Incorporation of Lead Phthalocyanine into Periodic Nanolayered Assemblies for Advanced Optical Systems

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ABSTRACT: Periodically structured polymeric materials can lead to the next generation of electro-optic and nonlinear optical devices for applications in information technology. Layer-multiplying melt coextrusion is an attractive method for fabricating periodic structures with thousands of alternating polymer microlayers or nanolayers. Many advanced applications for periodic polymeric structures would be enabled by locating a photoactive dye in one or both layers. However, it is anticipated that due to the thinness of the individual layers and the relatively low molecular weight of many dyes, a substantial fraction of the dye will diffuse from the doped layers into the undoped layers during melt coextrusion. In the present study, we demonstrate two methods for confining the activity of a photoactive dye, lead phthalocyanine, to the doped layers. Polycarbonate containing lead phthalocyanine was coextruded with undoped polyester as an assembly of 128 alternating 86 nm-thick layers. Using the absorption spectra, we demonstrated that a high concentration of the monomer form persisted in the polycarbonate layers, whereas the lead form was converted to the less active lead-free form in the polyester layers. Thus, the active monomer form of PbPc(β-CP)$_4$ was maintained selectively in the polycarbonate layers. In the second approach, the coextrusion process was altered so that the alternating polycarbonate and polyester layers were separated by a thin layer of a barrier polymer. The barrier layer prevented diffusion of the dye during melt coextrusion and the dye remained selectively in the polycarbonate layers. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2150–2159, 2009

Key words: lead phthalocyanine; coextrusion; nanolayers; dye diffusion

INTRODUCTION

Electro-optic and nonlinear optical devices are important for many applications in the area of information technology. Polymeric materials display significant advantages over currently employed inorganic crystals and are leading candidates for the next generation of devices.[1–3] In particular, periodically structured materials enable applications in photonic bandgap materials, phase-matched frequency conversion, tuned electro-optic devices, and 3-dimensional data storage.[4]

The fabrication of unique periodic structures of dissimilar polymers is possible by layer-multiplying coextrusion technology.[5,6] The extremely flexible, continuous process is readily translated into cost-effective production of commercial quantities. In contrast to the well-known concept of self-assembly, layer multiplication uses forced assembly to fabricate a wide variety of melt-processable polymers into continuous film with thousands of alternating microlayers or nanolayers. The thickness of individual continuous layers can be controlled from 10 nm to 100 μm. The first commercial applications of microlayered polymers exploited the vivid optical effects obtained from microlayer film of transparent polymers of different refractive indices for a variety of decorative products.[7] More recently, the use of microlayer technology in light management has extended to mirrors and laptop computer screens.[8]

An abundance of advanced applications for periodic polymeric structures would be enabled by locating functionality in one or both layers, Figure 1. Recently, we have been particularly interested in incorporating a non-linear dye or a photoreactive organic compound into one of the layers to create non-linear optical materials that function as optical switches and optical limiters,[9] and as light reflecting systems that can be patterned for information storage.[10] Incorporation of the appropriate functionalities could result in multilayer architectures with periodically reversing optical nonlinearity.[11,12]

Phthalocyanines have traditionally been used as dyes and colorants for the automotive, textiles, and paper industries.[13] Other applications include electrical conductors, gas sensors, optical data storage, photosensitizers, and optical limiters.[14] Phthalocyanines
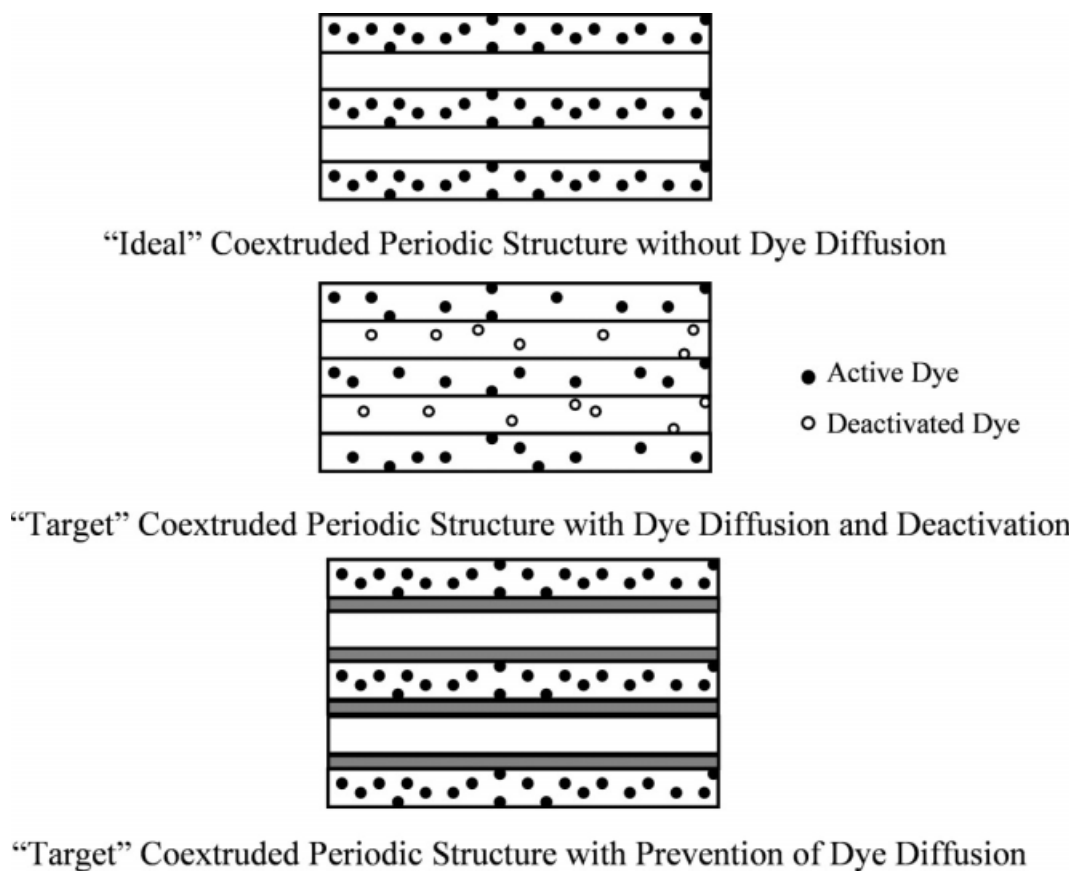
Figure 1 Schematics showing the ideal coextruded periodic structure, the coextruded periodic structure with dye diffusion and deactivation, and the coextruded periodic structure with barrier layers to prevent dye diffusion.

