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Optical Limiting Analysis of Phthalocyanines in Polymer Thin Films

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This paper reports on the effect of embedding twelve phthalocyanines containing In, Ga, Zn and Al as central metals in polymer thin films on their optical limiting abilities. This paper also examines the effect of forming a covalent link between zinc tetraamino phthalocyanine (**10**) and poly (methyl acrylic acid) (PMAA), and Zn (**11**) or OHAl (**12**) octacarboxy phthalocyanines with polyethylenimine (PEI). The average film thickness (for phthalocyanines mixed or linked to polymers) of each Pc/Polymer films on glass was 95 μm . The hyperpolarizability of the twelve phthalocyanines was found to be in the range of 10^{-26} to 10^{-24} esu.L. This is significantly higher than the hyperpolarizabilities of these phthalocyanines in solution, which ranged from 10^{-30} to 10^{-26} esu.L. Degradation studies seem to indicate that placing a phthalocyanine within a polymer thin film may protect it slightly from photo- and thermal degradation.

Keywords: Phthalocyanine, optical limiting, thin films, poly(methyl acrylic acid), Polyethylenimine

1 Introduction

The development of optical limiting (OL) materials has attracted considerable attention as a means of providing protection for light sensitive objects such as the eye from laser radiation (1–4). Materials with strong reverse saturable absorption (RSA) can effectively limit the output energy of incident light, hence such materials are of prime importance in optical limiting applications (5). Metallophthalocyanines (MPcs) have been shown to be excellent OL materials with a high absorption cross section ratio of excited triplet to ground states in the absorption range 400–600 nm (6–9). The nonlinear optical (NLO) properties of MPcs can be modified by substituting different metals into the ring or altering peripheral and axial functionalities (10).

The phthalocyanines that are mostly used as optical limiters are those containing heavy central metals such as indium, gallium, lead and antimony. These metals increase intersystem crossing and consequently triplet quantum yields. In addition, some of these metals do not fit into phthalocyanine central cavity, lowering the symmetry of the phthalocyanine, which has been determined to have a beneficial effect on the phthalocyanine's optical limiting ability. It is

also possible to utilize the peripheral groups to increase the ratio of excited state to ground state absorption cross sections (11–13) which also help with the solubility and disaggregation of the phthalocyanines.

Embedding the phthalocyanines within a transparent polymer thin film adds some protection to the phthalocyanines against degradation. OL studies of Pcs have been mainly done in solution (14, 15) with some reports investigating the solid state behaviour (16–22). A practical optical limiting device requires the casting of the optically active compounds in the solid state. A number of polymers have been employed for supporting phthalocyanines for OL applications with varying success in terms of OL parameters. These include PVC (poly vinylchloride) (23), polystyrene (24) and poly(methyl methacrylate) (PMMA) (25, 26). The latter polymer has been more extensively studied than the rest. This work compares the OL behavior of the phthalocyanine complexes (**1–12**, Fig. 1) embedded in PMAA (poly methyl acrylic acid), in branched PEI (polyethylenimine) and in PMMA, (Fig. 1). The covalent linking of tetraamino or octacarboxy phthalocyanines to PMAA and PEI, respectively, is reported here for the first time. The Pc complexes (Fig. 1) were chosen for their good solubility due to ring substitution (27) and limited aggregation behaviour in solution due to non-peripheral substitution (27). The central metals (In, Ga and Zn) were chosen for their size which will enhance intersystem crossing due to the heavy atom effect. The Pc complexes have been published before (28–34).

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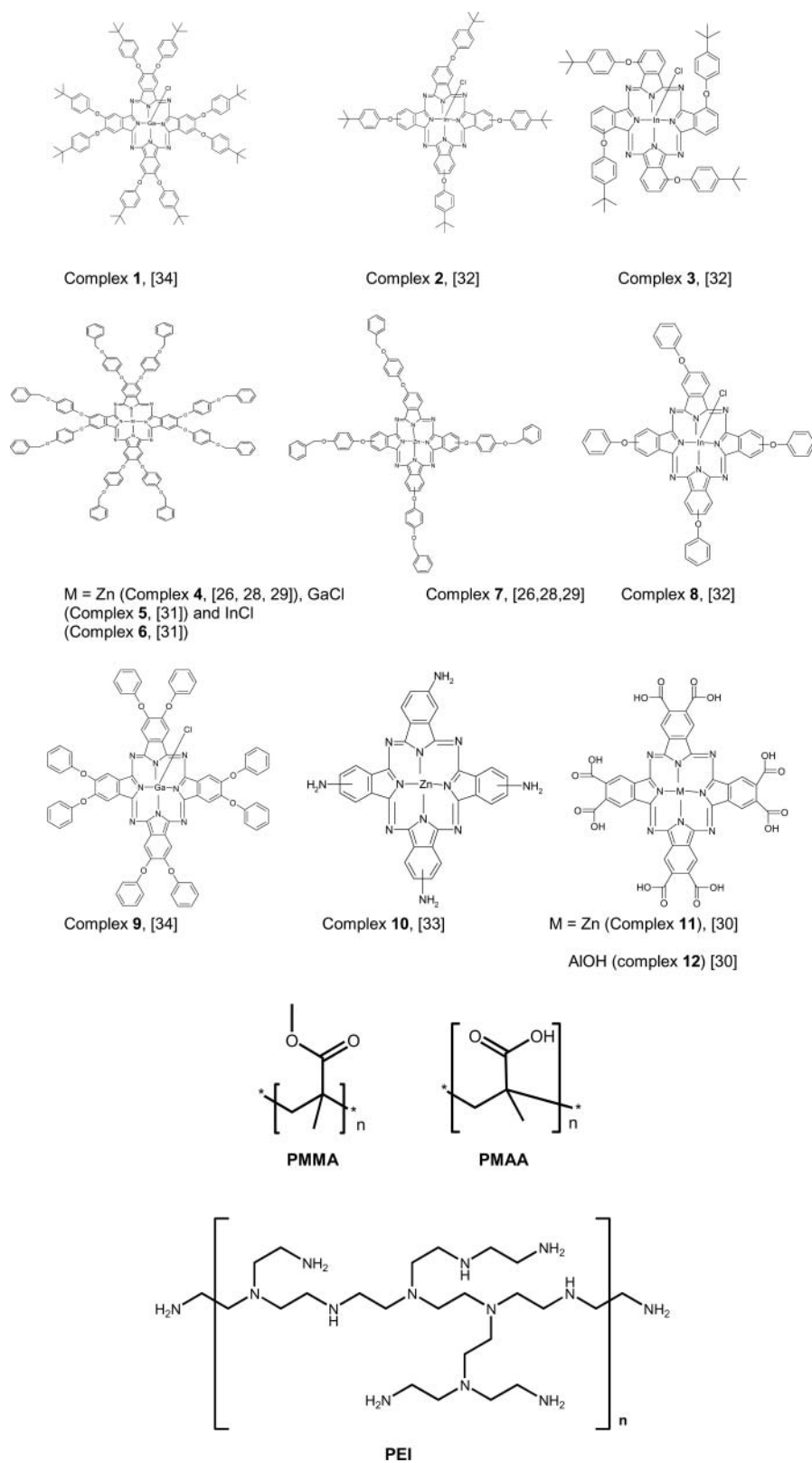


Fig. 1. Chemical structures of the studied phthalocyanines and the polymers. PMMA = Poly(methyl methacrylate), PMAA = poly(methyl acrylic acid), PEI = polyethylenimine.

