EQUIPMENT AND INSTRUMENTATION TO DEVELOP NONLINEAR OPTICAL MATERIALS FOR PHOTONIC AND LASER TECHNOLOGIES

Final Report

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Acquiring the necessary infra-structure for conducting research in the area of photonic and laser technologies, the major objective of this proposal, has been accomplished through the acquisition of a number of key instruments. Our newly established Laser Assisted Experiments (LAE) facility is now equipped to conduct experiments related to all three major nonlinear optical (NLO) phenomena of polymers: (i) second-order NLO effect, applicable to second-harmonic generation and linear electro-optic effect (ii) third-order NLO effect, applicable to integrated optics such as optical switching and optical data processing and (iii) photorefractive effect, applicable to real-time holography and optical phase conjugation.

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Acquiring the necessary infra-structure for conducting research in the area of photonic and laser technologies, the major objective of this proposal, has been accomplished through the acquisition of a number of key instruments. Our newly established Laser Assisted Experiments (LAE) facility is now equipped to conduct experiments related to all three major nonlinear optical (NLO) phenomena of polymers: (i) *second-order NLO effect*, applicable to second-harmonic generation and linear electro-optic effect (ii) *third-order NLO effect*, applicable to integrated optics such as optical switching and optical data processing and (iii) *photorefractive effect*, applicable to real-time holography and optical phase conjugation.

For second-order NLO measurements, we have acquired a powerful nanosecond Nd:YAG laser which can also be used to conduct photorefractive experiments. For third-order NLO properties, a picosecond Nd:YAG laser was purchased. A prism coupler which provides accurate values of the refractive index and thickness of polymer films (similar to an ellipsometer) has also been acquired to obtain supporting data for the calculation of NLO susceptibilities. We have already begun conducting experiments in our LAE facility which has, to date, resulted in one publication and another in preparation.

In addition, we have also strengthened our structural characterization infra-structure. Table 1 shows the list of instruments most of which have been purchased through the AFOSR grant. Additional support that was required to complete this project came from IIT's cost-sharing program, the PI's start-up funds and NALCO and Dreyfus Foundations.

Currently, there are several on-going projects that extensively utilize the above equipment. A brief description of each project is given below:

(1) Nonlinear Optical Vision Protection, Army TACOM: in this project we are developing new types of third-order NLO polymers for the protection of eyes and sensors from laser hazards.

(2) Nonlinear Optical Polymers, ONR AASERT support: the main theme of this project is to develop human resources in the area of NLO polymers.

(3) High performance Composites, ARO AASERT support: as above, but in the area of high-performance composites.

(4) Composite Polymers from Renewable Resources, Army-Natick: This project utilizes mainly thermal analysis systems.

(5) Novel Langmuir-Blodget Monomers, Army-Natick: This project utilizes mainly structural characterization equipment.

In addition, some of the structural characterization equipment is routinely used in our graduate-level polymer chemistry laboratory course, (CHEM 537: Polymer Chemistry Laboratory) and in our undergraduate course, (CHEM 334: Spectroscopic Identification of Organic Compounds).

In conclusion, this infra-structure support has greatly accelerated our research activities; this is evidenced by our recent communications provided for your review.

Table 1. Instrumentation Facility at the PI's Laboratories

Equipment	Features
Structural Characterization	
Perkin Elmer 2000 FT-IR with TGA Interface:	Computer scanning and identification of individual peaks as well as overlay plots for comparison purposes. This FT-IR system has a TGA interface that can collect data on evolved gases during a TGA experiment.
Perkin Elmer Lambda 19 UV/Vis/NIR Spectro:	Allows for absorption measurements over the entire UV/Vis/ NIR spectrum (175 to 3200 nm). Accessories include with an integrating sphere for measurements in reflectance mode.
Perkin Elmer Q-910 MS with Autosystem GC:	Molecular weights up to 650 amu can be identified. Both the purity and content of a reaction mixture as well as the rate of formation of a desired product can be determined by sampling the reaction mixture throughout the course of a reaction and analyzing on this system.
Perkin Elmer 2400 Elemental Analyzer:	Capable of measuring percent carbon, hydrogen, nitrogen, sulfur, and oxygen in high accuracy.
Wyatt Tech DAWN DSP-F Laser Photometer:	Determines absolute molecular weight of polymers.
Thermal Analysis	
Perkin Elmer Series 7 Thermal Analyzer:	The system comprising of a DSC, a TGA and a DMA is PC controlled and loaded with a number of software packages (e.g., DSC kinetics software, purity software, specific-heat software, and TGA decomposition kinetics software). Mechanical properties can be determined using a DMA and the configurations that can be adopted are three point bending, parallel stretching and parallel plate.
Processing	
Labconco 6 Class-100 Laminar Flow Station:	Placed in a clean room for processing of polymers. Eliminates problem of dust accumulation in films.
Headway EC-101 Spin Coater:	For the processing of polymers into thin films. Holds any substrates between 1/2" and 3.5". Adjustable speed and time of spinning.
Linear Optical Characterization	
Matricon 2010 Prism Coupler:	Accurately determines refractive index and thickness of both thick and thin films at 532 nm and 1064 nm. Measurements at other wavelengths are possible through a laser port.
Nonlinear Optical Characterization	
Quantel Brillient-20 Nanosecond Laser:	Mounted on a NewPort RS-4000 (4' x 8' x 8") optical table. Delivers 420 mJ/pulse at 1064 nm and 160 mJ/pulse at 532 nm wavelengths with a pulse duration of less than 7 ns. Equipped with most optics and detectors for second-order NLO properties.
Quantel 531-30 Picosecond Mode-locked Laser:	Mounted on a NewPort RS-4000 (5' x 12' x 12") optical table. Delivers 25 mJ/pulse at 1064 nm and 12 mJ/pulse at 532 nm with a pulse duration of less than 35 ps. Equipped with necessary optics and detectors for third-order NLO properties.

Third-order nonlinear optical response in a multilayered phthalocyanine composite

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The third-order nonlinear optical properties of multilayered films containing 23% by weight of an axially modified silicon phthalocyanine derivative have been measured by degenerate four-wave mixing at 532 nm with 70 ps full width at half maximum pulses. The average $\chi^{(3)}$of the films measured at $(1.33\pm0.15)\times10^{-11}$ esu using CS_2 as a standard and the cubic hyperpolarizability $\langle\gamma\rangle$ was calculated at $(1.97\pm0.22)\times10^{-32}$esu. The degenerate four-wave mixing signal profile indicates that the films have a response time better than 70 ps. © *1995 American Institute of Physics.*

Phthalocyanine (Pc) derivatives have generated much interest in the area of nonlinear optics due to their large and ultrafast third-order optical nonlinearities, low optical density in the visible spectral region [which render them suitable for nonresonant degenerate four-wave mixing (DFWM) measurements using a laser source in the visible such as a frequency doubled (YAG) laser], ease of derivatizing through peripheral and axial positions, and excellent chemical and thermal stabilities.[1] In order to exploit the full potential of Pc derivatives and to attain maximum possible $\chi^{(3)}$ values by enhancing intermolecular electron transfer, it is essential to design a Pc molecule that can be dissolved in concentrations higher than 10% by weight (~0.2 M) and/or processed into films containing covalently attached Pc molecules in high density.