are known to combine with a variety of metals and have strong absorption in the visible region.[15] Lead phthalocyanine in particular has good optical limiting properties due to the conjugation within the macro-cycle.[16] The optical properties of phthalocyanines have generally been studied in solution or as thin films.[17] However, the solid state applications of phthalocyanine compounds can be expanded by dispersing them in a transparent polymeric matrix. An important consideration in choosing a polymer for phthalocyanine blends is achieving good dispersion of the monomeric form, with conservation of the electronic structure. When lead phthalocyanine is blended with some aromatic polyesters, the central lead atom is replaced with hydrogen to give the less efficient lead-free form.[18] A particularly attractive feature of polycarbonate blends is the high concentration of lead phthalocyanine monomer. Dispersions of 1 wt % dye are possible without significant aggregation.[19,20]

An additional consideration arises if a dye is to be located in a specific layer of a periodic polymeric structure that is fabricated by layer-multiplying coextrusion. It is anticipated that due to the thinness of the individual layers in the layered assembly and the mobility of the relatively low molecular weight dye in the polymer melt, a substantial fraction of the dye will diffuse from the doped layer to the undoped layer. Diffusion of small molecular weight additives is often used to an advantage in applications such as cling film,[21] and GRIN optical fibers where a concentration gradient is desired.[22] In other situations, such as diffusion of additives or contaminants from recycled polymer, it is not a desired effect.[23] The advantages or disadvantages of dye diffusion in a periodic layered assembly derive from the dye properties in each of the layers. The diffusivity of a dye depends on the temperature and the affinity of the dye for the undoped layer.[24]

A variety of solutions to dye diffusion can be considered. For example, the dye might be immobilized in one layer by grafting or encapsulation. Two alternative approaches are examined in this study. The first is to combine the doped polymer with a polymer that interacts with the diffused dye so that the electronic structure is not conserved. Thus, the active monomer form of the dye is maintained only in the doped layer, as shown schematically in Figure 1. To demonstrate this approach, we combine layers of polycarbonate containing lead phthalocyanine with alternating layers of undoped polyester by layer-multiplying coextrusion in the anticipation that the fraction of dye that diffuses into the polyester layers
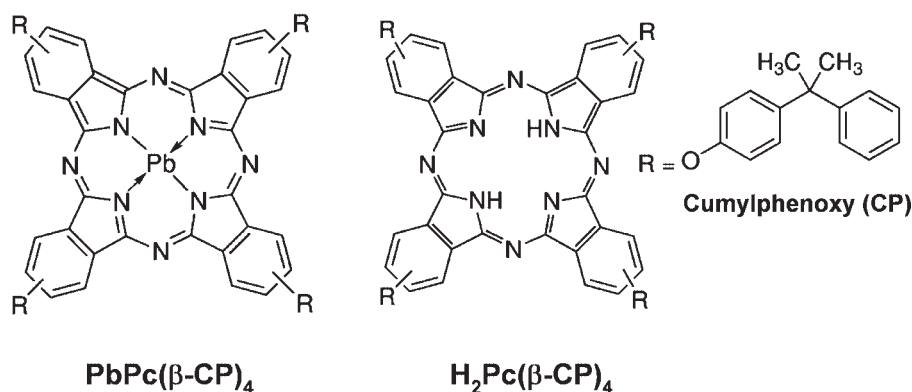
Figure 2 Chemical structures of lead tetracumylphenoxy phthalocyanine (PbPc(β-CP)$_4$) and metal-free tetracumylphenoxy phthalocyanaine (H$_2$Pc(β-CP)$_4$).

will be converted to the less active lead-free form, leaving the active lead form only in the polycarbonate layers. A second approach involves separating the doped polycarbonate layers and the undoped polyester layers with a thin layer of a third polymer as shown schematically in Figure 1. The third polymer acts as a barrier and prevents diffusion of dye between the doped and the undoped layers.

MATERIALS AND METHODS

Characterization of phthalocyanine in solution

Lead tetracumylphenoxy phthalocyanine (PbPc(β-CP)$_4$) and metal-free tetracumylphenoxy phthalocyanine (H$_2$Pc(β-CP)$_4$) were purchased from Sigma-Aldrich in powder form and used as received. The respective dye structures are shown in Figure 2. The UV/Vis absorbance spectra of the dyes in chloroform solutions were measured with an Ocean Optics spectrometer, SD 2000 fiber optic spectrometer and OOI Base 32 software.

To obtain the monomer extinction coefficient, low concentrations of PbPc(β-CP)$_4$ in chloroform ($<10^{-5}$ M) were used so that only the monomer form existed. The monomer was characterized by a main peak at 724 nm along with a small side peak at 650 nm, Figure 3. The extinction coefficient was taken from the slope of the linear plot of concentration versus absorbance at 724 nm for the low concentration solutions. The measured extinction coefficient of $1.50 \times 10^5 \, M^{-1}cm^{-1}$ for PbPc(β-CP)$_4$ in chloroform was consistent with values reported in the literature.[15,19] With increasing concentration of PbPc(β-CP)$_4$ in chloroform, a steady decrease in the monomer extinction at 724 nm was observed. Concurrently, a broad shoulder centered at 820 nm appeared and increased with increasing concentration. The emerging shoulder at 820 nm was attributed to the formation of the PbPc(β-CP)$_4$ dimer.[15]