2 Experimental

2.1 Materials

The syntheses of phthalocyanine complexes (**1** to **12**, Fig. 1) used in this work have been reported before (26, 28–34). Dimethylformamide (DMF) and dichloromethane (DCM) were obtained from Saarchem and dried over molecular sieves before use. Triply deionised water was employed for aqueous solutions. Poly(methyl methacrylate) (PMMA average molecular weight: ~ 120000 g/mol), poly(methyl acrylic acid, (PMAA oligomer, average molecular weights: 900 g/mol), polyethylenimine (branched PEI, average molecular weight: 25000 g/mol (determined by light scattering)) and

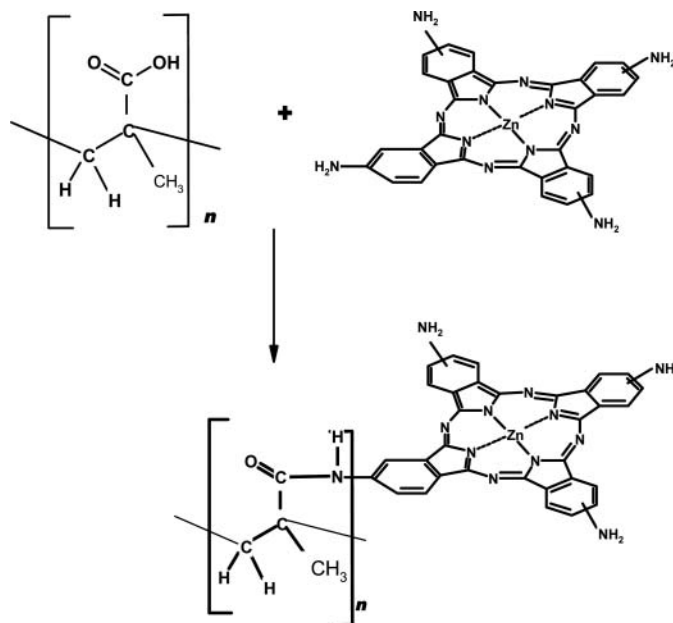
N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) were obtained from Aldrich. N-hydroxysuccinimide (NHS) was obtained from Fluka.

2.2 Preparation of the Phthalocyanine Thin Films

Fabrication of the solid state films of investigated phthalocyanines was done using a Pc/polymer solution in DCM (PMMA), DMF (PMMA) or DMF: water 2:1 (PEI and PMAA). The solvent employed depended on the solubility of both the phthalocyanine and the polymer. The DMF: water mixture, in particular, was used for the linkage formation studies because it was found that the phthalocyanines and polymers involved were not soluble in the same solvent, so a solvent mixture was necessary. The thin films of Pc alone or Pc with polymers were formed by placing a drop of the solution on a glass slide, followed by the evaporation of the solvent. Concentrations of phthalocyanines were of the order of 10^{-4} M. The polymer solution in which the phthalocyanines were dissolved was 15% by weight.

2.3 Covalent Linking of Phthalocyanines to Polymers

Amide linkages were formed between complex **10** (zinc tetraamino phthalocyanine, ZnTAPc, Scheme 1) and PMAA, as well as complexes **11** and **12** (metallo octacarboxyphthalocyanines, OCPcs, $M = \text{Zn, Al}$, Scheme 2) and PEI. The MOCPcs complexes **11** and **12** ($\sim 1.05 \times 10^{-4}$ Mol) were first dissolved in a DMF:water mixture (2:1) (4 mL), then EDC (5 mM) and NHS (2 mM) were added to convert the carboxylic group ($-\text{COOH}$) of the MPcs into an active carbodiimide ester group. The mixture was left to stir at room temperature under a nitrogen atmosphere for 1 h. After this time, 1 g (0.04–0.1 mmol) of PEI was added to the activated Pc and the mixture stirred for 1 h to allow for the conjugation of the Pc to the PEI to take place. For the conjugation of PMAA to complex **10** (ZnTAPc), the carboxylic group ($-\text{COOH}$) of the PMAA was first activated by stirring a mixture of the PMAA with EDC (5 mM) and NHS (2 mM) in DMF:water for 1 h, followed by addition