In the past decade, extensive effort has been made to produce highly soluble Pc derivatives.[2–4] Most of the highly soluble Pc derivatives made so far contain either electron donor substituents such as alkyl, alkoxy or phenoxy groups, or electron withdrawing substituents such as sulfonyl or carboxyl groups at the peripheral positions. In recent years, studies have been made on the effect of peripheral substituents,[5] additional conjugation such as in naphthalocyanine[5,6] and the central metal atom character[7] on $\chi^{(3)}$. Results indicate that peripheral substituents greatly improve the solubility of the Pc molecule and increase both the absorption in the visible region and to some extent the optical nonlinearities in molecules where electrons are permitted to flow in or out of cyclic π-conjugated rings. In extended π-conjugated systems such as naphthalocyanine the absorption in the visible region increases dramatically while $\chi^{(3)}$ shows about a 5–10 times enhancement in its value. Similarly, the nature of the central metal atom plays an important role in tuning both optical nonlinearities and absorption in the visible region. For instance, $\chi^{(3)}$ of Pc increases about 15 times by changing the central metal atom from silicon to vanadium[8] and similarly increases with a central heavy metal atom such as lead.[9] Axial derivatization through a certain metal atom such as silicon has also been found to increase the solubility of Pc molecules[10–11] and have little to no effect on the absorption behavior in the visible region depending on the axial substituents. However, lead and vanadium are not appropriate metal atoms for axial derivatization. Silicon has been chosen as a central metal atom for axial derivatization because of its tetravalency and ability to form strong and stable bonds with oxygen.[12]

Since it is convenient to perform nonlinear optical measurement in the visible region (e.g., at the YAG doubled frequency) due to the visibility of the laser light, availability of inexpensive laser light sources, and simplicity in measurements of signal, we planned to study nonlinear optical properties in the visible region of films containing a high concentration of Pc derivatives. A series of axially modified silicon phthalocyanine (SiPc) derivatives which are highly soluble in organic solvents like dioxane and chloroform, and easily processable into multilayered films using a commercially available reactive silane, has been synthesized.[13] In this letter, we describe the results of DFWM measurements using picosecond pulses on a representative SiPc derivative. A detailed account of the syntheses of these molecules, electronic spectra, and DFWM measurements of both solutions and films with respect to concentration will be reported separately.[14]

The structure of an axially modified SiPc derivative, SiPcTEA, synthesized for this study is shown in Fig. 1. The molecule is very soluble in common organic solvents. For example, the solubility of this derivative was measured at 12.15×10^{-2} gm per milliliter in chloroform (~0.15 M),[15] which is about three times greater than that of previously reported soluble Pc derivatives.[2,3,5,7] Also, the molecule is highly soluble in a commercially available spin-on-glass (SOG)[16] solution and the resulting solution is processable into thin films. Such films, upon curing, produce a crosslinked polymeric system in which the phthalocyanine derivative is covalently linked with a polysiloxane network. Covalent linkages are formed by the reaction of hydroxyl functionalities in SiPcTEA and reactive polysiloxane present in SOG and therefore the formation of microcrystallites at higher concentrations is unlikely. Indeed, the cured films

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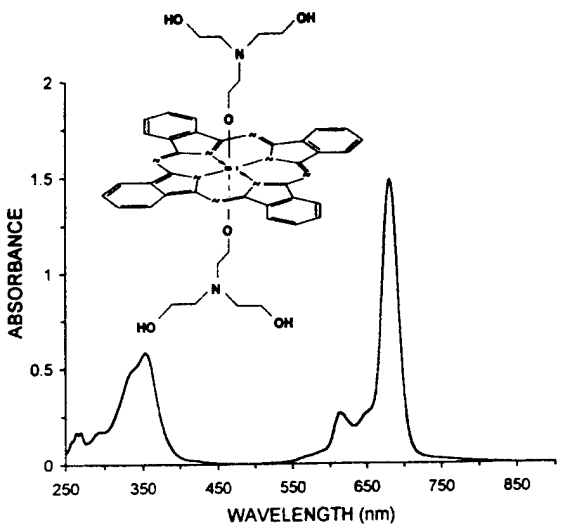

FIG. 1. Chemical structure of SiPcTEA and absorption spectrum of SiPcTEA-SOG composite thin film.

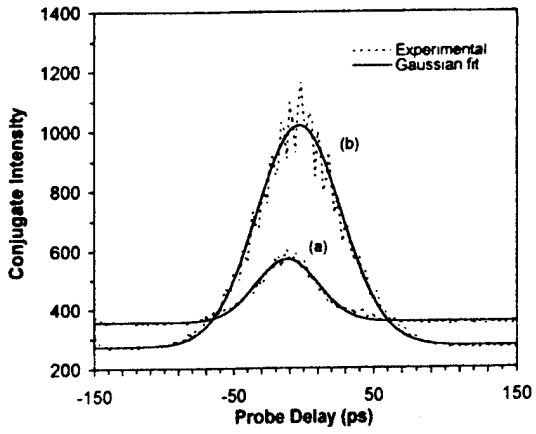

FIG. 2. Typical phase conjugate signal $I_4(\omega)$: (a) for SiPcTEA-SOG composite film. (b) for CS_2.

possess valued characteristics such as optical clarity, robustness, and rigidity.

Thick and uniform films are desirable for certain nonlinear optical applications such as optical limiting devices for vision and sensor protection. Spin casting from solution is a fairly simple and convenient technique to make uniform films having thicknesses of about 1 μm. The unique property of the SiPcTEA and SOG mixture is its allowance to easily cast multiple layer coatings without producing interlayer phase separation. It was possible to obtain optical quality thick films through multiple coatings. Furthermore, the multilayer formation capabilities of this mixture may also be exploited in certain device designs such as in "bottleneck" optical limiters,[17] where multilayered films with varied concentrations and thicknesses at each layer are required.

For this study, a solution was made by mixing 60 mg each of SiPcTEA and polyethylene glycol ($M_w \sim 10\,000$, Aldrich Chemical Co.) in 2 mg of SOG solution (Allied Signal). The solution was filtered through a 0.2 μm syringe filter prior to spin coating in a class-100 clean room. Typical processing conditions for obtaining films of 1 μm thickness was a 1200 rpm spin speed for a duration of 30 s. Multiple coating requires curing the film after each coating at 200 °C for 10 min followed by cooling to room temperature. For DFWM experiments, films of thicknesses ranging from 1.15 to 4.05 μm were prepared over microscope slides by casting multiple layers with identical materials. The thickness of the films was measured by surface profilometry with an error of $\pm 10\%$. The film contained about 23% by weight of SiPcTEA.

It was possible to cast films from SOG solutions containing up to 40% by weight of SiPcTEA. Cured films experienced severe cracking at concentrations of over 10% by weight of SiPcTEA. Addition of polyethylene glycol in equal weight proportion to SiPcTEA is absolutely necessary to obtain crack-free films. The UV-Vis absorption spectrum of a thin film was recorded on a Perkin-Elmer Lambda-19 spectrometer and is shown in Fig. 1. The refractive index of the multilayered film was measured at 1.623 at 532 nm.