Dilute solutions of H$_2$Pc(β-CP)$_4$ in chloroform with concentrations similar to those of the PbPc(β-CP)$_4$ solutions were used to obtain the monomer spectrum and to determine the extinction coefficient. The H$_2$Pc(β-CP)$_4$ monomer was characterized by double peaks at 705 nm and 670 nm, together with two smaller side peaks at 645 nm and 610 nm, Figure 4.[15] The calculated extinction coefficient of 1.57×10^5 $M^{-1}cm^{-1}$ for H$_2$Pc(β-CP)$_4$ in chloroform at 705 nm was close to the value of $1.59 \times 10^5 \, M^{-1}cm^{-1}$ reported previously.[15] As the concentration of H$_2$Pc(β-CP)$_4$ in chloroform increased, a decrease in extinction of the main monomer peaks was observed. The decrease in the main peaks was accompanied by broadening of the 645 nm and 610 nm peaks into a single peak. The changes in the spectra were attributed to dimer formation.[15]

The spectra of the PbPc(β-CP)$_4$ and H$_2$Pc(β-CP)$_4$ dimers in chloroform were obtained by subtracting a fraction of the monomer spectrum, $\varepsilon_1(\lambda)$ (designated as the spectrum of the solution with the lowest dye
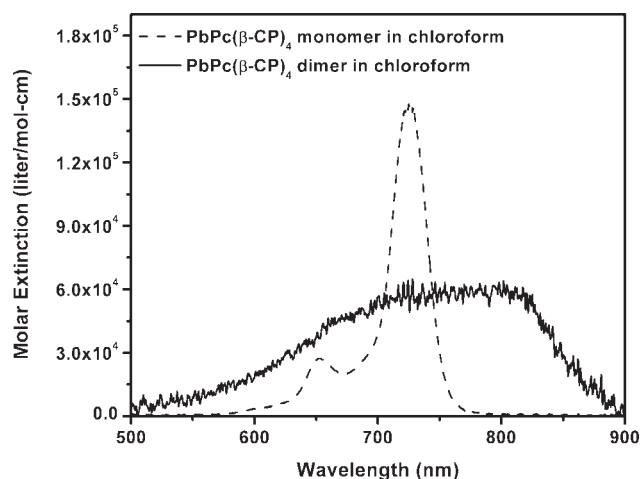

Figure 3 Measured spectrum of the (PbPc(β-CP)$_4$) monomer and the calculated spectrum of the (PbPc(β-CP)$_4$) dimer in chloroform solution.
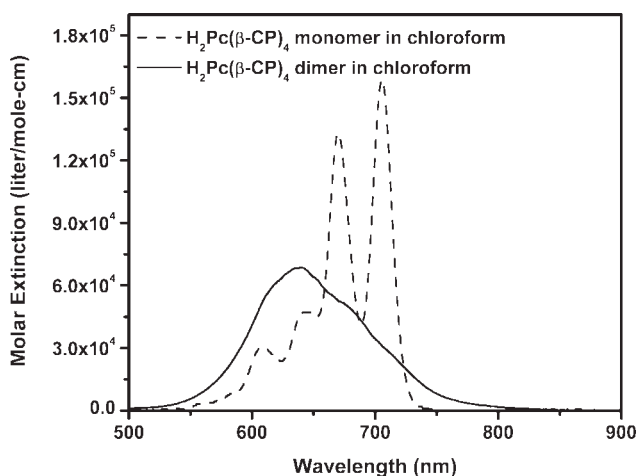
Figure 4 Measured spectrum of the (H$_2$Pc(β-CP)$_4$) monomer and the calculated spectrum of the (H$_2$Pc(β-CP)$_4$) dimer in chloroform solution.

concentration, 1.59×10^{-6} M), from the spectrum of the solution with the highest concentration, $\varepsilon_H(\lambda)$ (2.68×10^{-3} M), until a smooth dimer spectrum, $\varepsilon_2(\lambda)$, was achieved that closely fit the reported dimer spectrum[15,19]

$$\varepsilon_2(\lambda) = \frac{\varepsilon_H(\lambda) - f_m \varepsilon_1(\lambda)}{1 - f_m} \quad (1)$$

where f_m is the fraction of the monomer spectrum that was subtracted. The resulting dimer spectra are included in Figures 3 and 4.

After the monomer and dimer spectra were determined, all other measured spectra, $\varepsilon(\lambda)$, were deconvoluted by adding fractions of the monomer and dimer spectra until a good fit was achieved

$$\varepsilon(\lambda) = f_m \varepsilon_1(\lambda) + (1 - f_m)\varepsilon_2(\lambda) \quad (2)$$

From the resulting monomer and dimer concentrations, the equilibrium constant for dimer formation in chloroform at 25°C, K_{eq}, was calculated at each concentration according to

$$K_{eq} = \frac{C_d}{C_m^2} = \frac{1 - f_m}{2C_o f_m^2} \quad (3)$$

where C_m and C_d are the monomer and dimer concentrations, respectively, C_o is the total concentration of dye in the solution, and $C_m = C_o f_m$ and $C_d = C_o (1 - f_m)/2$. The average equilibrium constant for PbPc(β-CP)$_4$ in chloroform was 310 and comparable to the literature reports.[15,19] The equilibrium constant of 6100 obtained for H$_2$Pc(β-CP)$_4$ was also comparable to the literature report.[14,15] It was an order of magnitude higher that of PbPc(β-CP)$_4$, confirming that H$_2$Pc(β-CP)$_4$ formed dimer more readily than PbPc(β-CP)$_4$ in chloroform.

Phthalocyanine blends

The dyes were blended with polycarbonate (Calibre 200-15, provided by the Dow Chemical Company in pellet form) and polyethylene terephthalate glycol (Eastar 6763, provided by the Eastman Chemical Company in pellet form). Master batches of 20 wt % PbPc(β-CP)$_4$ in PC, PbPc(β-CP)$_4$ in PETG, and H$_2$Pc(β-CP)$_4$ in PETG were solution blended in chloroform at ambient temperature. The solution blends were dried in a vacuum oven overnight (12 h) at 60°C. The master batches were diluted by melt blending with pellets of the same polymer in a DACA mini twin screw extruder at 270°C with a residence time of 5 min. The melt blends had target concentrations of 0.1, 0.2, 0.5, 1, 2, and 4 wt % dye.