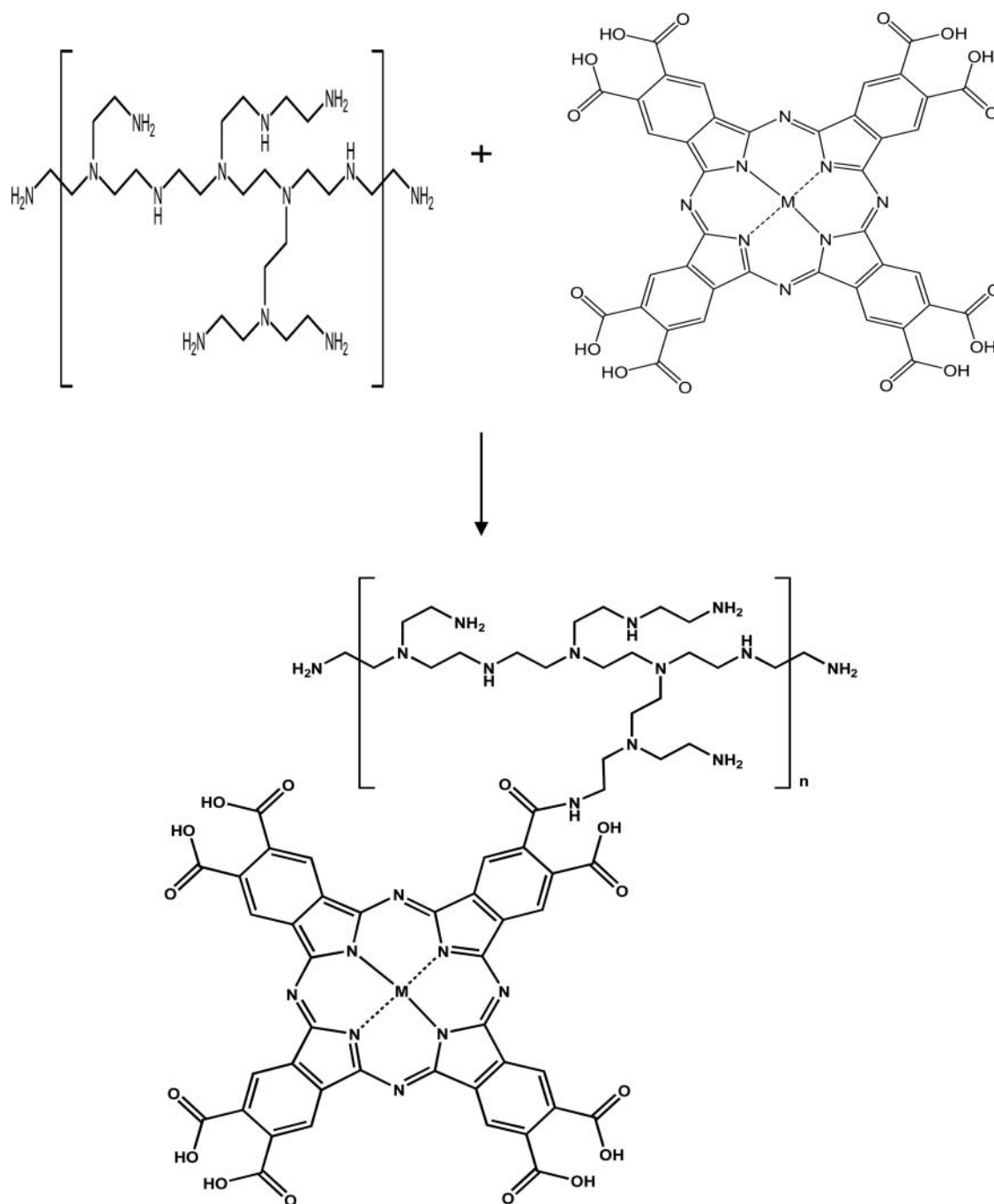


Sch. 1. Formation of the amide linkage between ZnTAPc (**10**) and PMAA.

of ZnTAPc and further stirring for 1 h. The linked Pc-polymers were separated from the unlinked polymer and phthalocyanines by size exclusion chromatography using Biobeads and DMF as the eluent. The linked complex was then formed into a thin film for analysis, along with the thin film of a mixture of these two compounds without a chemical bond. The molar ratio of PEI or PMAA to Pc was kept the same for the linked and mixed complexes. However, the ratio of polymer to Pc in the linked and mixed complexes will differ in the final product due the activation and purification steps in the former.

2.4 Equipment

A convenient and fast experimental method to assess materials for NLO (including optical limiting) is the open aperture Z-scan experiment. This measures the total transmittance through the sample as a function of incident laser intensity while the sample is gradually moved through the focus of a lens (along the z-axis). The Z-scan equipment employed in this work was fabricated at the University of Stellenbosch in South Africa. All experiments described in this study were performed using a tunable laser system consisting of an Nd:YAG laser (355 nm, 135 mJ/4–6 ns) pumping an OPO (30 mJ/3–5 ns) with a wavelength range of 420–2300 nm (NT-342B, Ekspla). UV-visible spectra were recorded on a Shimadzu UV-2550 spectrophotometer. A Bruker D8 Discover X-ray diffraction (XRD) equipped with a LynxEye detector, using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405$ Å, nickel filter) was employed for XRD data. Data were collected in the range from $2\theta = 15^\circ$ to 60° , scanning at 1° min^{-1} with a filter time-constant of 2.5 s per step and a



Sch. 2. Formation of the amide linkage between MOCPCs (**11**, **12**) and PEI.

slit width of 6.0 mm. Samples were placed on a zero background silicon wafer slide. A knife-edge attachment was used to determine the film thickness.

Infra-red spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR Spectrometer. Bruker RAM II Raman spectrometer (equipped with a 1064 nm Nd:YAG laser and a liquid nitrogen cooled germanium detector) was used to collect Raman data. Scanning electron microscope (SEM) images were obtained using a JOEL JSM 840 scanning electron microscope. Mass spectral data were collected

with a Bruker AutoFLEX III Smartbeam TOF/TOF Mass spectrometer. The instrument was operated in negative ion mode. The spectra were acquired using dithranol as the MALDI matrix, and with a 355 nm Nd:YAG laser as the ionizing source. Thermal gravimetric analysis (TGA) was carried out using a Shimadzu Simultaneous Thermogravimetry/Differential Thermal Analyzer, Model DTG-60H at a heating rate of $10^{\circ}\text{C min}^{-1}$ in a high-purity nitrogen atmosphere. For photodegradation studies, the polymers were irradiated at room temperature and in air

using a General Electric Quartz lamp (300W, 120 V). The white light from the lamp was used with only water filtering the light, for infrared radiation. Light intensities were measured with a POWER MAX5100 (Molelectron detector incorporated) power meter and were found to be 3.657×10^{15} photons $\text{s}^{-1} \text{cm}^{-2}$. The thin films of phthalocyanine alone (complex **4** was used as an example for these studies) or Pc mixed with polymer were mounted at about 3 cm before the light. This allowed the thin film of Pc/polymer or phthalocyanine alone to be exposed to the full electromagnetic spectrum generated by the lamp, as well as causing an increase in heat to the analysed substances. This setup should therefore cause thermal and light stresses upon the thin film of Pc/polymer or phthalocyanine alone as thin films, allowing us to examine the protection the polymer offers to the phthalocyanine within it compared to the same phthalocyanine alone on a glass side.

2.5 Nonlinear Optical Parameters

The imaginary component of the third order susceptibility ($\text{Im}[\chi^{(3)}]$) is representative of the nonlinear absorption per mole, Equation 1 (35):

$$\text{Im}[\chi^{(3)}] = \eta^2 \varepsilon_0 c \lambda \beta / 2\pi \quad (1)$$

where η and c are the linear refractive indices and the speed of light, respectively, and ε_0 is the permittivity of free space. λ is the wavelength of the incident light. The β term, is the nonlinear absorption coefficient of the compound and is essentially the nonlinear version of α (the linear absorption coefficient), and is determined using the Z-scan.