Third order nonlinear optical susceptibility $\chi^{(3)}$ was measured by DFWM experiments in optical phase conjugate (OPC) geometry. In OPC geometry, also known as backward DFWM, two counterpropagating intense laser beams (I_1 and I_2) of frequency ω are used as pump beams while a third laser beam (I_3) at the same frequency incident at a small angle with respect to the pump direction is used as a probe. The fourth beam (I_4), phase conjugate to I_3, propagates opposite to the probe direction. A mode-locked Q-switched and frequency doubled Nd:YAG laser (Coherent Antares) was used as the source at 532 nm radiation. The laser output pulse consisted of the picosecond pulses under the Q-switched envelope. The most energetic picosecond pulse was extracted from the Q-switched envelope by a Pockel's cell pulse extractor. The extracted pulses had an average pulse energy of 90 μJ and the full width at half maximum (FWHM) of 70 ps at a repetition rate of 1 kHz. The output beam from the pulse extractor was then split into three beams and each beam was focused by a lens of 10 cm focal length and spatially overlapped near the focal points. Temporal overlap was achieved by introducing appropriate delay among the three beams. The phase conjugate signal was reflected away by a beam splitter and measured by a photodiode detector. Another photodiode was used to monitor the laser intensity. The photodiode signals were sent to a boxcar integrator which was interfaced to a personal computer for data acquisition and analysis. The signal was analyzed as a function of probe delay and is shown in the Fig. 2.

The intensity of the conjugate beam is given by

$$I_4(\omega) = \left(\frac{\omega}{2\epsilon_0 c n^2}\right)^2 |\chi^{(3)}|^2 l^2 I_1(\omega) I_2(\omega) I_3(\omega), \qquad (1)$$

where I_1, I_2, and I_3 are the intensities of the forward and backward pumps and the probe beam, respectively, l is the interaction length and n is the refractive index of the medium. The correlation between the signal and the laser intensity was checked by varying the laser intensity via neutral density filters and the cubic power dependence was established for the reference sample as well as the multilayered films. CS_2 was used as a reference material in order to esti-

mate the effective $\chi^{(3)}$ of the film and avoid the direct evaluation of all the parameters in Eq. (1). The experimentally measured $\chi^{(3)}$ of the sample compared to CS_2 can be given by the following [Eq. (2)]:[18]

$$\chi^{(3)}=\chi^{(3)}_{\text{ref}}\left(\frac{I_4/I_0^3}{I_{4\ \text{ref}}/I_{0\ \text{ref}}^3}\right)^{1/2}\left(\frac{n}{n_{\text{ref}}}\right)^2\left(\frac{l_{\text{ref}}}{l}\right)\times\left(\frac{\alpha l}{e^{-\alpha l/2}(1-e^{\alpha l})}\right), \tag{2}$$

where $\chi^{(3)}_{\text{ref}}=\chi^{(3)}_{CS_2}=6.8\times10^{-13}$ esu; l is the interaction path length of the sample; I_4 and $I_0$are the intensities of the phase conjugated signal and the signal proportional to the laser intensity and α is the absorption coefficient of the sample at the laser wavelength in cm^{-1}. The subscript "ref" refers to the reference material which in this case is CS_2. The reference medium was assumed to have no absorption at the laser wavelength. Based on the properties of the laser and the optical geometry used in the experiment, the interaction path length for CS_2 in a 1 mm path cuvette is 0.10 ± 0.01 mm. Since the thickness of the films is much smaller than 0.1 mm, actual film thickness was used. I_4 was collected as a function of time delay of the probe beam I_3, while the two pump beams stayed at zero delay time.

The experimentally obtained signal as a function of time delay of the probe beam can be well described by a Gaussian profile

$$F(C,\sigma,a,b)=\frac{C}{\sigma\sqrt{2\pi}}e^{-0.5(t-a)^2/\sigma^2}+b, \tag{3}$$

where a,b,C, and σ are the constants treated as adjustable parameters and t is the equivalent time variable. The average peak intensity of the signal is taken as peak height of the fitted Gaussian $[(C/\sigma\sqrt{2\pi})]$.

The second hyperpolarizability $\langle\gamma\rangle$ of the molecule in an isotropic media is related to the third-order macroscopic susceptibility by the equation:[19]

$$\langle\gamma\rangle=\frac{\chi^{(3)}}{L^4N}, \tag{4}$$

where N is the number density of the molecules in cm^{-3} and L is the local field correction factor given by $[(n^2+2)/3]$. Based on the measurements for the five films with thicknesses ranging from 1.15 to 4.05 μm, the average $\chi^{(3)}$ and $\langle\gamma\rangle$ values were obtained at $(1.33\pm0.15)\times10^{-11}$esu and $(1.97\pm0.22)\times10^{-32}$esu, respectively. The $\chi^{(3)}$ value of CS_2 was taken as 6.8×10^{-13}esu. A typical DFWM signal profile from the Pc-film and signal profile from CS_2 is shown in Fig. 2. The FWHM for the Pc-film signal is about 52 ps, which is shorter than that of the laser pulse (~70 ps). This indicates that the Pc film has an ultrafast response and is essentially limited by laser pulse width. The signal profile from the film was found sharper than that from CS_2. It is premature with the limited data available at this stage to comment on the origin of this shorter time response as compared to CS_2. However, we anticipate that reverse saturable absorption (RSA), which results in the increase of absorption with the intensity of excitation, partially accounts for this observed behavior.[20] Although Pc based materials exhibit weak absorption in the visible (400–600 nm) spectral range, they show strong RSA in this spectral regime. The RSA may manifest in enhanced third-order nonlinearity resulting in a DFWM signal with a narrower time response than the laser pulses. Experiments utilizing subpicosecond laser pulses and the measurements of optical nonlinearities at 1064 nm (the region where the Pc film is completely transparent) are underway to further investigate phenomena in these films and will be reported in the subsequent publications. To our knowledge this is the first report of a multilayered film containing phthalocyanine derivatives in high density. The details of the nonlinear optical response and optical limiting effects with the multilayered films containing higher concentrations of macrocyclic rings are under investigations.

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Polyhydroxysilicon Phthalocyanine and Bis-phthalocyanine Derivatives: New Monomers for Third-Order Nonlinear Optical Polymers

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A series of new silicon phthalocyanine [$SiPc(OR)_2$] and silicon bis-phthalocyanine [$RO(SiPcO)_2R$] derivatives containing two or more hydroxyl groups has been synthesized by axial etherification of [$PcSi(OH)_2$] or [$HO(SiPcO)_2H$] with various multi-functional alcohols, where R is a residue generated from the corresponding alcohol namely, triethanolamine, triethylene glycol or N,N-bis (2-hydroxyethyl isonicotinamide). These derivatives can be processed into thin polymeric films by reacting with isophorone diisocyanate. Many of the derivatives demonstrated high solubility in common organic solvents such as chloroform and dioxane, and exhibit low absorptions in the visible region.

Phthalocyanine (Pc) derivatives have emerged as one of the most promising classes of materials in the area of nonlinear optics due to their large and ultrafast third-order optical nonlinearities.[1] Although the molecular design requirements for practical third-order nonlinear optical materials are poorly understood, a combination of long π-conjugation lengths and low HOMO-LUMO gaps appear to be important. Presently, we and others have been interested in developing prototype devices for the protection of vision and sensors against short, intense laser pulses using Pc compounds due to their favorable transparency in the visible spectral range.[2-4] To provide efficient vision protection a material should possess (i) high nonresonant nonlinear optical susceptibility ($\chi^{(3)}$) which is directly proportional to the number density of the π-conjugated molecules (ii) be easily processable into thin films and (iii) be

optically transparent in the visible region. However, the practical applicability of many Pc derivatives is hindered due to their low solubility in common organic solvents and incompatibility with vinyl polymers which prevent thin film processing.