To determine the actual dye concentration of the blends, the blends were dissolved in chloroform with dye concentrations $<10^{-5}$M to ensure that only the monomer form was present. For each UV/Vis measurement, a reference solution containing a similar concentration of the polymer in chloroform was used. The actual dye concentration was determined using Beer's law and the previously determined monomer extinction coefficient. Densities of 1.19 and 1.27 gcm^{-3} for PC and PETG were used to convert from molar concentration to weight percentage, Tables I–III. Subsequent analyses of the blends were based on the measured concentrations.

For UV/Vis measurements on the polymer blends, thin films of each blend were compression molded at 270°C for 3 min and cooled in the press by circulating water. Good quality optical films were obtained by pressing the blends between glass slides that were coated with a thin layer of silicone mold release spray. To avoid signal saturation in the UV/Vis measurements, the film thickness was less than 50 μm and decreased as the dye concentration increased. A digital micrometer was used to measure the film thicknesses.

A PC blend with 4 wt % PbPc(β-CP)$_4$ was coextruded with undoped PETG in a 50/50 composition using the layer-multiplying coextrusion process described previously.[25] The coextrusion system consisted of two extruders and six multiplying elements, which produced a 129-layer assembly with the dye in alternating layers. A sacrificial skin layer of polyethylene was added before the exit die to improve surface quality and handling of the thin films. The core film thickness excluding the skin layers was 11 μm, giving a nominal layer thickness of 86 nm.

Additional films were coextruded using the three-component layer multiplying process described previously.[25] The films consisted of 129 alternating layers of a PC blend with 4 wt % PbPc(β-CP)$_4$ and undoped PETG separated by 128 thin tie-layers of a fluorinated terpolymer, Dyneon THV 220G (THV).

TABLE I
Concentration of PbPc(β-CP)₄ in Pc Blends

Target concentration (wt %)	Measured concentration (wt %)	Difference from target[a] (%)
0.1	0.11	10
0.2	0.22	10
0.5	0.59	18
1	1.14	14
2	2.15	7
4	3.68	8

[a] % Difference from Target $= \frac{\text{Target}-\text{Measured}}{\text{Target}} \times 100$.

The composition was PC/THV/PETG 42/16/42. A sacrificial skin layer of polyethylene was added before the exit die. One film was extruded with a core film thickness excluding the skin layers of 564 μm, giving nominal layer thicknesses of 2 μm for the PC and PETG layers, and 0.38 μm for the THV layers. Another film was extruded with a core film thickness of 23 μm, giving nominal layer thicknesses of 150 nm for the PC and PETG layers, and 28 nm for the THV layers.

RESULTS AND DISCUSSION

Blends of PbPc(β-CP)₄ with polycarbonate

The concentration of PbPc(β-CP)₄ in the PC blends, which was determined from a dilute solution ($<10^{-5}$M) of the blend in chloroform, was generally slightly higher than the target concentration, Table I. The measured concentrations were used for the subsequent analysis of the absorption spectra of the blends. Comparison of the PbPc(β-CP)₄ spectra in the PC blends with those in chloroform solutions revealed that the dye existed as monomer in the lowest concentration blend film (nominally 0.1 wt %) with the main peak at 724 nm and a small side peak at 650 nm. The extinction coefficient obtained from the PC blend was 1.27×10^5 M^{-1}cm^{-1}, which was only slightly lower than the extinction coefficient of PbPc(β-CP)₄ in chloroform.

With increasing dye concentration in the PC blend, the PbPc(β-CP)₄ remained primarily in the monomer form, Figure 5a. However, a broad shoulder at 820 nm appeared on the high wavelength side of the monomer peak as evidence of some aggregation. A gradual increase in the extinction at 820 nm was accompanied by a decrease in the monomer peak extinction. Two isosbestic points at 635 nm and 748 nm showed that an equilibrium existed between the two dye states, monomer and dimer, which was similar to the behavior seen for this dye in chloroform.[15]

The dimer spectrum in PC was obtained according to eq. (1) and is included in Figure 5b. The broad dimer spectrum in PC corresponded with that

reported previously,[19] but differed in intensity and shape from the dimer spectrum in chloroform (Fig. 3). The extinction was considerably lower in the PC spectrum and the strong contribution in the 800 nm region of the chloroform spectrum was not seen in the PC spectrum.

The relative amounts of dimer in the intermediate concentrations were calculated by deconvoluting the film spectra following the method used for chloroform solutions. A slope of 2 in the logarithmic plot of monomer concentration versus dimer concentration was evidence that a 2-component equilibrium existed with very few, if any, higher order aggregates present in the films. Based on the amounts of monomer and dimer, the equilibrium constant for the PC blends was calculated from eq. (3) to be about 27. The concentration at which noticeable aggregation occurred in the PC blends ($\sim 2 \times 10^{-3}$ M) was two orders of magnitude higher than in solution ($\sim 2 \times 10^{-5}$M). As noted previously,[19] when the blend was quenched from the melt, the equilibrium established at the melt temperature was
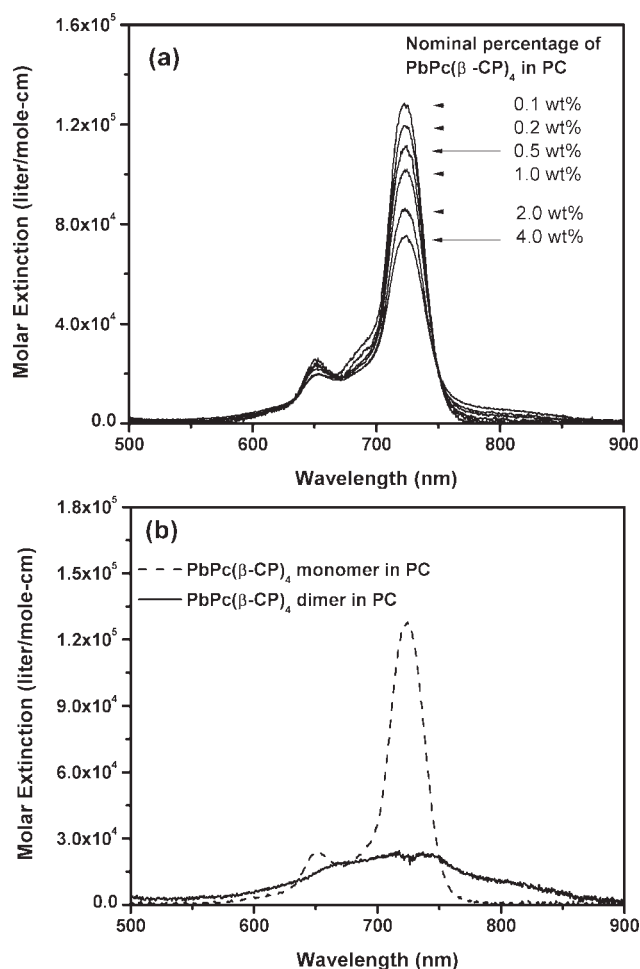