Another term to consider is called hyperpolarizability (γ), which gives the nonlinear absorption per mole of compound, which is useful when it comes to comparison of the effectiveness of multiple compounds. Hyperpolarizability (γ) is calculated using Equation 2 (36, 37):

$$\gamma = \frac{\text{Im}[\chi^{(3)}]}{f^4 C_{mol} N_A} \quad (2)$$

where N_a is Avogadro's constant, C the concentration of the active species in the triplet state and f is Lorentz local field factor, (Eq. 3):

$$f = (\eta^2 + 2)/3 \quad (3)$$

3 Results and Discussion

3.1 Characterization of Phthalocyanines-Polymer Linked Conjugates

The conjugation of Pcs with the polymers took place through an amide bond formation between the NH_2 group of ZnTAPc (**10**) and the COOH group of the PMAA, or the COOH groups of MOCPC complexes (**11**, **12**) and the NH group of PEI. Conjugates formed may be represented by

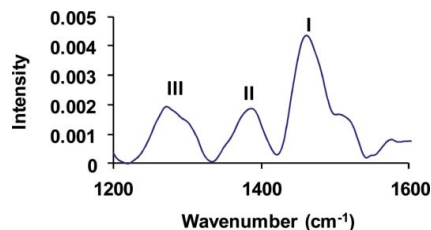


Fig. 2. Raman spectra of ZnOCPc (**11**) linked to PEI.

Schemes 1 and 2. In the IR spectra (Fig. 1, supporting documentation), the amide bond is observed at 1652 cm^{-1} for the conjugate of PMAA with ZnTAPc, which is shifted from $\text{C}=\text{O}$ vibration of PMAA alone at 1666 cm^{-1} , confirming amide bond formation. There is also a shift of the N-H peak position from 3331 cm^{-1} (for ZnTAPc) to 3371 cm^{-1} for the conjugate. For conjugates of PEI with phthalocyanines **11** and **12**, the IR spectra showed an amide vibrational band near 1640 cm^{-1} , which was not observed with Pc or PEI alone, confirming amide bond formation.

The covalent linkage of ZnOCPc (**11**) to PEI through an amide bond was further ascertained using Raman spectroscopy. Raman bands were observed in the amide (38) region 1200 to 1600 cm^{-1} , (Fig. 2). The bands are weak, however, the amide bonds I, II and III are clearly visible in Figure 2.

Figure 3 shows the XRD patterns of **11** or **12** when mixed or linked with PEI and **10** when mixed or linked with PMAA. The XRD spectra of **12** mixed and linked with PEI are shown in Figure 3A. The peak at $2\theta = 22^\circ$ was the only pronounced peak on the XRD spectrum of PEI alone (Fig. 3A(i)) and it is close to the (002) reflection of carbon (39). The broad nature of this peak underlines the substantial amorphous nature of PEI. The peak for the Pc alone was observed near 25° for complexes **10-12**, as is typical of phthalocyanines (40) (XRD pattern not shown in Fig. 3). Thus, the peaks for the conjugate (or mixture) of Pc and PEI in the 24 to 25° region are expected to be an overlap with the Pc peak.

The peak at 22° for the PEI alone is slightly shifted in the **12**/PEI covalently linked conjugate due to the possible binding interaction between **12** and PEI, along with the emergence of four relatively sharp peaks of crystalline nature (Fig. 3A (ii)). A similar XRD shift was observed for **11**/PEI, but no new sharp peaks emerged. When mixed (without a chemical bond) the spectra of **12**/PEI (or **11**/PEI) are similar to that of complexes **11** or **12** linked to PEI, (Fig. 3A and B (iii)) except that the sharp peaks were less intense for **12** and there was a shoulder near 40° for **11**. It has been reported that both the degree of crystallization and the interplanar space changes, imply a new crystal form or a new compound in phthalocyanines (41). The theory behind the use of XRD was that due to the potential cross linking between the polymer strands caused by the phthalocyanines, there may be an alteration in the

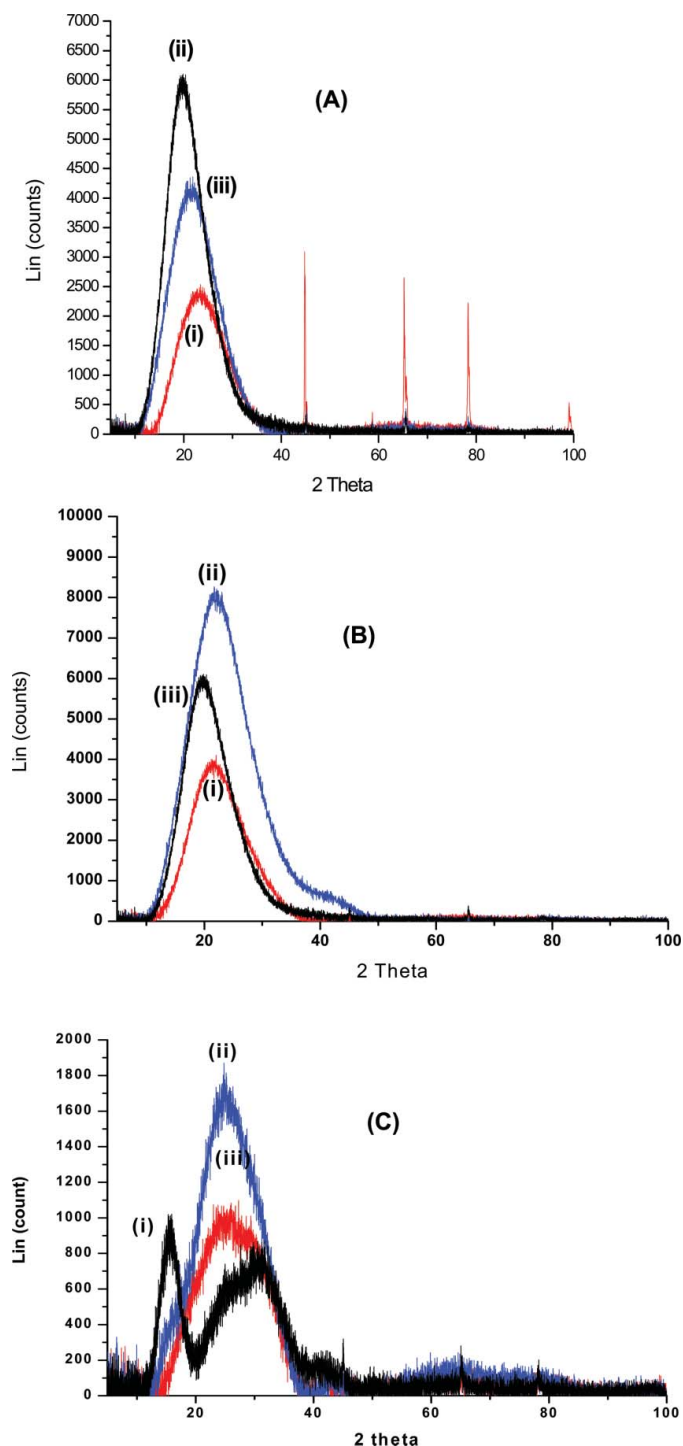


Fig. 3. XRD spectra of (A) AlOCPc (**12**) in PEI, (B) ZnOCPc (**11**) in PEI and (C) ZnTAPc (**10**) in PMAA. (i) polymers alone, (ii) Pcs linked to the polymers and (iii) Pcs mixed into the polymers.

crystallinity of the polymer, as observed in Figure 3A and B. The XRD trace for ZnTAPc (**10**) and PMAA shows that the two amorphous peaks for PMAA alone (at 15 and 29°) form into a singular amorphous peak when **10** was mixed into or linked to PMAA.