In the past decade, extensive effort has been made to produce soluble Pc derivatives.[5-11] Most of the highly soluble Pc derivatives made so far contain either electron donor substituents such as alkyl, alkoxy or phenoxy groups, or electron withdrawing substituents such as sulfonyl or carboxyl groups at the peripheral positions. In recent years, several studies concerning the effect of peripheral substituents[12], additional conjugation such as in naphthalocyanine[12,13] and the central metal atom character[3,14] on $\chi^{(3)}$ have been conducted. Results indicate that peripheral substituents greatly improve the solubility of the Pc molecule and increase both the absorption in the visible region and to some extent the optical nonlinearities in molecules where electrons are permitted to flow in or out of cyclic π-conjugated rings. In extended π-conjugated systems such as naphthalocyanine, the absorption in the visible region increases dramatically while $\chi^{(3)}$ shows about a 5-10 times enhancement in its value. Similarly, the nature of the central metal atom plays an important role in tuning both optical nonlinearities and absorption in the visible region. For instance, $\chi^{(3)}$ of Pc increases about 15 times by changing the central metal atom from silicon to vanadium[15] and similarly increases, albeit not as drastically, with a central heavy metal atom such as lead.[16] Axial derivatization through a metal atom such as silicon has also been found to increase the solubility of Pc molecules[17-19] and have little to no effect on the absorption behavior in the visible region, depending on the axial substituents.

In this communication, we present a facile synthetic route for a series of axially modified phthalocyanine and bis-phthalocyanine derivatives which contain two or more hydroxyl groups and comply with the processing and optical transparency requirements for materials to be used for vision protection from laser radiation. The polyhydroxy derivatives were made by

axial etherification of dihydroxysilicon phthalocyanine (DHPc) or dihydroxysilicon bis-phthalocyanine (DBPc) with a multi-functional alcohol. The structures of the molecules are shown in Scheme 1. In order to obtain high yields and to develop a generalized procedure for axial etherification using polyhydroxy compounds we modified the procedure reported for etherification using mono-functional alcohols.[18,20,21] We noticed that if we add DHPc (or DBPc) into a refluxing solution of a multi-functional alcohol and pyridine (twenty times and equivalent molar amount, respectively) in a high boiling solvent such as *o*-dichlorobenzene (*o*-DCB), the desired product in high yield was obtained in less than one hour. Since the starting material, DHPc (or DBPc), is insoluble in common organic solvents the product obtained was reasonably pure (ca. 95%) after work-up. Further purification of the derivatives were performed by dissolving in chloroform and precipitating from hexane. Purification using column chromatography was fruitless due to the decomposition of the product. In general, liquid alcohols afforded higher yields than did solid ones. Analytical data of both monomers (**1a-c**) and dimers (**2a-c**) are presented in Table 1. The FT-IR bands at 830 and 3535 cm^{-1} due to Si-O-H group observed in both DHPc and DBPc were absent in the monomers and dimers, instead a new sharp band appeared at 3435 cm^{-1} due to aliphatic hydroxyl groups. The major difference in the FT-IR spectra of the monomers and dimers is the presence of a sharp band at 988 cm^{-1} due to -Si-O-Si bond in the dimers. The IR absorptions attributed to the Pc ring in both monomers and dimers in the 1150-650 cm^{-1} range remain essentially unchanged.

INSERT Scheme 1 and INSERT Table 1

Some of the derivatives have emerged as the best known soluble phthalocyanine and bis-phthalocyanine derivatives (Table 2). For instance, the solubility of compound **1a** was measured at 12.1 x 10^{-2} gm per milliliter in chloroform (~0.15 M), which is about three times greater than that of previously reported soluble Pc derivatives.[5,22] Surprisingly, the derivatives generated from N,N-bis (2-hydroxyethyl isonicotinamide), **1c** and **2c**, showed

incredibly high solubility in a variety of organic solvents such as chloroform. It is important to note that the previously reported phthalocyanine monomers and dimers derived from mono-functional alcohols such as $Si[C(CH_3)_3](CH_3)_2OH$ were soluble only in basic organic solvents such as pyridine and quinoline, and somewhat less soluble in polar solvents such as chloroform and dioxane.[20]

INSERT Table 2

The most interesting feature of these derivatives is their facile processability into thin polyurethane films. The hydroxyl groups of these Pc derivatives react with a reactive diisocyanate compound such as isophorone diisocyanate to form urethane linkages. The films were made in such a proportion that the number of isocyanate groups were equal to the number of hydroxyl groups. The kinetics of polymerization using a representative example of each category is shown in Fig.1. Although both monomers and dimers require less than 10 min for complete conversion, we set the curing condition at 125°C for 1 h to ensure complete curing. We also used triethanolamine (one-half molar equivalent of isophorone diisocyanate) as a processing aid to improve the quality of the films such as crack resistance. The resulting polyurethane films possess high resistance to low impact scratches and thermostability at 125°C for over 10 hours.

INSERT Fig. 1

FT-IR spectroscopy was also used to monitor the curing of the films by observing the sharp peak at 2261 cm^{-1} due to C=N bond of the isocyanate group over time. The absorption peak gradually decreased with the progress of curing. The peak due to the C=O bond of the isocyanate group which appeared at 1702 cm^{-1} was almost unchanged after curing. The disappearance of the O-H band which seems to overlap with the N-H band in the 3100-3700 cm^{-1} region was also noticed as a result of the sharpening of the N-H band at 3326 cm^{-1} (Fig. 2).

INSERT Fig. 2

Preliminary studies of the polymer films (of about 1 μm thickness) containing 23% by weight of phthalocyanine or bis-phthalocyanine derivatives indicate no observable microcrystallization or phase-segregation. The electronic absorption spectra of the films also indicate high optical transparency in the visible region (Fig. 3). Interestingly, the Q- and B-band transitions of the dimers show a dramatic shift to the blue region relative to the monomers. This shift is accounted for by the excitation coupling of neutral excitation transition between the Pc rings of the dimer.[20]

INSERT Fig. 3

To our knowledge, no bis-phthalocyanine derivative either covalently incorporated in a polyurethane matrix or highly soluble in common organic solvents has been reported thus far. Studies on the third-order nonlinear optical properties of the films as a function of the concentrations of the monomers and dimers are in progress in order to appraise which derivative exhibits superior properties for laser protection devices.

The authors wish to thank Dr. B. Bihari and Dr. M. Kamath for their technical assistance, and Dr. K. Katti (University of Missouri) and Dr. T. Hsieh (Sandoz, Desplaines, Illinois) for their generous help for obtaining ^{1}H-NMR and FAB-Mass spectra. This work is supported by the U. S. Army Tank-Automotive Command (Warren, Michigan) under the contract # DAAE07-93-C-R138. Acknowledgment is also made to AFOSR for providing funds (grant # F49620-9310-583) for instruments used in this study.

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Legend to Scheme

Scheme 1. Synthesis of monomers and dimers.

Legend to Figures

Fig. 1 Kinetics of Polymerization.