Figure 5 Spectra of (PbPc(β-CP)₄) in PC blends: (a) the concentration dependence; and (b) the measured monomer spectrum and the calculated dimer spectrum.
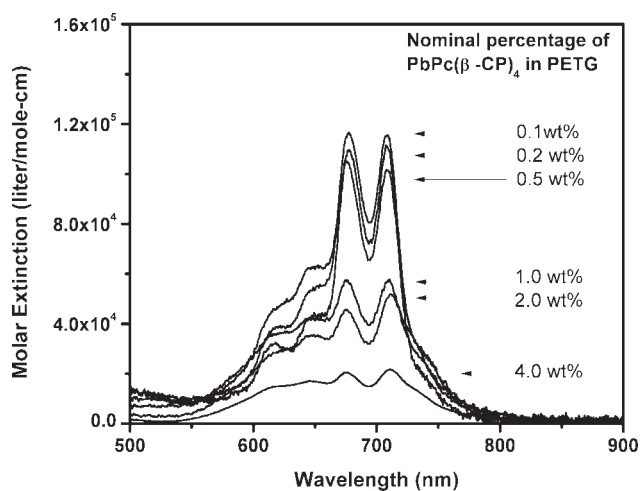
Figure 6 The concentration dependence of the (PbPc(β-CP)$_4$) spectrum in PETG blends.

preserved in the solid state glass. The rigid polymer chains prevented aggregation and the high monomer concentration was stable below the glass transition temperature of the polymer matrix.

Blends of PbPc(β-CP)$_4$ and H$_2$Pc(β-CP)$_4$ with PETG

The UV/Vis spectrum of PbPc(β-CP)$_4$ in PETG was very different from the spectrum in PC. Rather, the spectrum with two main peaks and two side peaks, Figure 6, closely resembled the spectrum of H$_2$Pc(β-CP)$_4$ in chloroform. It appeared that a substantial fraction of the Pb-form was transformed to the H$_2$-form in PETG, probably as a result of metal extraction by the hydroxyl end groups of the copolyester.

Dissolution of the blends in chloroform at low concentration ($<10^{-5}$M) revealed a mixture of PbPc(β-CP)$_4$ and H$_2$Pc(β-CP)$_4$ in the monomer forms, as indicated by a shoulder on the high wavelength side of the main double peaks of the H$_2$Pc(β-CP)$_4$. To determine the dye concentrations, deconvolution of the spectra was conducted using the monomer spectra in chloroform. Approximately half of the target concentration was consistently converted to H$_2$Pc(β-CP)$_4$ and approximately 20% remained in the original

PbPc(β-CP)$_4$ form, Table II. The dye mixture demonstrated that melt processing with PETG permanently converted the lead phthalocyanine to the metal free phthalocyanine. In addition, apparently 30% of the dye was lost in PETG blends, which was attributed to thermal degradation of the H$_2$Pc(β-CP)$_4$ that formed during melt processing.

It appeared that PbPc(β-CP)$_4$ changed to the metal-free H$_2$Pc(β-CP)$_4$ on melt blending with PETG. For comparison, H$_2$Pc(β-CP)$_4$ was blended with PETG under the same conditions used to prepare the blends of PbPc(β-CP)$_4$ in PETG. The actual H$_2$Pc(β-CP)$_4$ concentration was determined from the spectra of dilute solutions of the blends in chloroform. The H$_2$Pc(β-CP)$_4$ spectrum was identical to that of the monomer in chloroform, showing that the H$_2$-form was conserved in the blend. However, the measured dye concentration was about 30% less than the target concentration, Table III. The difference between the measured and targeted concentrations was attributed to thermal degradation of the H$_2$Pc(β-CP)$_4$ during blending. It has been reported that the phthalocyanine ring can be degraded into components that do not absorb in the spectral regions studied.[26–28]

The film with the lowest concentration of H$_2$Pc(β-CP)$_4$ in PETG showed similar spectral characteristics as H$_2$Pc(β-CP)$_4$ in chloroform solution. The two main peaks of the monomer were present, along with the two lower wavelength side peaks, Figure 7. However, the intensities and positions of the two main peaks were slightly different from those in solution (Fig. 4). Of the two main peaks, the lower wavelength peak was stronger in the PC blend, whereas the higher wavelength peak was stronger in the chloroform solution. The high wavelength peak was at 707 nm in PC, slightly higher than the 705 nm in solution. The low wavelength peak was also slightly higher than the 670 nm in solution and showed a slight blue shift as the concentration increased: from 680 nm in the 0.11 wt % film to 676 nm in the 2 wt % film. With increasing dye concentration, dimer formation caused the 680 nm peak to broaden, which resulted in the apparent blue shift. The film spectra also showed a broadening of the two side peaks that was attributed

TABLE II
Concentration of PbPc(β-CP)$_4$ in PETG Blends

Target concentration (wt %)	Measured H$_2$Pc(β-CP)$_4$ concentration (wt %)	Measured PbPc(β-CP)$_4$ concentration (wt %)	Total dye concentration (wt %)	Difference from target (%)
0.1	0.048	0.0091	0.0571	−43
0.2	0.093	0.037	0.130	−35
0.5	0.25	0.12	0.37	−26
1	0.50	0.23	0.73	−27
2	0.94	0.45	1.39	−31
4	2.22	0.71	2.93	−26

TABLE III
Concentration of $H_2Pc(\beta\text{-}CP)_4$ in PETG Blends

Target concentration (wt %)	Measured concentration (wt %)	Difference from target (%)
0.1	0.075	−25
0.2	0.14	−30
0.5	0.36	−28
1	0.91	−9
2	1.89	−5.5
4	2.97	−25

to dimer formation. In addition, a small shoulder appeared on the high wavelength side of the main peaks. The shoulder disappeared when the blends were dissolved in chloroform, giving rise to the possibility that the shoulder resulted from some specific interaction between $H_2Pc(\beta\text{-}CP)_4$ and PETG.