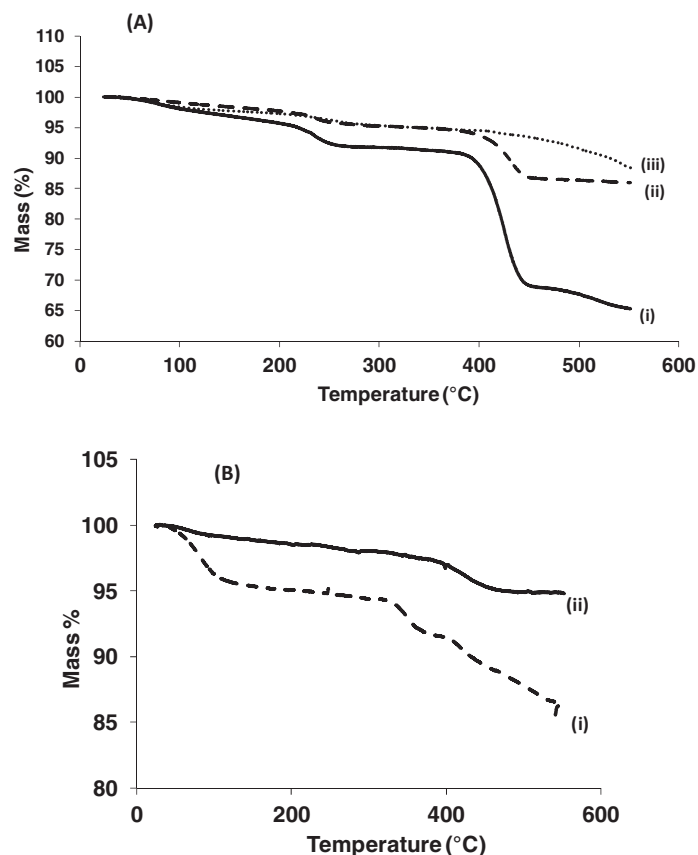


Fig. 4. TGA profiles of (A) (i) PMAA alone, (ii) PMAA mixed with ZnTAPc and (iii) ZnPc alone; (B) (i) PMAA mixed with ZnTAPc and (ii) PMAA linked to ZnTAPc.

As stated above, crosslinking is a possibility when ZnTAPc is linked to PMAA or MOCs are linked to PEI. Thermogravimetric Analysis was successfully employed to determine the extent of crosslinking in polymers (42). A completely crosslinked polymer does not show a loss of mass in TGA traces. Figure 4 shows the TGA profiles of PMAA, ZnTAPc and the latter mixed or chemically linked to PMAA. The initial mass loss (Fig. 4A and B) experienced around 100°C may be attributed to solvent losses (e.g. water). PMAA alone shows two decomposition steps at 250 and then at 450°C, while ZnTAPc alone shows a single step at 250°C (Fig. 4A). Upon mixing the PMAA and ZnTAPc, the mass losses due to PMAA are still evident, Fig. 4B. However, when the two are covalently linked there is a significant decrease in mass loss which is attributable to crosslinking (42), Figure 4B in the ZnTAPc-PMAA conjugate. Crosslinking results in the restriction of the flexibility of the polymer chain. An explanation for the increased rigidity could be that the linked phthalocyanine is sterically hindering the movement of the PMAA strands when the Pc is linked. This could then potentially result in an increase in the temperature at which mass loss occurs at within the Pc-polymer conjugate. The TGA data, however, shows clearly

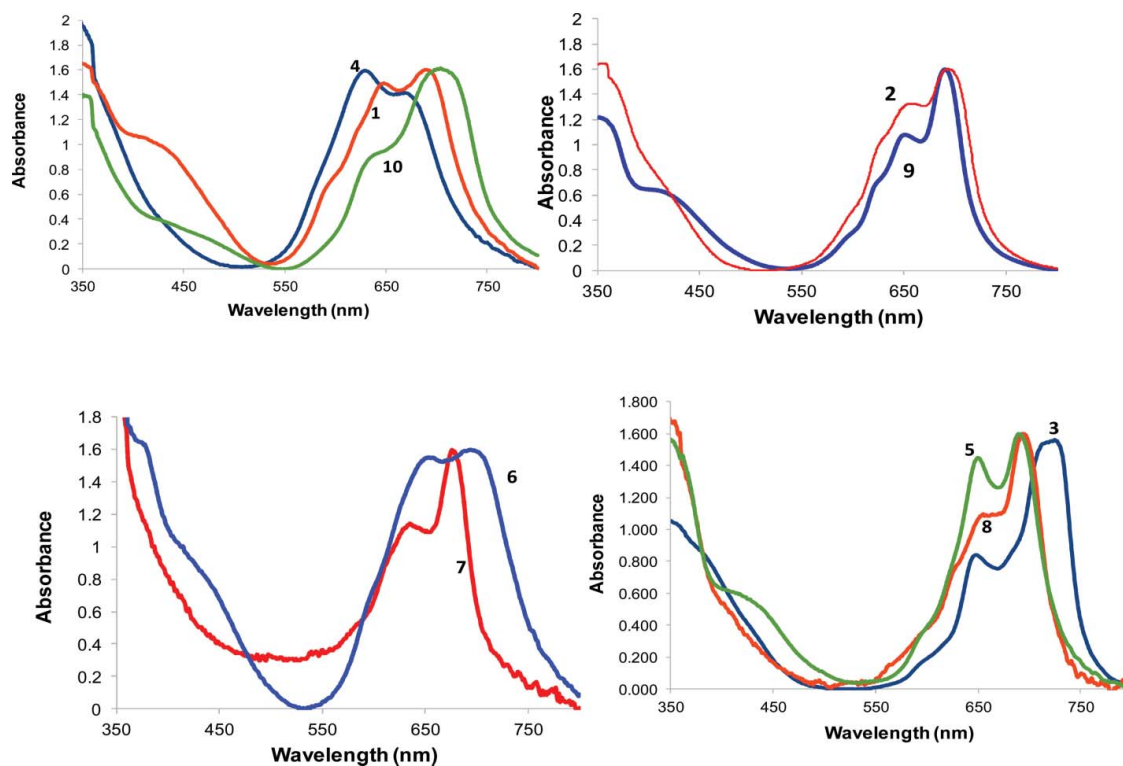


Fig. 5. UV-Visible spectra of phthalocyanines 1-10 in PMMA thin films.

that the polymer has changed markedly. The rigidity of Pc environment has been shown to decrease the probability of non-radiation relaxation, increasing the population of the singlet excited state, and subsequently intersystem crossing to the triplet state (43). This results in the improvement of optical limiting properties. Thus, crosslinking of the Pc-polymer conjugates may lead to improved optical limiting behavior due to reduction in flexibility of the chain.