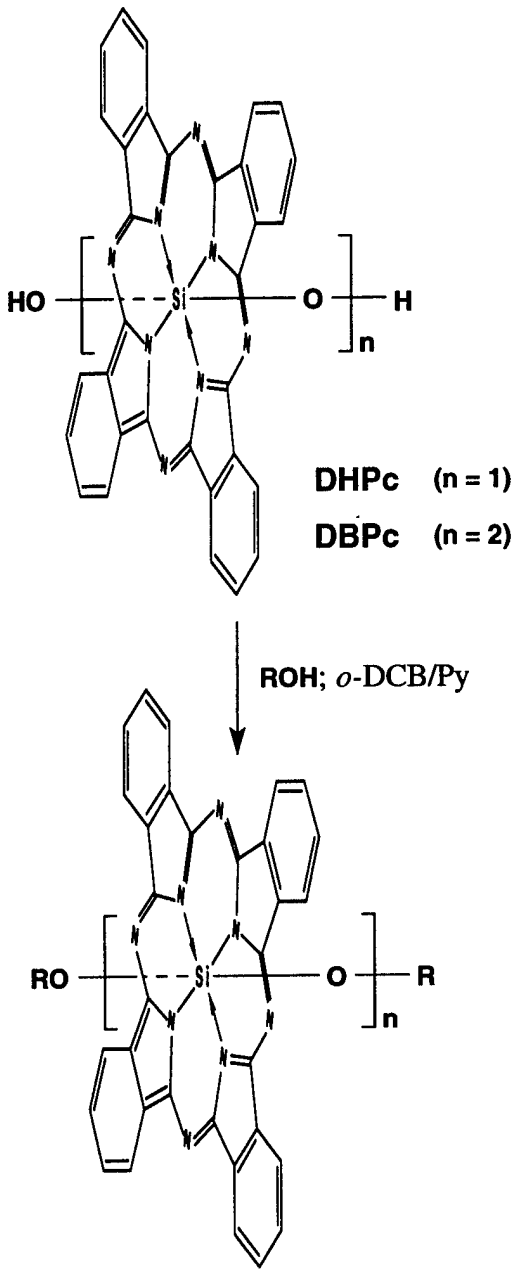
Fig. 2 FT-IR spectra of compound **2a**, isophorone diisocyanate and triethanolamine mixture: (a) before curing; (b) after curing.

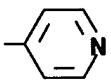
Fig. 3 Electronic absorption spectra of polymer films (ca. 1 μm thickness) containing 23% (w/w) of compounds **1a** (——) and **2a** (- - - -).

Legend to Tables

Table 1 Analytical Data of Monomers and Dimers

Table 2 Electronic Spectra[a] and Solubilities of Monomers and Dimers



Compound	R	n
1a	$CH_2CH_2N(CH_2CH_2OH)_2$	**1**
1b	$CH_2CH_2OCH_2CH_2OCH_2CH_2OH$	**1**
1c	$CH_2CH_2N(CH_2CH_2OH)CO$ 	**1**
2a	Same as **1a**	**2**
2b	Same as **1b**	**2**
2c	Same as **1c**	**2**