It is useful to compare blends of $H_2Pc(\beta\text{-}CP)_4$ in PETG with the blends of $PbPc(\beta\text{-}CP)_4$ in PETG, where it appeared that a large fraction of the Pb-form was converted to the H_2-form. Both exhibited about a 30% loss in dye when compared to the target concentrations. This was in contrast to $PbPc(\beta\text{-}CP)_4$ in PC where the measured concentration was generally higher than the target concentration. Therefore, the 30% loss in PETG was attributed to degradation of the $H_2Pc(\beta\text{-}CP)_4$ at the elevated temperatures encountered during melt blending.

The spectra of both PETG blends resembled those of the $H_2Pc(\beta\text{-}CP)_4$ in chloroform with two main peaks and two lower wavelength side peaks, although the positions and intensities varied somewhat. Some differences between the spectra of $PbPc(\beta\text{-}CP)_4$ in PETG and those of $H_2Pc(\beta\text{-}CP)_4$ in PETG were attributed to the presence of unconverted $PbPc(\beta\text{-}CP)_4$. It appeared that $H_2Pc(\beta\text{-}CP)_4$ readily aggregated in PETG, as indicated by the rapid decrease in intensity
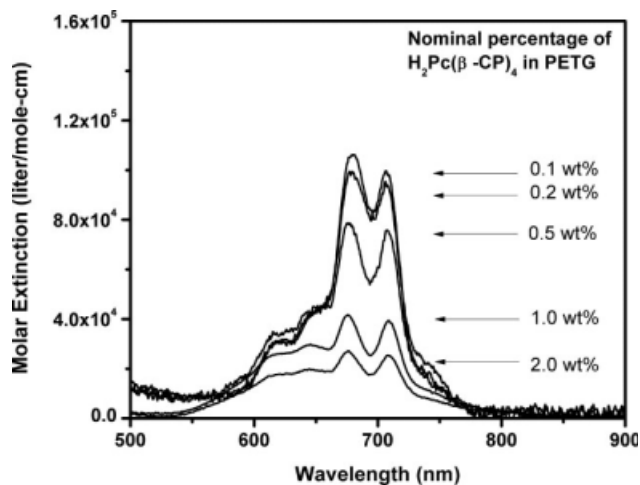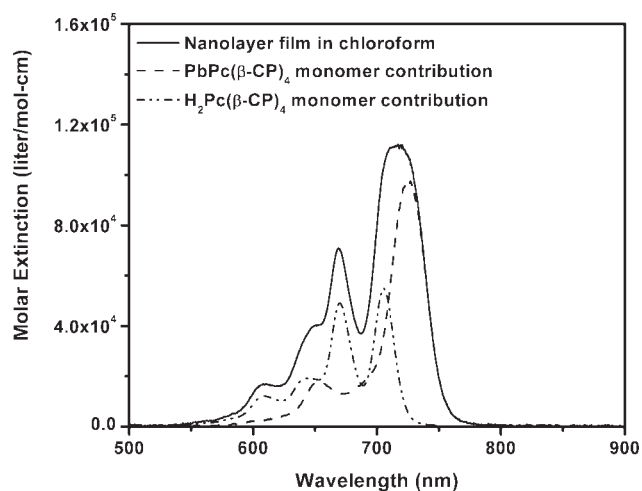

Figure 8 Spectrum of the nanolayer film in dilute chloroform solution deconvoluted into the contributions of $(PbPc(\beta\text{-}CP)_4)$ and $(H_2Pc(\beta\text{-}CP)_4)$.

of the monomer peaks with increasing blend concentration. However, it proved difficult to deconvolute the spectra of the PETG blends into the individual monomer and dimer components primarily because of the shifts that occurred in the main peaks.

Nanolayer coextruded films

The coextruded films consisted of 129 alternating nanolayers of PC with 4 wt % $PbPc(\beta\text{-}CP)_4$ and nanolayers of PETG without dye. It was anticipated that due to the thinness of the individual nanolayers in the coextruded assembly, which was nominally 86 nm, and the mobility of the relatively low molecular weight dye in the polymer melt, a substantial fraction of the dye would diffuse from the PC layers
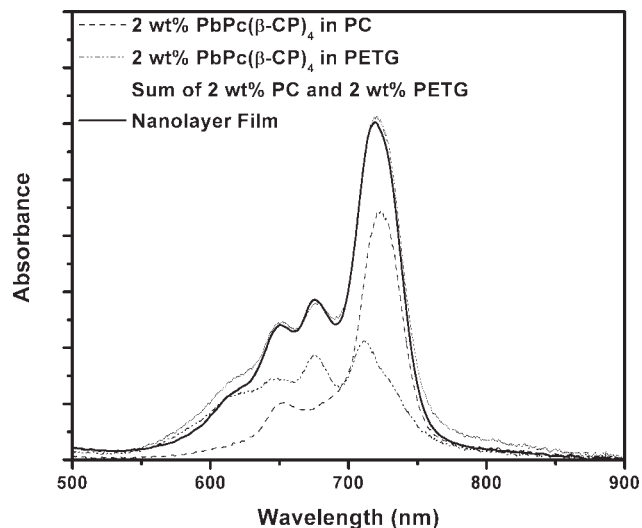

Figure 7 The concentration dependence of the $(H_2Pc(\beta\text{-}CP)_4)$ spectrum in PETG blends.

