Synthesis and Properties of Novel Crosslinkable Phthalocyanine Monomers

B. K. MANDAL,* A. K. SINHA, and M. KAMATH

*Department of Chemistry, Illinois Institute of Technology,
Chicago, Illinois 60616, U.S.A.*

(Received December 9, 1994)

ABSTRACT: Polymer films incorporating phthalocyanine rings are useful for third-order nonlinear optical applications. Two axially modified silicon phthalocyanine monomers containing crosslinkable sites have been synthesized. A monomer containing acrylate groups was crosslinked thermally whereas a monomer containing cinnamate groups was crosslinked both thermally and photochemically. Both monomers can be made into solid polymeric films incorporating over 20% (w/w) of the phthalocyanine ring with no observable phase segregation. Elemental analysis, ^1H NMR, FT-IR, and UV-Vis spectroscopy were employed for the structural characterization of the monomers. The kinetics of crosslinking such as reaction conversion *versus* time and temperature, heat of reaction (ΔH), activation energy (ΔE) and reaction order (n), and the thermal properties of the crosslinked films have also been investigated.

KEY WORDS Crosslinkable Phthalocyanine / Third-Order Nonlinear Optical Properties / Thermal and Photochemical Crosslinking Reactions /

There exists an increasing interest in phthalocyanine (Pc) derivatives in the area of nonlinear optics due to excellent opportunities for further molecular engineering leading to large and ultrafast third-order optical nonlinearities.^{1–5} In recent years, enhancement of the nonlinear optical (NLO) properties of phthalocyanine has been accomplished by substituting donor or acceptor groups at the peripheral positions,^{4,6} extending conjugation such as in naphthalocyanine^{7,8} and incorporating a heavy metal atom at the center.^{7,9–12} However, due to their low solubilities in common organic solvents and incompatibility with vinyl polymer hosts, the exploration of NLO properties in the solid state or in solutions with high concentrations of Pc rings is hindered. A medium containing a high density of Pc rings will not only lead to higher values of macroscopic third-order nonlinear susceptibility, $\chi^{(3)}$, but also will allow more intermolecular interactions and aggregation which may cause an inherent increase in molecular

hyperpolarizability, γ .

In the past, most NLO studies with Pc compounds have been performed in dilute solutions. The solid state NLO properties of polymeric films containing such macrocyclic compounds have been the subject of several recent reports.^{4,13,14} Polymeric films containing high concentrations of Pc rings essentially require covalent attachment of Pc rings with the polymer matrix in order to avoid the formation of microcrystallites that are prevalent in the case of guest–host systems. In addition to flexibility in device fabrication, faster response time is another anticipated attribute of solid Pc-polymeric films. In this paper we report the synthesis and characterization of two new Pc monomers which can be processed into crosslinked polymeric thick or thin films incorporating high concentrations of Pc rings by thermal or photochemical crosslinking reactions. The syntheses of the monomers is described in Figure 1.

* To whom correspondence should be addressed.

Figure 1. Synthesis of crosslinkable silicon phthalocyanine derivatives.

MATERIALS AND METHODS

Materials and Instrumentation

Cinnamoyl chloride, methacryloyl chloride,

methylmethacrylate (MMA), poly(methylmethacrylate) (PMMA, $M_w \sim 100000$), triethylamine, 4-dimethylaminopyridine (DMAP), dioxane, and chloroform were all purchased from

Aldrich Chemical Co. Azobisisobutyronitrile (AIBN) was obtained from Eastman Kodak Co. All reagents were used as received except MMA, triethylamine, dioxane, and chloroform which were freshly distilled prior to use. ^1H NMR spectra of the compounds were obtained from outside facilities. All other characterizations were carried out using Perkin-Elmer systems: elemental analysis (PE-2400); FT-IR (System 2000); TGA (Series 7); DSC (Series 7); and UV-Vis (Lambda 19).