Scheme - 1 Sinha & Mandal

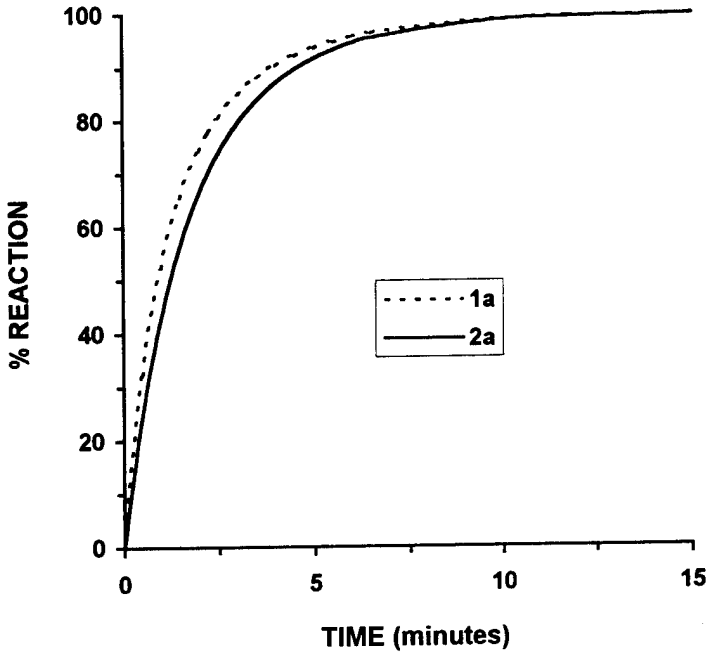


Fig. 1 of 3

Sinha and Mandal

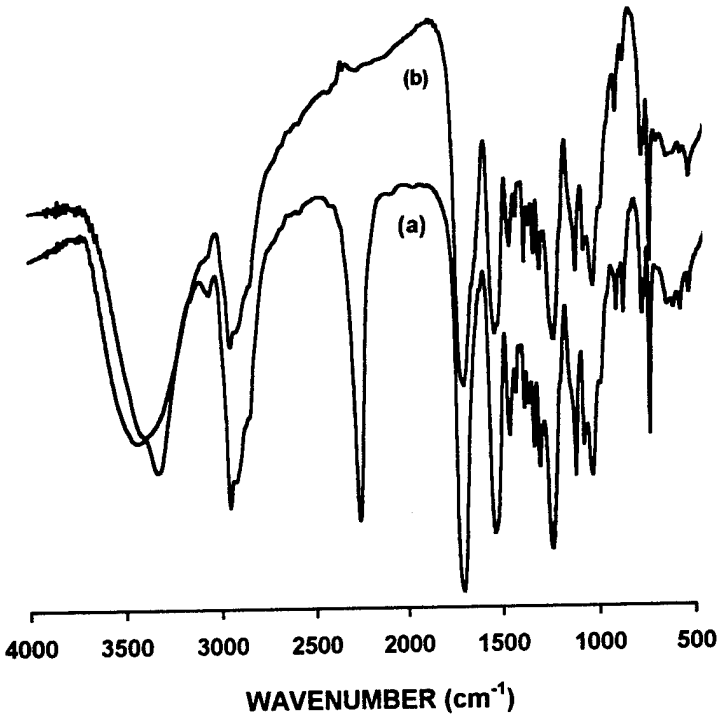


Fig. 2 & 3 Sinha and Mandal

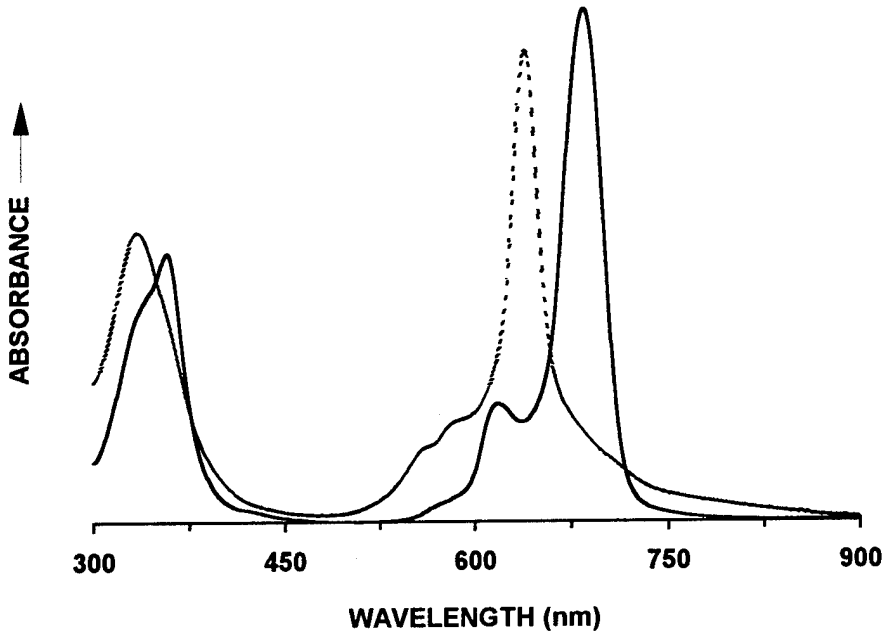


Fig. 3 of 3 Sinha and Mandal

Table 1. Analytical Data of Monomers and Dimers

Compound	Yield	Analysis[a]			^{1}H-NMR ($CDCl_3$)	FAB-MS
	%	C, %	H, %	N, %	δ, ppm	m/z
1a	75	63.51 (63.14)	4.98 (5.30)	16.69 (16.73)	-2.02 (t, 4H), -0.22 (t, 4H), 0.85 (t, 8H), 1.99 (t, 8H), 8.37 (m, 8H), 9.68 (m, 8H)	837, 688, 557
1b	84	63.33 (62.99)	5.03 (5.05)	13.12 (13.36)	-1.89 (t, 4H), 0.49 (t, 4H), 2.43 (m, 8H), 2.95 (t, 4H), 3.32 (t, 4H), 8.36 (m, 8H), 9.66 (m, 8H)	839, 689, 556
1c	70	64.97 (65.12)	4.55 (4.41)	17.58 (17.52)	-2.0 (t, 4H), -1.71 (t, 4H), 0.52 (t, 4H), 1.27 (t, 4H), 8.39 (m, 8H), 8.66 (m, 4H) 9.04 (m, 4H), 9.67 (m, 8H)	959, 854, 749 556
2a	63	65.21 (65.50)	4.58 (4.34)	17.98 (18.09)	-3.70 (t, 4H), -1.26 (t, 4H), 0.00 (t, 8H)[b], 1.28 (t, 8H), 8.34 (m, 8H), 9.05 (m, 8H)	- - - -
2b	72	65.33 (65.41)	4.36 (4.19)	15.98 (16.06)	-3.62 (t, 4H), -0.61 (t, 4H), 2.46 (m, 8H), 2.94 (t, 4H), 3.62 (t, 4H), 8.34 (m, 8H), 9.04 (m, 8H)	- - - -
2c	62	66.37 (66.51)	4.05 (3.85)	18.68 (18.55)	-3.61 (t, 4H), -3.45 (t, 4H), 0.46 (t, 4H), 1.25 (t, 4H), 8.08 (m, 8H), 8.32 (m, 4H) 8.39 (m, 4H), 9.03 (m, 8H)	- - - -

[a] Figures in the parentheses represent required values. [b] Signal merged with TMS. The triplet was apparent in the expanded spectrum.

Table 1 of Sinha and Ho et al

Table 2. Electronic Spectra[a] and Solubilities of Monomers and Dimers

Compound	Wavelength, nm (10^{-4} ε, mol^{-1} cm^{-1})			Solubility, gm/L[b]
1a	677 (21.1084)	649 (2.9795)	610 (3.3731)	121.5 (0.145)
	356 (6.9402)	288 (2.1438)		
1b	674 (17.9275)	645 (2.3412)	607 (2.7461)	64.0 (0.076)
	353 (5.3799)	280 (1.7930)		
1c	677 (12.8583)	638 (4.5367)	610 (2.7112)	143.0 (0.149)
	355 (5.4310)	289 (2.2720)		
2a	635 (33.158)	587 (5.5765)	561 (3.9954)	38.6 (0.028)
	331 (16.8562)	284 (11.4221)		
2b	635 (72.5280)	588 (1.9195)	561 (1.4425)	11.8 (0.008)
	330 (43.1991)	285 (3.3188)		
2c	636 (20.1947)	587 (4.1231)	562 (3.0501)	126.7 (.084)
	331 (11.2921)	284 (6.9204)		

[a] The electronic spectra were recorded in chloroform.

[b] Measured from a saturated solution at 25°C, where c = A/εl and l = 1 cm.

Figures in the parentheses represent molarity of corresponding saturated solutions in mol/L.

Table 2 of 2 Sinha & Mandal

Thin Film Processing of Axially Modified Phthalocyanine Derivatives

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SYNOPSIS

A new class of polyhydroxy phthalocyanine derivatives has been prepared by axial etherification of dihydroxysilicon phthalocyanine. Some of these derivatives exhibit very high solubility in common organic solvents and possess adequate optical transparency for use as nonlinear optical materials in vision protection against laser light. Crosslinked polyurethane films containing covalently linked phthalocyanine rings have been made by heating mixtures of a polyhydroxy phthalocyanine derivative, triethanolamine and isophorone diisocyanate. The films possess high impact resistance, thermostability at 125°C for over 10 hours and low absorption in the visible region. Solid polymeric films incorporating over 20% (w/w) of phthalocyanine rings were prepared without phase segregation. The kinetic parameters of polymerization, such as reaction conversion versus time and temperature, heat of reaction (ΔH), activation energy (ΔE) and reaction order (n) have been investigated.

Keywords: nonlinear optical properties . axially modified phthalocyanine . polyurethane . vision protection

INTRODUCTION

Polymers containing high concentration of phthalocyanine (Pc) rings are sought for nonlinear optical applications; specifically, those that are useful for human vision protection against high intensity tunable and fast pulsed lasers.[1] To provide efficient vision protection a material should possess high nonresonant nonlinear optical susceptibility ($\chi^{(3)}$), be easily processable into thin films, and be optically transparent in the visible region. It is predicated (equation 1) that such polymer films will not only possess 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.

$$\chi^{(3)} = N L^4 \langle\gamma\rangle \qquad \ldots\ldots\ldots \quad (1)$$

In this equation N is the molecular number density and L is the Lorentz local field factor.[2,3] In addition to increased flexibility in device fabrication, faster response time is another anticipated attribute of solid polymeric films containing macrocyclic rings in high density. Due to their incompatibility with common vinyl polymers, however, covalent attachment of macrocyclic rings with the polymer matrix is essential in order to avoid the formation of microcrystallites that are prevalent in the case of guest-host systems.

In past decades, a number of soluble Pc derivatives containing a variety of peripheral and axial groups and central metal atoms have been synthesized.[4-10] To our knowledge, none of these derivatives are soluble in over 10% (w/w) concentrations in common organic solvents such as chloroform, and until recently, none could be easily processed into optical quality films containing covalently attached Pc rings with common organic polymers such as poly(methylmethacrylate).[11,12] In this paper, we report a facile synthetic route for obtaining soluble, axially modified Pc derivatives and the processing of a representative derivative into thin polyurethane films by reaction with triethanolamine and isophorone diisocyanate.

EXPERIMENTAL

Materials

Dihydroxysilicon phthalocyanine (DHPc), triethanolamine (TEA), isophorone diisocyanate (IDI), ethylene glycol, glycerol, triethylene glycol, N,N-bis (2-hydroxyethyl)-isoniconamide], 1,4-bis (2-hydroxyethyl)-piperazine, pyridine, *o*-dicholorobenzene (*o*-DCB) and chloroform were all purchased from Aldrich and used without further purification.