Figure 9 Absorbance spectrum of the nanolayer film compared with the calculated spectrum.
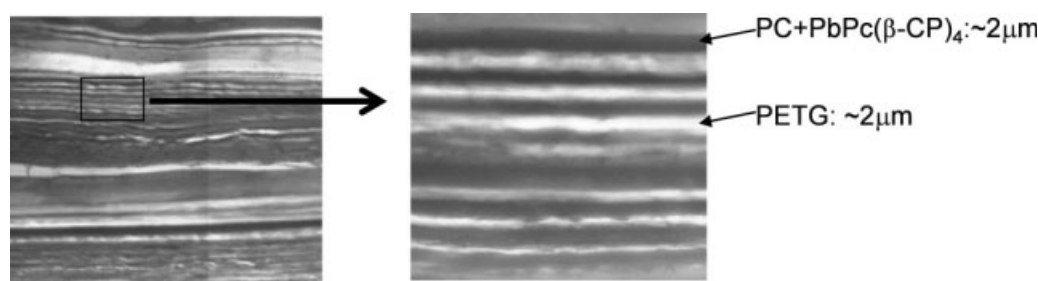
Figure 10 Optical micrograph of a nanolayered film with THV barrier layers. The nominal thickness of the PC and PETG layers was 2 μm and the nominal thickness of the THV layers was 0.38μm.

into the PETG layers where most of it would be irreversibly converted to $H_2Pc(\beta\text{-CP})_4$.

The dye content of the nanolayer film was obtained by dissolving the film in chloroform following the methodology used with the compression molded blend films. A dilute solution of the coextruded film in chloroform gave a UV/Vis spectrum with the combined features of $PbPc(\beta\text{-CP})_4$ and $H_2Pc(\beta\text{-CP})_4$ monomers, Figure 8. Deconvoluting the spectrum gave the actual dye concentrations in the film as $PbPc(\beta\text{-CP})_4$ (50% or 2 wt %) and $H_2Pc(\beta\text{-CP})_4$ (32% or 1.3 wt %), for a total of 82% of the target concentration. It was assumed that most of the $PbPc(\beta\text{-CP})_4$ was the dye that remained in the PC layers whereas the $H_2Pc(\beta\text{-CP})_4$ represented the dye that diffused from the PC layers into the PETG layers where it was converted to the H_2-form. If the dye loss occurred predominately by degradation of $H_2Pc(\beta\text{-CP})_4$ in the PETG layers, it appeared that about half of the $PbPc(\beta\text{-CP})_4$ diffused into the PETG layers. Thus, the dye concentration was nominally 2 wt % in both PC and PETG layers, although degradation decreased the active dye concentration in the PETG layers. The small amount of $PbPc(\beta\text{-CP})_4$ that might have been present in the PETG layers was neglected.

The UV/Vis spectrum of the dye in the nanolayer film was noticeably different from the spectrum in chloroform solution due to the presence of dimer especially in the PETG layers, Figure 9. In particular, $H_2Pc(\beta\text{-CP})_4$ dimer formation significantly reduced the monomer peaks. The dye content calculated from the chloroform solution was used to estimate the UV/Vis spectrum of the nanolayer film. According to the solution spectrum, the dye was approximately equally distributed between the PC and PETG layers at a nominal concentration of 2 wt %. Furthermore, the nanolayer film had equal volumes of PC and PETG. Therefore, the absorbance spectra of the nominally 2 wt % blends of $PbPc(\beta\text{-CP})_4$ in PC and in PETG were multiplied by a factor of 0.5 and combined to produce the calculated nanolayer film spectrum in Figure 9. The calculated spectrum closely corresponded to the measured spectrum, thereby confirming that when the dye diffused from the PC layers

to the PETG layers, it largely converted to the H_2-form, leaving the functionality of the Pb-form only in the alternating PC layers

Nanolayer coextruded films with a barrier layer

Additional coextruded films consisted of 128 alternating nanolayers of PC with 4 wt % $PbPc(\beta\text{-CP})_4$ and nanolayers of PETG without dye, each separated by a thin barrier layer of THV. To determine whether the $PbPc(\beta\text{-CP})_4$ had diffused from the doped PC layers to the undoped PETG layers, optical micrographs of microlayer films were examined. From the image in Figure 10, the individual 2 μm thick PC and PETG layers are clearly discerned. The PC layers appear dark due to the presence of the $PbPc(\beta\text{-CP})_4$. The undoped PETG layers are white in the image, indicating the lack of diffused dye and the barrier effect of the THV layer. It is not possible to discern the 0.38 μm THV layers either because they are too thin or because
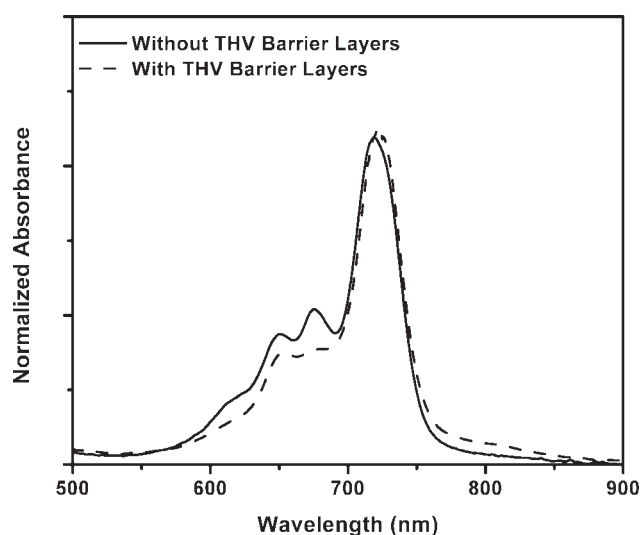

Figure 11 Spectra of nanolayered films with and without the THV barrier layers. In the film with THV barrier layers, the nominal thickness of the PC and PETG layers was 150 nm and the nominal thickness of the THV layers was 28 nm. In the film without the THV barrier layers, the nominal thickness of the PC and PETG layers was 86 nm.

there is not enough contrast to differentiate them from the PC or PETG layers.