Experimental Procedure

Compound **1** was prepared by reacting dihydroxysilicon phthalocyanine with triethanolamine following a general procedure for axial etherification described previously.¹⁵ Monomers **2** and **3** were synthesized from compound **1** by esterification with methacryloyl chloride and cinnamoyl chloride respectively. In a typical procedure, methacryloyl chloride (1.24 g, 11.94 mmol) in 10 ml chloroform was added dropwise to a solution of compound **1** (1 g, 1.19 mmol) and a catalytic amount of DMAP dissolved in 40 ml of chloroform and 5 ml of triethylamine at 0°C under nitrogen. After stirring the mixture overnight at room temperature the solution was washed several times with water and the organic layer dried over anhydrous sodium sulfate and evaporated under reduced pressure. The impurities were removed by soxhlet extraction with hexane and monomer **2** was obtained by extracting the residue with chloroform which removes the monomer in high purity (following evaporation of chloroform). Monomer **3** was made by the same procedure using cinnamoyl chloride.

Thin Film Processing

Thin film processing of monomer **2** was performed by two methods. In one method, a crosslinked matrix was made by dissolving the monomer (100 mg), in AIBN (20 mg) and MMA (560 mg) in an ultrasonicator followed by heating at 80°C under nitrogen in a water bath for 15 min at which time the solution

became viscous. The solution was film-cast or spin-cast on glass slides and baked overnight at 80°C under nitrogen (film-I). In another method a solution made by dissolving PMMA (560 mg), monomer **2** (100 mg), and AIBN (20 mg) in 4 ml of dioxane was film-cast over glass slides followed by baking at 80°C overnight under nitrogen (film-II). Thin film processing of monomer **3** was performed by dissolving the monomer (100 mg) and PMMA (560 mg) in 4 ml of dioxane followed by spin-casting over glass slides. The curing was performed by heating the film at 100°C for 3 h (film-III) and by irradiating UV-light (Multi-Ray) with an intensity of $\sim 2 \text{ mW cm}^{-2}$ around 254 nm for five hours at room temperature (film-IV).

RESULTS AND DISCUSSION

The synthesis of monomers **2** and **3** requires the presence of a large excess of base such as triethylamine, otherwise the breaking of Si-O-C bonds was observed leading to the formation of insoluble dihydroxysilicon phthalocyanine. In addition, the presence of a catalytic amount of DMAP, a well-known hypernucleophile, is required for enhancing the rate of reaction.¹⁶ The monomers obtained were reasonably pure as inferred from analytical data (Table I) and were used to study both solution and solid-state properties. Further purification using column chromatography leads to the breakdown of the molecules. The yield of both monomers was around 90%. Monomer **2** was found to crosslink slowly at room temperature over the course of a few days and therefore was stored in a refrigerator.

The proposed structures of the two monomers are in good agreement with the analytical data (Table I). In their FT-IR spectra, monomer **2** showed a characteristic methacrylate C=C peak at 1637 cm^{-1} and C=O peak at 1721 cm^{-1} while monomer **3** showed cinnamate C=C peak at 1634 cm^{-1} and C=O peak at 1703 cm^{-1} . Both monomers showed a sharp

Table I. Analytical data of crosslinkable silicon phthalocyanine monomers

Monomer	Yield		Analysis			¹ H-NMR (CDCl ₃)		Wavelength ^a	Solubility
	%		C/%	H/%	N/%	δ/ppm		nm (10 ⁻⁴ ε, mol ⁻¹ cm ⁻¹)	g ml ⁻¹
2	91	Exptl	64.45	5.36	12.34	-2.01 (t, 4H), -1.85 (t, 4H),		677 (22.4136) 646 (3.0280)	207.9 (0.190)
		Calcd	64.97	5.45	12.63	0.81 (t, 8H), 1.57 (s, 12H), 2.80 (t, 8H), 5.24 (d, 4H), 5.54 (d, 4H), 8.33 (m, 8H), 9.62 (m, 8H)		608 (3.4136) 355 (7.0673) 287 (2.3339)	
3	87	Exptl	70.39	5.43	10.14	-1.91 (t, 4H), -0.31 (t, 4H),		679 (28.9182) 647 (4.3533)	81.4 (0.058)
		Calcd	70.78	5.05	10.32	0.80 (t, 8H), 2.85 (t, 8H), 6.01 (d, 4H), 6.55 (d, 4H), 7.38 (m, 10H), 8.29 (m, 8H), 9.63 (m, 8H)		610 (4.6597) 354 (9.3020) 276 (14.2857)	