Synthesis of Polyhydroxy Pc Derivatives

In this study, a variety of silicon phthalocyanine derivatives which contain two or more hydroxyl groups has been synthesized by axial etherification of DHPc. The structures of the polyhydroxysilicon phthalocyanine (PHPc) derivatives are shown in Figure 1. In a typical experiment DHPc (1 g, 1.74 mmol) was added to a refluxing solution of TEA (5 g, 33.5 mmol) in *o*-DCB (40 mL) and pyridine (5 mL) in a 100-mL three-necked round-bottomed flask fitted with a condenser and a nitrogen inlet. After 1 h of refluxing, the mixture was filtered while hot to separate the compound from unreacted dihydroxysilicon phthalocyanine (separation of product was observed in some instances, in which case the residue was washed with 100 mL chloroform). The filtrate on washing with 3x100 mL water followed by drying over $MgSO_4$ and subsequent evaporation of solvent under reduced pressure gave a blue colored product **1** which was purified by recrystallization from a toluene:hexane mixture. Yield: 1.09 g (75%) of blue crystal. All compounds appear deep blue except **6** which shows a purple color.

Insert Fig. 1

Thin Film Processing of PHPc Derivatives

Films were made by casting a solution of a Pc derivative, TEA and IDI in an organic solvent such as dioxane. In a typical procedure, compound **1** (0.5 g, 0.6 mmol) in 10 mL of dioxane was added to a mixture of 0.63 g (4.2 mmol) TEA and 1.65 g (7.4 mmol) IDI, mixed throughly for 10 min in an ultrasonicator and filtered through a 0.2 μm syringe filter. The solution was cast into films over glass slides using both film-casting and spin-casting techniques in a Class-100 clean room. The films were dried under vacuum overnight prior to curing. All films were made in such a proportion that the number of isocyanate groups were equal to the number of hydroxyl groups. Some of the PHPc derivatives such as **1** were found soluble in the TEA/IDI mixture and therefore it was possible to cast films in the absence of a solvent. The Pc content in all films was over 20% by weight. All films are named after the Pc compound number given in Figure 1 except film-IT which was made by heating a mixture of x mole of IDI and 3x/2 mole of TEA.

Measurements

The structures of PHPc derivatives were confirmed by ^{1}H-NMR (outside facility), FT-IR (Perkin-Elmer 2000) and FAB-Mass spectroscopy (outside facility) and elemental analysis (Perkin-Elmer 2400). The electronic spectra of the derivatives in both solution and solid polymeric film were recorded with a Lambda-19 (Perkin-Elmer) spectrophotometer. The kinetics of polymerization and the thermostability of the films were determined using a Perkin-Elmer Series-7 differential scanning calorimeter and thermogravimetric analyzer, respectively.

RESULTS AND DISCUSSION

The synthesis of highly soluble PHPc derivatives which qualify for potential vision protection materials involves axial modification of DHPc with a multi-functional alcohol. The molecular design permits smooth reaction between isocyanate groups of IDI and hydroxyl groups of PHPc derivative leading to a crosslinked polyurethane (Figure 2).

Insert Figure 2

In order to obtain high yields and to develop a generalized procedure for axial etherification using multi-functional alcohol we modified the procedure of Kenney et al.[13] reported for etherification using mono-functional alcohols. The reaction proceeds through a siliconium ion intermediate which reacts with alcohol to form soluble Pc derivatives. We noticed that if we add DHPc into a refluxing solution of a multi-functional alcohol in a high boiling solvent such as *o*-dichlorobenzene, the desired product formed in less than one hour. Since the starting material, DHPc, is insoluble in common organic solvents the product obtained was very pure after work-up. In general, liquid alcohols afforded higher yields than did solid ones.

The proposed structures of all PHPc derivatives are in good agreement with the analytical data (Table I). The FT-IR spectra of all derivatives indicated the absence of a sharp band at 839 cm^{-1} observed in DHPc for the Si-O bond. The IR absorptions attributable to the Pc ring in the 1150-650 cm^{-1} range remain essentially unchanged. The ^{1}H-NMR spectra of PHPc derivatives show that the Pc ring produces, not surprisingly, a large ring current effect on axially linked α- and β-methylene protons compared to peripherally substituted[7] methylene protons. The resonance of α-methylene protons of all compounds occurs around -2 ppm

while that of β-methylene protons varies from compound to compound and occurs closer to the negative side of the TMS peak. On the other hand, the resonances of peripheral aromatic protons are almost the same for all compounds, 8.4 ppm and 9.7 ppm for 4,5-Pc and 3,6-Pc protons respectively.[14] Negative FAB-Mass spectral analysis of the Pc derivatives showed predominant ions corresponding to the fragments consistent with the assigned molecular ions (Table I).

Insert Table I

Analysis of the optical spectra of phthalocyanine is well reported[15] and is characterized by two major bands, the Q-band and B-band corresponding to absorptions at 670 nm and 340 nm, respectively. Solution optical spectra of the PHPc derivatives show a sharp Q band transition at ca. 675 nm with the shoulders at ca. 642 nm and 609 nm which are likely of vibronic origin (Table II). Quite unlikely, compound **6** showed a large relative change in intensity of the peak at 636 nm with increase in solution concentration without any shifts of the other major bands (Figure 3). The B-band region of the Pc derivatives was found to be quite similar for all compounds except for compound **6** which shifted slightly towards blue.

Insert Figure 3

Solubility studies in common organic solvents such as chloroform have been performed. These Pc derivatives exhibit much higher solubility in common organic solvents than both axially and peripherally modified Pc derivatives reported so far (Table II). For instance, the solubility of compound **1** was measured at 12.1 x 10^{-2} gm per milliliter in chloroform (~0.15 M), which is about three times greater than that of previously reported soluble Pc derivatives.[4,16,17]

Insert Table II

Differential scanning calorimetry (DSC) was used to study the kinetics of curing for all Pc films. The DSC studies indicate that the formation of the carbamate group begins slowly at room temperature and becomes more pronounced over 50°C. In view of this, three temperatures (75°, 100° and 125°C) were selected to study the kinetics of curing for each film. Curing studies of the film containing only IDI (x mole) and TEA (3x/2 mole) were also performed alongside. It is surprising to note that the complete conversion of the films containing PHPc derivatives required much less time than those without the derivative at 75°C. The reaction without PHPc derivative is, however, very fast at 125°C (Figure 4). The reaction leading to film-5 was found to occur at least two times faster than those of other Pc films at all three temperatures selected for this study. To ensure complete curing, however, the curing conditions were set at 125°C for 1 h, although the DSC traces of all films at 125°C indicate an optimum cure time of 5 to 20 min. It is worthwhile to note that the curing of PHPc derivatives in the presence of a small amount of TEA produces crack-free optical quality films.

Insert Figure 4

FT-IR spectroscopy was also used to monitor the curing of the films by observing the sharp peak at 2261 cm^{-1} due to C=N bond of the isocyanate group (Figure 5a). The absorption peak gradually decreased with the progress of curing. The peak due to the C=O bond of the isocyanate group which appeared at 1702 cm^{-1} was almost unchanged after curing. The disappearance of the O-H band which seems to overlap with the N-H band in the 3100-3700 cm^{-1} region was also noticed as a result of the sharpening of the N-H band at 3326 cm^{-1} (Figure 5b). The IR absorptions attributable to the Pc ring in the 1150-650 cm^{-1} range remain essentially unchanged.