Any dye that diffused through the THV layer would have been converted to the hydrogen form in the PETG layer. Thus, the amount of hydrogen form in the nanolayer film was a measure of the extent of dye diffusion. It was not possible to dissolve the films and determine the dye composition from the solution UV/Vis spectrum because a common solvent for PC, PETG, and THV was not found. However, comparing the spectra of nanolayer films with and without the barrier layers demonstrated major differences in the 600–700 nm region, Figure 11. In particular, the reduced intensity of the $H_2Pc(\beta\text{-CP})_4$ monomer peak at 675 nm confirmed that the amount of hydrogen form was much lower in the nanolayer film with the barrier layer and, therefore, the THV layers effectively prevented diffusion of dye into the PETG layers.

The dye content of the PC and PETG layers in the nanolayer film was estimated by fitting the UV/Vis absorbance spectrum with the spectra of the $PbPc(\beta\text{-CP})_4$ blends. The dye was assumed to be only in the PC and PETG layers, not in the THV barrier layers. The best fit for a nanolayer film with equal volumes of PC and PETG was obtained by combining the absorption spectra of nominally 4 wt % $Pb_2Pc(\beta\text{-CP})_4$ in PC and 0.2 wt % $PbPc(\beta\text{-CP})_4$ in PETG, each multiplied by a factor of 0.5. The good correspondence between the measured spectrum of the nanolayer film and the calculated spectrum, shown in Figure 12, indicated that only about 5% of the $PbPc(\beta\text{-CP})_4$ diffused from the PC layers into the PETG layers where it was converted to $H_2Pc(\beta\text{-CP})_4$. Most of the dye remained in the alternating PC layers. This was
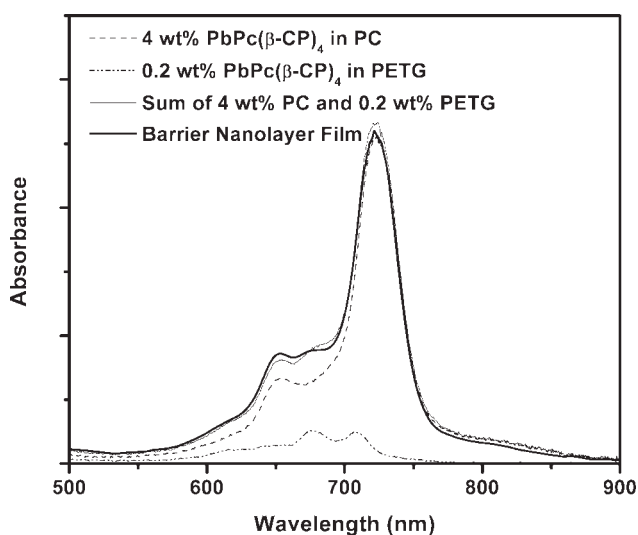

Figure 12 Absorbance spectrum of the nanolayer film with THV barrier layers compared with the calculated spectrum. The nominal thickness of the PC and PETG layers was 150 nm and the nominal thickness of the THV layers was 28 nm.

in strong contrast to the nanolayer film without the barrier layer, and demonstrated that dye migration from one layer to another during coextrusion could be prevented.

CONCLUSIONS

Periodically structured polymeric materials can lead to the next generation of electro-optic and nonlinear optical devices for applications in information technology. An attractive approach for fabricating layered polymeric materials is layer-multiplying coextrusion. This extremely flexible, continuous process combines two or three polymers into continuous film with thousands of alternating microlayers or nanolayers. Many advanced applications for periodic polymeric structures would be enabled by locating a photoactive dye in one or both layers. However, it is anticipated that due to the thinness of the individual layers in the layered assembly and the mobility of the relatively low molecular weight dye in the polymer melt, a substantial fraction of the dye will diffuse from the doped layers to the undoped layers. In the present study, we demonstrate two methods for confining the activity of the dye to the doped layers.

A high concentration of the photoactive monomer form of lead phthalocyanine ($PbPc(\beta\text{-CP})_4$) was obtained in polycarbonate (PC). The concentration that could be achieved in the PC blends before noticeable aggregation occurred ($\sim 2 \times 10^{-3}$ M or 1 wt %) was two orders of magnitude higher than in solution ($\sim 2 \times 10^{-5}$ M). The monomer-dimer equilibrium favored the monomer at higher temperatures. Hence, when the blend was quenched from the melt, the equilibrium established at the melt temperature was preserved in the solid state glass.

In contrast to the polycarbonate blends, it appeared from the absorbance spectra that $PbPc(\beta\text{-CP})_4$ was converted to the less active lead-free form ($H_2Pc(\beta\text{-CP})_4$) in a polyester (PETG). This was confirmed by examining the absorbance spectra of $H_2Pc(\beta\text{-CP})_4$ in solution and in PETG blends. The absorption spectrum of $H_2Pc(\beta\text{-CP})_4$ in chloroform was retained in the PETG blends. Moreover, the absorption spectrum of $H_2Pc(\beta\text{-CP})_4$ in PETG closely reproduced the spectrum of $PbPc(\beta\text{-CP})_4$ in PETG. Transformation of a substantial fraction of the Pb-form to the H_2-form in PETG probably resulted from metal extraction by the hydroxyl end groups of the polyester.

Subsequently, PC containing $PbPc(\beta\text{-CP})_4$ was nanolayered with undoped PETG to create a periodic structure of 129 alternating 86 nm-thick layers. From the absorbance spectrum of the coextruded film, it was determined that about half the dye diffused from the PC layers into the PETG layers,

where it was substantially converted to the lead-free form. Thus, the active monomer form of PbPc(β-CP)$_4$ was maintained selectively in the PC layers.

In a second approach, the layered films were coextruded with the doped PC layers and the undoped PETG layers separated by a thin layer of a third polymer. A fluorinated terpolymer was found to be an effective barrier layer and prevented diffusion of the PbPc(β-CP)$_4$ from the doped PC layers into the undoped PETG layers. As a result, the dye remained selectively in the alternating polycarbonate layers.

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