Mass spectra were employed to estimate the number of phthalocyanines coordinated to the polymer. PMAA and ZnTAPc conjugate was again used as an example. The MALDI-TOF MS data of the PMAA alone shows peaks corresponding to 8 (675 amu), 10 (889 amu) and 13 (1124 amu) monomer units (Fig. 2A, supporting information), with the mixture with ZnTAPc showing the same set of peaks, though with some enhanced (Fig. 2B, supporting information). However, upon comparison of the mass spectra of the PMAA alone (Fig. 2A, supporting information), the mixture (Fig. 2B, supporting information) and the covalently linked Pc (Fig. 2C, supporting information), additional peaks corresponding to the 8, 10 and 13 monomer units plus a Pc ($M+Na$) moiety (at 1347, 1560 and 1795 amu respectively) are observed. This may suggest that there is one Pc unit per every 2 or 3 polymer units. The increase in mass of the polymer was not observed when phthalocyanines were simply mixed (i.e. without formation of a chemical bond). The mass spectral results seem to reinforce the explanation provided by the TGA results, i.e.

some carboxylic acid groups on the polymer chain remain unlinked and intact.

3.2 Characterization of Thin Films of Pcs with Polymers

Film thickness was determined by utilization of the knife-edge attachment of the XRD to physically measure the thickness of the films that were removed from the glass slides. Several measurements were taken of various films, and an average film thickness of each Pc/Polymer on glass was $95 \mu\text{m}$.

The UV-Vis spectra of phthalocyanines 1-10 embedded in PMMA polymer thin films, (Fig. 5), show aggregation as expected in the solid state. However, complexes 11 and 12 showed no aggregation when linked or mixed with the polymer, Figure 6 (A and B). Both of these complexes are octasubstituted with COOH and are known not to aggregate in solution (44). Figure 6A and B shows that the spectra of polymer mixed and linked complexes 11 and 12 are red shifted compared to solution spectra as is typical for solid state (45). Complexes 2, 3, 7, 8, 9 and 10 showed a monomer peak (lower energy) which was more intense than the aggregate (higher energy), (Fig. 5). Complexes 4, 5, 6 all octa substituted with benzyloxy phenoxy groups shows the aggregate peak equal to, or more intense than, the monomer peak, (Fig. 5), suggesting that octa-substitution with this substituent encourages aggregation especially in the solid state. Complex 10 showed extensive aggregation

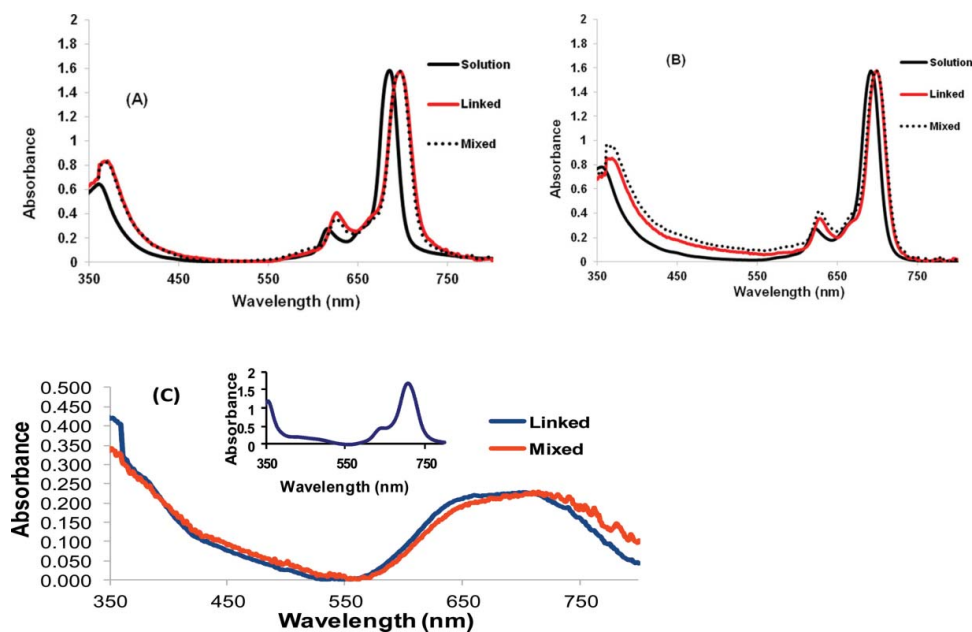


Fig. 6. UV-Visible spectra of phthalocyanines (A) **12**, (B) **11** and (C) **10** mixed and linked to polymers (PMAA for **11** and **12**, and PEI for **10**). Solution spectra for **11** and **12** were recorded in water, (pH 10). The spectra of mixed or linked complexes were of films (therefore solid state). Insert in C is the spectrum of **10** in a DMSO solution.

when linked or mixed with the PMAA, compared to the DMSO solution (insert), (Fig. 6C).