^a The electronic spectra of monomers were recorded in chloroform. ^b Measured from a saturated chloroform solution at 25°C, where $c = A/\epsilon l$ and $l = 1$ cm. Figures in parentheses represent molarity of corresponding saturated solutions in mol l⁻¹.

decrease in the intensity of the O-H band around 3450 cm⁻¹ in comparison to compound **1** due to the formation of ester linkages. The IR absorptions attributable to the Pc ring in the 1150–650 cm⁻¹ range were also slightly changed with respect to compound **1**.

The ¹H NMR spectra of the monomers show that the Pc ring produces, not surprisingly, a large ring current effect on axially linked α- and β-methylene protons compared to peripherally substituted¹⁷ methylene protons. The resonance of α- and β-methylene protons of both monomers occurred at the negative side of the TMS peak. The vinyl protons of the acrylate group in monomer **2** are anisotropic and each appeared as a doublet at 5.24 and 5.54 ppm. This difference is due to additional deshielding of one proton by the acrylate carbonyl group. The two *trans* vinyl protons of the cinnamate group also appeared as doublets but at relatively lower fields, at 6.01 and 6.55 ppm. In general, the protons in both the acrylate and cinnamate groups appeared in higher fields compared to the derivatives containing no Pc rings.^{18,19} The resonances of peripheral aromatic protons are almost the same for all compounds; 8.3 ppm and 9.6 ppm for 4,5-Pc and 3,6-Pc protons respectively (Table I).

Solution optical spectra of monomers **2** and

3 showed a sharp Q band transition at *ca.* 677 nm with shoulders at *ca.* 646 and 608 nm which are likely of vibronic origin (Table I). The B-band region of the monomers showed two weak bands at *ca.* 355 and 285 nm. The monomers did not display appreciable band-shifts in comparison to compound **1** except for an intense band at 276 nm for monomer **3**. This is probably due to partial overlap of the B-band absorption with that of the cinnamate group. Studies on solubility in common organic solvents such as chloroform have been performed. Monomer **2** exhibited solubility much higher than compound **1** which was measured at 12% (w/w) in chloroform (Table I). Monomer **3** which showed 8% (w/w) solubility is still more soluble than the derivatives reported in the literature.^{20–22}

Solid polymer films of the monomers were prepared and characterized. Film-I was a cross-linked copolymer of monomer **2** and MMA while films II–IV were semi-interpenetrating polymer networks (semi-IPNs) in which PMMA is embedded into a crosslinked network of monomer **2** or **3**. All films were cured thermally except film-IV which was cured photochemically. The kinetics of thermal cross-linking resulting in semi-IPN films II and III were monitored by differential scanning calo-

Table II. Kinetics of curing and thermal properties^a of crosslinked films

Film	Pc content %	DSC ^b			TGA ^b			
		ΔE^c	ΔH	n^c	PDT ^d	Isothermal heating ^e		
		kJ mol^{-1}	J g^{-1}			125°C	150°C	175°C
I	17.9	—	—	—	418	1.8	2.7	5.2
II	17.9	123.4	48.6	1.1	380	1.8	2.4	5.3
III	17.9	153.1	81.9	1.1	378	1.6	5.5	7.3
IV	17.9	—	—	—	345	2.0	4.9	6.7

^a All experiments were performed under nitrogen. ^b Heating rate, $10^\circ\text{C min}^{-1}$. ^c Anticipated error is with in $\pm 6\%$.

