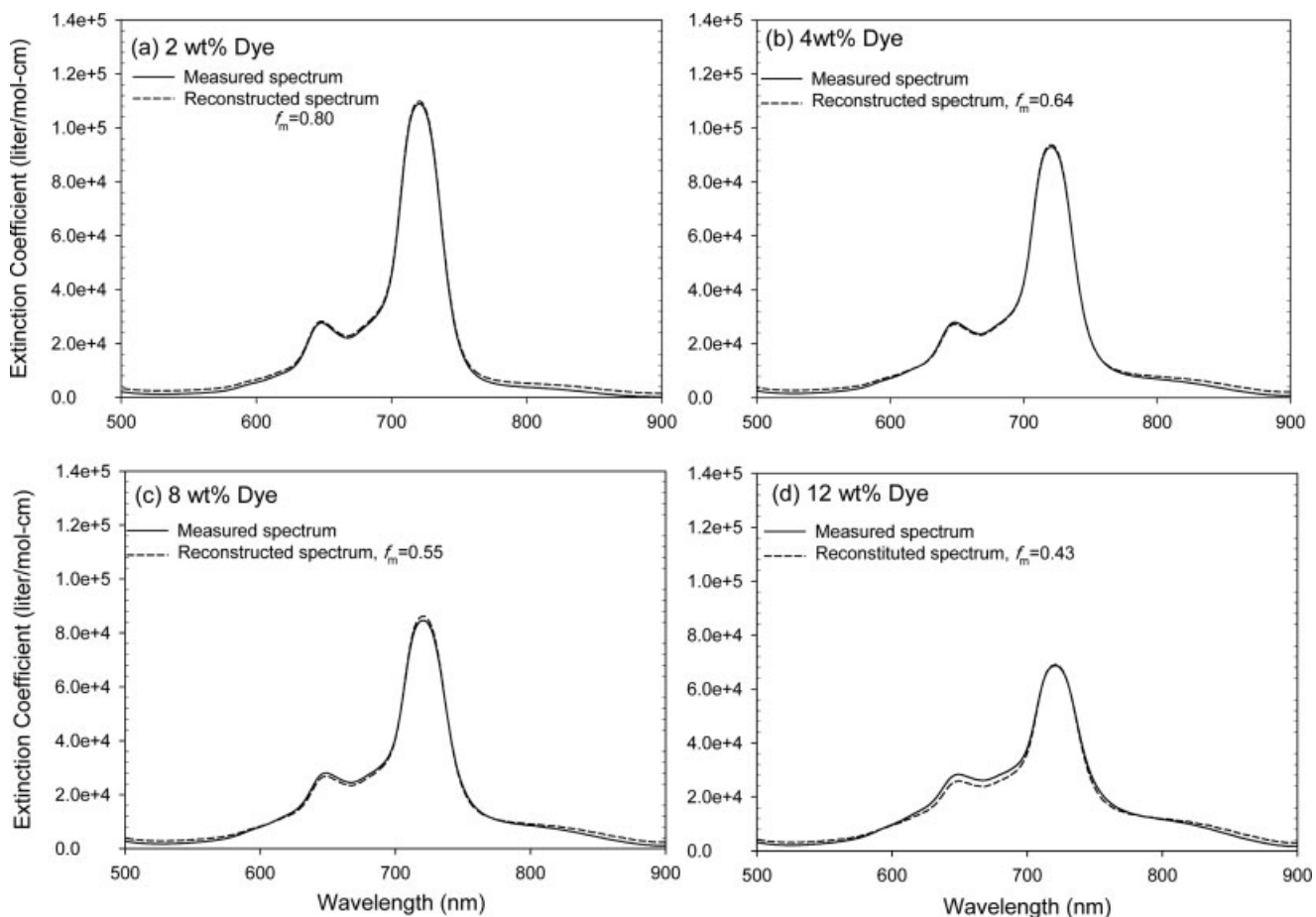


Figure 3 The measured UV-VIS spectrum at various concentrations compared with the reconstituted spectrum from eq. (2).

with the best fits according to eq. (2), and the values of f_m are summarized in Table I.

The monomer-dimer equilibrium is expressed as

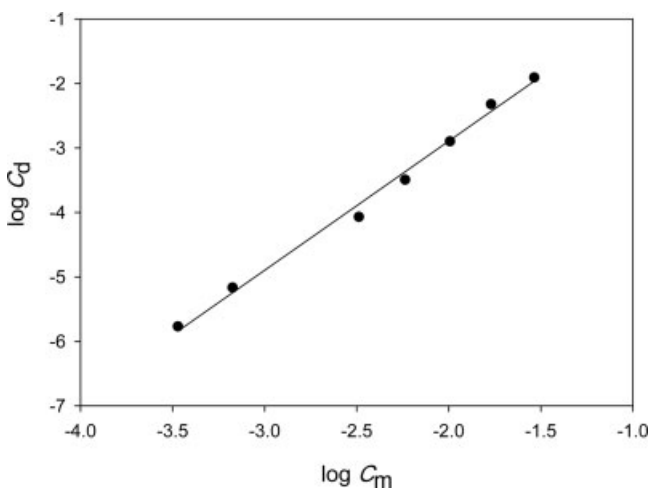


Figure 4 The relationship between monomer concentration C_m and dimer concentration C_d . Results for blends with up to 8 wt % PbPc(β -CP) $_4$ are plotted. The slope from the least squares fit is 2.00 with $R^2 = 0.99$.