3.3 Optical Limiting Examination of Phthalocyanines 1–10 in PMMA Thin Film

Figure 7A shows the Z scan plot of complex **8** in a PMMA thin film as a representative for all films. Table 1 gives the optical limiting parameters calculated for the different thin films. Hyperpolarizability (γ), which is generally regarded as a better parameter to use for comparison purposes, exhibited values (10^{-26} to 10^{-25}) of the order of about 100 to 10000 \times greater than those found in DMSO solutions

($\sim 10^{-30}$) for the same complexes (46) (Table 1). The values of $\text{Im}[\chi^{(3)}]/\alpha$ were also larger than in solution. Thus, Pcs in thin films are considered to be better OL than in solution. Part of the reason for this could be due to contribution of the polymer to a reduction in transmission, or it could be the greater amount of aggregation that the phthalocyanines experience in thin films, which in turn leads to greater optical limiting. Liu et al. (21) examined indium phthalocyanine, both in solution and in a PMMA polymer film, and observed a significant increase in optical limiting ability, along with observations of phthalocyanine aggregation in the polymer film. It was also mentioned (21) that PMMA has no optical limiting ability of its own, but that

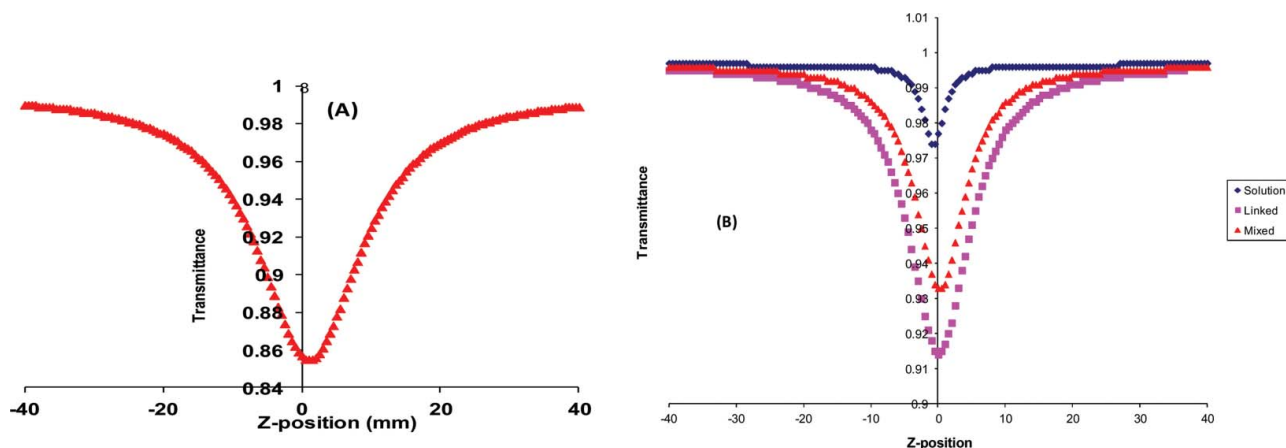


Fig. 7. Z-scan spectra of (A) **8** in PMMA thin film and (B) **12** mixed and linked to PEI as thin films, as well as in solution (water).

Table 1. Optical Limiting Parameters for Phthalocyanine Complexes mixed with PMMA and as Thin Films

Thick Films	$Im[\chi^{(3)}] (esu)^a$	$\gamma (esu.L)$	$Im[\chi^{(3)}]/\alpha$
(1) PMMA	$6.21 \times 10^{-4} (8.54 \times 10^{-11})$	$6.49 \times 10^{-25} (2.39 \times 10^{-30})$	$7.53 \times 10^{-6} (2.67 \times 10^{-11})$
(2) PMMA	$1.17 \times 10^{-4} (8.97 \times 10^{-11})$	$9.64 \times 10^{-26} (2.09 \times 10^{-30})$	$1.18 \times 10^{-6} (3.46 \times 10^{-11})$
(3) PMMA	$1.12 \times 10^{-4} (4.37 \times 10^{-11})$	$4.54 \times 10^{-26} (1.02 \times 10^{-30})$	$6.78 \times 10^{-7} (1.46 \times 10^{-11})$
(4) PMMA	$4.70 \times 10^{-4} (2.88 \times 10^{-11})$	$3.63 \times 10^{-25} (2.17 \times 10^{-30})$	$5.67 \times 10^{-6} (3.28 \times 10^{-11})$
(5) PMMA	$6.22 \times 10^{-5} (3.95 \times 10^{-11})$	$7.87 \times 10^{-26} (1.69 \times 10^{-30})$	$6.92 \times 10^{-7} (1.44 \times 10^{-11})$
(6) PMMA	$4.01 \times 10^{-4} (9.21 \times 10^{-11})$	$9.31 \times 10^{-25} (4.12 \times 10^{-30})$	$8.18 \times 10^{-6} (3.50 \times 10^{-11})$
(7) PMMA	$3.70 \times 10^{-5} (4.81 \times 10^{-11})$	$1.40 \times 10^{-25} (1.30 \times 10^{-30})$	$1.95 \times 10^{-6} (1.74 \times 10^{-11})$
(8) PMMA	$8.18 \times 10^{-5} (5.62 \times 10^{-11})$	$1.71 \times 10^{-25} (1.78 \times 10^{-30})$	$2.93 \times 10^{-6} (2.09 \times 10^{-11})$
(9) PMMA	$1.28 \times 10^{-4} (4.53 \times 10^{-11})$	$8.53 \times 10^{-26} (1.15 \times 10^{-30})$	$1.61 \times 10^{-6} (2.08 \times 10^{-11})$
(10) PMMA	$8.84 \times 10^{-4} (7.82 \times 10^{-11})$	$1.47 \times 10^{-25} (1.82 \times 10^{-30})$	$5.19 \times 10^{-6} (5.41 \times 10^{-11})$

^aValues in brackets are in DMSO solution from reference 44.

the crystallization and morphology of the polymer could not be discounted to contribute towards the improvement in γ and $Im[\chi^{(3)}]$ values.

The $Im[\chi^{(3)}]$ values obtained in this work in solution are similar to the values reported for InPc derivatives (21). The values increased 200 fold when the complexes were placed in PMMA thin films (21), whereas the increase in this work is much larger, Table 1. It was reported that in some cases the InPc complexes decomposed under laser irradiation. However comparing our results with those of the ZnPc derivatives embedded in PMMA (47), similar values of $Im[\chi^{(3)}]$ were obtained. The values obtained in ref. 47 and this work are very high, showing good optical limiting behavior.