^d Temperature of 5% weight loss. ^e Weight loss in % after 10 h of heating.

Figure 2. Kinetics of crosslinking reactions.

rimetry (DSC) which indicates that the polymerization of acrylate monomer **2** is much faster than the cinnamate monomer **3** (Figure 2). The activation energy (ΔE) of curing, heat of reaction (ΔH) and order of reaction (n) were also determined and are presented in Table II. As expected, the ΔE value of the thermal polymerization reaction involving cinnamate groups was higher than the reaction involving acrylate groups. The thermal polymerization reaction was found to be exothermic and the ΔH of cinnamate polymerization was about two times that of acrylate polymerization. However, the n values of both the reactions were the same. Kinetic studies for the forma-

tion of crosslinked film-I was not performed due to the high volatility of the MMA monomer.

The thermal stability of films I–IV was measured by thermogravimetric analysis (TGA). The product decomposition temperature (PDT) values obtained from the TGA thermograms indicate that film-I possesses higher thermostability than the other films (Table II). The results of isothermal heating at 125°C of all Pc films indicate resistance to thermal breakdown for up to 5 h and show weight losses of less than 2% after 10 h. However, the decomposition due to aliphatic segments becomes apparent when heated over 150°C for long durations. The complete degradation of the aliphatic segments which constitute about 80% of the total weight of the film occurred around 400°C for all Pc films.

FT-IR spectroscopy was also used to monitor the thermal curing of the films containing monomer **2** by the observation of the methacrylate $\text{C}=\text{C}$ peak at 1637 cm^{-1} over times. The peak was found to decrease gradually and a new sharp $\text{C}=\text{O}$ peak appeared at 1735 cm^{-1} with the progress of curing. The IR absorptions attributable to the Pc ring in the $1150\text{--}650\text{ cm}^{-1}$ range were also slightly changed.

The photocrosslinking of monomer **3** leading to film-IV was monitored by UV-Vis spectroscopy (Figure 3). Observation of the gradual

Figure 3. Change in UV-Vis spectra with the progress of crosslinking leading to formation of film-IV. Irradiation time, min: 0, 10, 20, 45, and 75.

decrease in intensity around 276 nm (which corresponds to the cinnamate group) with irradiation time, indicated the depletion of double bonds and the formation of a four-membered ring as a result of 2+2 photo-dimerization. UV-Vis spectra were also indicative of a very slow crosslinking of cinnamate groups compared to the crosslinking behavior observed in other polymers bearing cinnamate groups.^{19,23} This is probably due to the partial overlap of the B-band absorption of the Pc ring with the cinnamate group, which prevents the funneling of energy to the double bonds to promote 2+2 photo-dimerization. The absorption spectra of the monomers incorporated in polymer films were found unchanged when compared to their absorption behavior in solution. The absorption electronic spectra of the Pc films ($\sim 1 \mu\text{m}$ thick) exhibit low absorptions in the visible region. For instance, the OD of all films varied from 0.001–0.06 at 532 nm. Films I–IV apparently showed no sign of microcrystallization which was observed after drying of the film containing compound **1** in PMMA. Nonlinear optical properties of crosslinked films with respect to concentration of Pc rings are under current investigation.

CONCLUSIONS

We presented a convenient synthetic procedure for obtaining thermally and photochemically crosslinked phthalocyanine derivatives which can be processed into crosslinked polymeric films. The films containing 18% (w/w) of phthalocyanine derivatives exhibit high optical transparency in the visible region and show no observable phase-segregation.

Acknowledgments. The authors wish to thank Dr. B. Bihari for his insightful comments, and Dr. K. Katti (University of Missouri) for his generous help for obtaining ^1H NMR spectra. This work is supported by the U.S. Army Tank-Automotive Command Warren, Michigan) under contract #DAAE07-93-C-R138. Acknowledgment is also made to AFOSR for providing funds (grant #F49620-9310-583) for instruments used in this study.