with equilibrium constant

$$K_{eq} = \frac{C_d}{C_m^2} = \frac{(1 - f_m)}{2C_0 f_m^2} \tag{4}$$

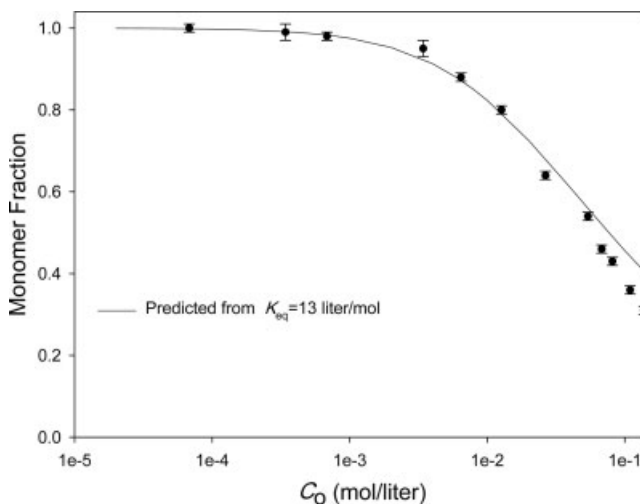


Figure 5 The monomer fraction f_m as a function of PbPc(β -CP) $_4$ concentration C_0 .

TABLE II
Effect of Temperature on Monomer Fraction and Dimer Formation Constant of
PbPc(β -CP)₄ in Polycarbonate Blends

PbPc(β -CP) ₄ in PC (wt %)	Temperature (T) (°C)	C _o at T (mol/L)	f _m	K _{eq} (L/mol)
0.94	270	6.40 × 10 ⁻³	0.90 ± 0.01	9.65
	240	6.55 × 10 ⁻³	0.87 ± 0.01	13.1
	210	6.66 × 10 ⁻³	0.84 ± 0.01	17.0
	180	6.79 × 10 ⁻³	0.80 ± 0.01	23.0
1.85	270	1.26 × 10 ⁻²	0.80 ± 0.01	12.4
	240	1.29 × 10 ⁻²	0.74 ± 0.01	18.4
	210	1.31 × 10 ⁻²	0.70 ± 0.01	23.3
	180	1.34 × 10 ⁻²	0.65 ± 0.01	30.9

where

$$C_d = \frac{C_o(1 - f_m)}{2} \quad (5)$$

is the concentration of dimer, and

$$C_m = C_o f_m \quad (6)$$

is the concentration of monomer. C_o is the concentration of PbPc(β -CP)₄ in the blend. It was assumed that the state of aggregation in the blends reflected the equilibrium condition at the melt temperature of 270°C. The PbPc(β -CP)₄ concentration C_o as moles per liter at that temperature was estimated as

$$C_o = \frac{10 \text{ (wt \%)}}{M_{\text{dye}} v_{\text{blend}}} \quad (7)$$

where M_{dye} is the molecular weight of PbPc(β -CP)₄ (M_{dye} = 1561) and v_{blend}, which is the specific volume of the blend at 270°C, is estimated from the density ρ measured at 25°C as

$$v_{\text{blend}} = \frac{1}{\rho} + \Delta v \quad (8)$$

where $\Delta v = v_{270} - v_{25}$ is the difference in specific volume of PC between 270 and 25°C and is taken as 0.1032 cm³/g from the reported thermal expansion.⁸ The values of K_{eq} calculated from eq. (4) are included in Table I. The K_{eq} values tend to increase with increasing C_o.

It is thought that higher aggregates form as the dye concentration increases, although the changes to the dimer spectrum are relatively small. One method of determining whether monomer and dimer are the only significant species in a concentration range is a simple logarithmic plot of monomer versus dimer concentration. A slope of 2 demonstrates that higher aggregate formation is not significant.⁹ A plot of data for blends with 0.01 to 8 wt % dye is linear with a least squares slope of 2.00, as seen in Figure 4. The

extracted value of K_{eq} is 13.0 L/mol. The effect of higher aggregate formation is most readily seen by plotting the monomer fraction as in Figure 5. Deviation from the curve calculated for K_{eq} = 13.0 becomes significant for compositions greater than 8 wt %.

The effect of melt temperature on the absorption spectrum was studied with 1 and 2 wt % blends. Quenching the blend from a lower melt temperature increased the fraction of dimer as indicated by increasing intensity in the 800 nm region. The spectra were deconvoluted to obtain f_m, Table II. The resulting values of K_{eq} were plotted according to the traditional ln K_{eq} versus 1/T form to obtain the enthalpy of dimerization. Although the values of K_{eq} were slightly different for the two blend compositions, the temperature dependence was essentially the same giving an average ΔH of 19.8 ± 0.3 kJ/mol. Extrapolation of the temperature dependence to 25°C yielded an equilibrium constant of 480, which was very close to the value of 400 reported for chloroform solution.³ The solvent would have affected aggregation through its impact on the π - π interaction between phthalocyanine chromophores. In this regard, polycarbonate and chloroform were comparable as indicated by similarity in the equilibrium constants and correspondence in the monomer spectra.

CONCLUSIONS

The nonlinear optical dye PbPc(β -CP)₄ shows good solubility in polycarbonate. Melt blends with up to 20 wt % dye can be readily prepared. An important objective in the choice of solvents for PbPc(β -CP)₄ is achieving dispersion in the monomer form, with conservation of the electronic structure. An attractive feature of the polycarbonate blends is the high concentration of monomer. Blends with up to 1 wt % show the dye to be primarily in the monomer form. At higher concentrations, the dye aggregates to form dimer and higher order species. The concentration effect is satisfactorily described by the monomer/dimer equilibrium. As a solvent for PbPc(β -CP)₄, polycarbonate is similar to chloroform in the close resemblance of the

monomer spectra and correspondence in the monomer/dimer equilibrium constants. However, when the blend is quenched from the melt, the equilibrium established at the melt temperature is preserved in the solid state glass. The rigid polymer chains prevent aggregation and the high monomer concentration is stable at ambient conditions.

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