Comparing complexes **2** and **3** both containing In central metal and the same substituents, but one peripherally (**2**) and the other non-peripherally (**3**) substituted (and embedded in PMMA polymer), shows that peripheral substitution results in larger values of both $Im[\chi^{(3)}]/\alpha$ and γ as was the case for the solution studies, (Table 1). Comparing **1**, **5** and **9** (all containing Ga central metal) but octasubstituted with different groups (and embedded in PMMA), shows an decrease in $Im[\chi^{(3)}]/\alpha$ and γ for **5** and **9** substituted with benzyloxyphenoxy or phenoxy groups in comparison to **1** which is substituted with *tert*-butylphenoxy groups. Thus, *tert*-butylphenoxy improves these parameters compared to benzyloxyphenoxy or phenoxy substituents. There could possibly be a slight alteration of symmetry of the phthalocyanine when *tert*-butylphenoxy is used as a substituent due to its bulkiness. This could account for the improvement in $Im[\chi^{(3)}]/\alpha$ and γ for complex **1**. However comparing complex **2** and **8** in PMMA, containing In central metal and tetrasubstituted with *tert*-butylphenoxy and phenoxy substituents, respectively, larger values of $Im[\chi^{(3)}]/\alpha$ and γ are obtained for complex **8** containing the phenoxy substituent. Thus the effects of the substituents on the optical limiting parameters could also depend on the central metal and on the number of substituents. There are increases in $Im[\chi^{(3)}]/\alpha$ and γ (Table 1) on going from the Ga (complex **5**) to the Zn (complex **4**) to In (complex **6**), all con-

taining the same substituent (and embedded in PMMA), showing the effects of the heavy atom effect. Comparing peripheral tetrasubstitution (complex **7**) with peripheral octasubstitution (complex **4**) with the same substituent (benzyloxyphenoxy) and central metal (Zn), there is a slight decrease in $Im[\chi^{(3)}]/\alpha$ and γ for the tetrasubstituted complex **7** compared to **4**. We have previously shown that octasubstitution gives better optical limiting behavior than tetrasubstitution (34). Complex **10** containing amino groups shows that the $Im[\chi^{(3)}]/\alpha$ and γ values are comparable to all of the other complexes even though amino groups are known to quench excited states (48).

Complex **10** showed the phthalocyanine to start behaving like a saturable absorber instead of a reverse saturable absorber (figure not shown). This means that the linked complex becomes utterly saturated by the intense laser light and can no longer absorb any more light. Table 2 gives the calculated optical limiting value of the mixed thin film of **10** (no value was calculated for the covalently linked thin film because it underwent saturable absorption), which was higher than the other thin films examined in this report (see Table 1).

Table 2. Optical Limiting Parameters of MOCPC (M = Zn (**11**), Al (**12**)) complexes mixed and linked to PEI, and dissolved in water (pH 10) and **10** mixed with PMAA in DMF/water mixture

Thick Films	$Im[\chi^{(3)}] (esu)$	$\gamma (esu.L)$	$Im[\chi^{(3)}]/\alpha$
Linked AlOCPc (12) PEI	5.32×10^{-5}	6.42×10^{-26}	9.65×10^{-7}
Mixed AlOCPc (12) PEI	4.74×10^{-5}	6.40×10^{-26}	9.63×10^{-7}
Linked ZnOCPc (11) PEI	4.00×10^{-5}	4.31×10^{-26}	7.27×10^{-7}
Mixed ZnOCPc (11) PEI	1.13×10^{-5}	1.64×10^{-26}	2.76×10^{-7}
AlOCPc (12) water	1.37×10^{-7}	8.20×10^{-27}	8.8×10^{-8}
ZnOCPc (12) water	3.94×10^{-7}	1.18×10^{-26}	1.41×10^{-7}
Mixed (10) PMAA	5.45×10^{-4}	2.59×10^{-24}	7.07×10^{-5}

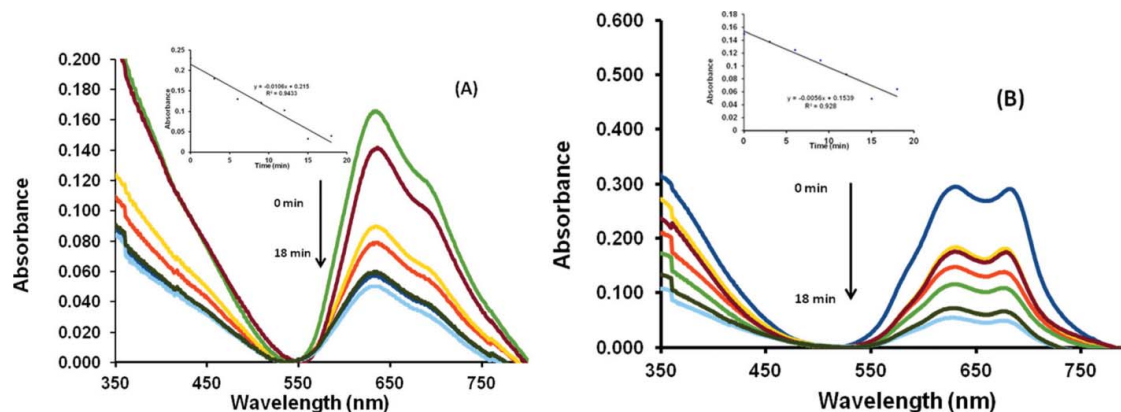


Fig. 8. UV-Visible spectra of phthalocyanine **4** (A) deposited on a glass slide from a DMSO solution and (B) in PMMA thin film exposed to white light. Insert: plot absorption alteration over time (in minutes) of **4** in PMMA thin film.

The Z scans of the linked or mixed complex **12** are shown in Figure 7B, together with the solution scan (in DMSO). The same behavior was observed for **11**. Table 2 gives comparative data from the hyperpolarizability and third order susceptibility values. It shows that simply placing these phthalocyanines in a PEI thin film has increased their optical limiting ability compared to that in aqueous solution. A slight increase in hyperpolarizability and $\text{Im}[\chi^{(3)}]/\alpha$ was also observed for linked samples when compared with the mixed samples of each phthalocyanine, indicating that the link formation may have further improved the thin films as optical limiters. This cannot be taken as definitive however because there are too many variables (including different amounts of Pcs in the linked and mixed conjugates) that could exist between the mixed and linked thin films that could account for the differences.

3.4 Photodegradation of Phthalocyanine 4 Alone on Glass Slide and Within a PMMA Thin Film

Figure 8 shows the photodegradation of phthalocyanine in **4** alone on a slide and within a PMMA thin film. In both figures, UV-Visible spectra show a decrease in absorption over time and the inserts show the linear decrease in absorption with time. Both samples were exposed to a quartz lamp and a water filter for IR radiation. The rate of degradation of the phthalocyanine on its own was observed to be slightly faster than when in a polymer matrix. Similar degradation behavior was observed for the phthalocyanines embedded in PMMA, with slight differences depending on the ring substituent. Photodegradation of phthalocyanines is through the singlet oxygen produced by them. This confirms that embedding the phthalocyanines in a polymer either improves stability or it is limiting their interaction with atmospheric oxygen to form into singlet oxygen.

4 Conclusions

Complexes **1-12** were studied for their optical limiting behavior as thin films when mixed or linked (only for com-

plexes **10-12**) with polymers. Covalent linking increased optical limiting behavior. Phthalocyanine **4** was employed to test whether a polymer matrix affords any protection against photodegradation of the phthalocyanine. Degradation studies seem to indicate that placing a phthalocyanine within a polymer thin film may slightly protect it from photo- and thermal degradation.

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