REFERENCES

1. Z. Z. Ho, C. Y. Ju, and W. M. Hetherington, *J. Appl. Phys.*, **62**, 716 (1987).
2. J. W. Wu, J. R. Helfin, R. A. Norwood, K. Y. Wong, O. Zamani-Khamiri, A. F. Garito, P. Kalyanaraman, and J. Sounik, *J. Opt. Soc. Am.*, **B6**, 707 (1989).
3. J. S. Shirk, J. R. Lindle, F. J. Bartoli, Z. H. Kafafi, and A. W. Snow, in "New Materials for Nonlinear Optics," S. R. Marder, J. E. Sohn, and G. D. Stucky, Ed., American Chemical Society, Washington, D.C., 1991.
4. M. Hosoda, T. Wada, T. Yamamoto, A. Kaneko, A. F. Garito, and H. Sasabe, *Jpn. J. Appl. Phys.*, **31**, 1071 (1992).
5. H. S. Nalwa, *Adv. Mater.*, **5**, 341 (1993).
6. H. S. Nalwa, A. Kakuta, and A. Mukoh, *Chem. Phys. Lett.*, **203**, 109 (1993) and references therein.
7. N. Q. Wang, Y. M. Cai, J. R. Helfin, and A. F. Garito, *Mol. Cryst. Liq. Cryst.*, **189**, 39 (1990).
8. H. S. Nalwa, A. Kakuta, and A. Mukoh, *J. Phys. Chem.*, **97**, 1097 (1993).
9. H. S. Nalwa, *Appl. Organomet. Chem.*, **5**, 349 (1991).
10. J. S. Shirk, J. R. Lindle, F. J. Bartoli, Z. H. Kafafi, A. W. Snow, and M. Boyle, *Int. J. Nonlinear Opt. Phys.*, **1**, 699 (1992).
11. J. S. Shirk, J. R. Lindle, F. J. Bartoli, and M. E. Boyle, *Int. J. Phys. Chem.*, **96**, 5847 (1992).
12. H. Hoshi, K. Kohama, S. Fang, and Y. Maruyama,

- Appl. Phys. Lett.*, **63**, 3080 (1993).
13. R. A. Norwood and J. R. Sounik, *Appl. Phys. Lett.*, **60**, 295 (1992).
14. J. R. Sounik, G. Khanarian, J. Popolo, and S. Meyer, *Chem. Mater.*, **5**, 1253 (1993).
15. R. D. Joyner and M. E. Kenney, *Inorg. Chem.*, **1**, 236 (1962).
16. I. McCulloch, H.-T. Man, B. Marr, C. C. Teng, and K. Song, *Chem. Mater.*, **6**, 611 (1994).
17. M. Hanack, A. Gul, A. Hirsch, B. K. Mandal, L. R. Subramanian, and E. Witke, *Mol. Cryst. Liq. Cryst.*, **187**, 365 (1990).
18. C. Xu, B. Wu, O. Todorova, L. R. Dalton, Y. Shi, P. M. Ranon, and W. H. Steier, *Macromolecules*, **26**, 5303 (1993).
19. H. R. Allcock and C. G. Cameron, *Macromolecules*, **27**, 3125 (1994).
20. E. A. Cuellar and T. J. Marks, *Inorg. Chem.*, **20**, 3766 (1981).
21. V. Ahsen, E. Yilmazer, M. Ertas, and O. Bekaroblu, *J. Chem. Soc., Dalton Trans.*, 401 (1988).
22. M. J. Cook, A. J. Dunn, S. D. Howe, and A. J. Thomson, *J. Chem. Soc., Perkin Trans. 1*, 2453 (1988).
23. B. K. Mandal, J. Kumar, J.-C. Huang, and S. Tripathy, *Makromol. Chem. Rapid. Commun.*, **12**, 63 (1991).