Insert Figure 5

The activation energy (ΔE) of curing, heat of reaction (ΔH) and order of reaction (n) were also determined and are presented in Table III. The ΔE values of the reactions leading to Pc films were found to be about three times less than for reactions of IDI and TEA. The reaction between isocyanate and the hydroxyl groups was exothermic. The ΔH and n values of all reaction mixtures involving Pc derivatives were less than the IDI/TEA mixture alone. It is important to note that ΔH of the reaction mixture leading to film-5, which requires a shorter curing time, was found to be very low in comparison to the other reaction mixtures.

Insert Table III

The thermal stability of the films was measured by thermogravimetric analysis (TGA). The product decomposition temperature (PDT) values obtained from the TGA thermograms indicate that films-3 and 6 have higher PDTs in comparison to films-1 and 5 which surprisingly have lower PDTs than a polyurethane film containing no Pc rings (Table III). The results of isothermal heating at 125°C of all Pc films indicate resistance to thermal breakdown for up to 10 h and show weight losses of less than 2% after 15 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. The results of isothermal heating of the polyurethane films showed that they are more stable than polyurethane film-IT.

The absorption electronic spectra of the Pc films (~1 μm thick) exhibit low absorptions in the visible region. For instance, the OD of all films varied from 0.001 - 0.06 at 532 nm. Absorption characteristics of all Pc films were found to be similar to their absorption behavior in solution. The Pc films are hydrophobic, do not scatter light, and resistant to low impact scratches. Since the crosslinking reaction does not evolve any by-products, the fabrication of optical quality thicker films (over 1 mm) is attainable using a preconfigured mould.

CONCLUSIONS

We presented a modified synthetic procedure for obtaining polyhydroxysilicon phthalocyanine derivatives which are highly soluble and processable into polymeric thin films. To our knowledge no Pc derivative which is freely soluble in over 10% (w/w) concentrations in common organic solvents has been reported in the literature. Further molecular engineering of these derivatives leading to photocrosslinkable and thermally crosslinkable polymers, and the measurement of their nonlinear optical properties and that of similar polymeric films derived from aromatic alcohols and isocyanate derivatives are in progress.

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Legend to Figures

Figure 1. Synthesis of PHPc derivatives.

Figure 2. Schematic of the processing of PHPc derivatives into crosslinked polyurethane films.

Figure 3. Electronic absorption spectrum of compound **6** with variation in concentration: (a) 1.22×10^{-6} M; (b) 1.72×10^{-5} M; (c) 2.58×10^{-5} M.

Figure 4. Kinetics of crosslinking reactions.

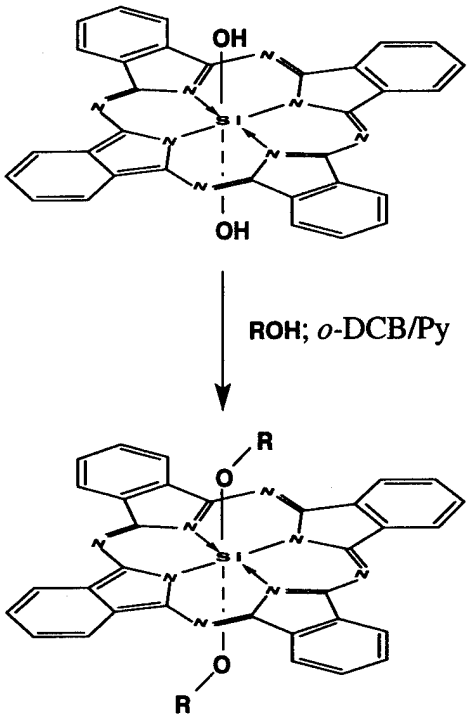
Figure 5. FT-IR spectra of compound **1**, IDI and TEA mixture: (a) before curing; (b) after curing.

Legend to Tables

Table I. Analytical Data of PHPc Derivatives

Table II. Electronic Spectra[a] and Solubilities of PHPc Derivatives

Table III. Kinetics of Curing and Thermal Properties[a] of Polyurethane Films



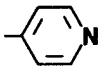
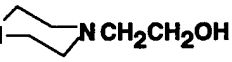
Compound	R
1	$CH_2CH_2N(CH_2CH_2OH)_2$
2	$CH_2CH(OH)CH_2OH$
3	$CH_2CH_2OCH_2CH_2OCH_2CH_2OH$
4	CH_2CH_2OH
5	$CH_2CH_2N(CH_2CH_2OH)CO$ 
6	CH_2CH_2  CH_2CH_2OH

Figure 1. Synthesis of PHPc derivatives.

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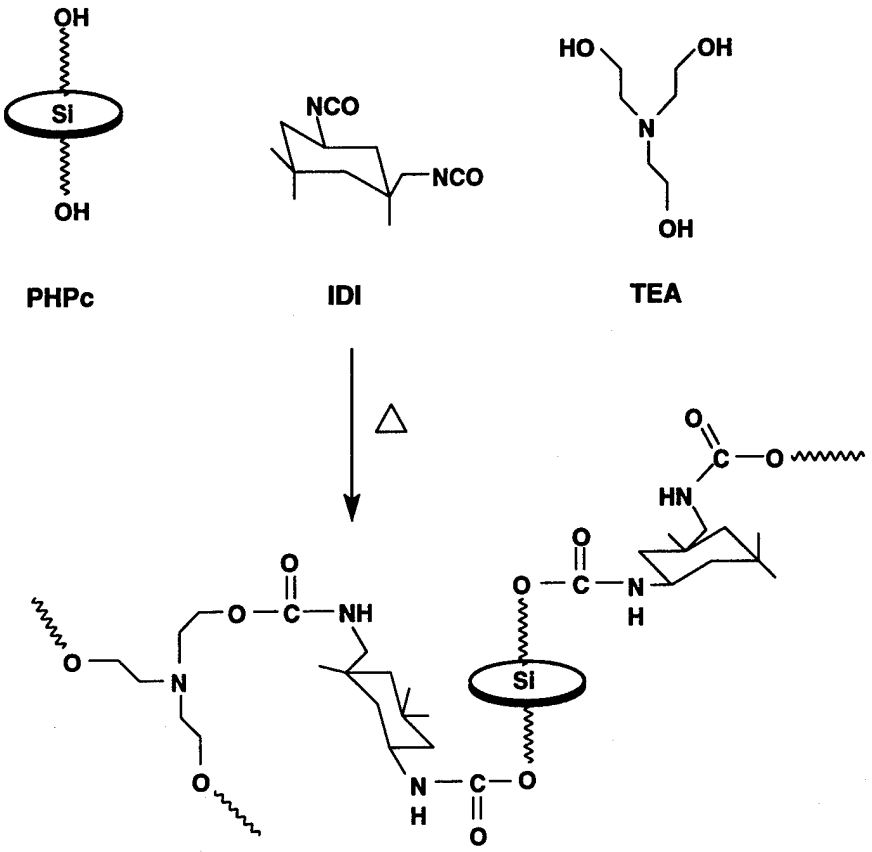

Crosslinked Polyurethane

Figure 2 of 5 Mondal et al.

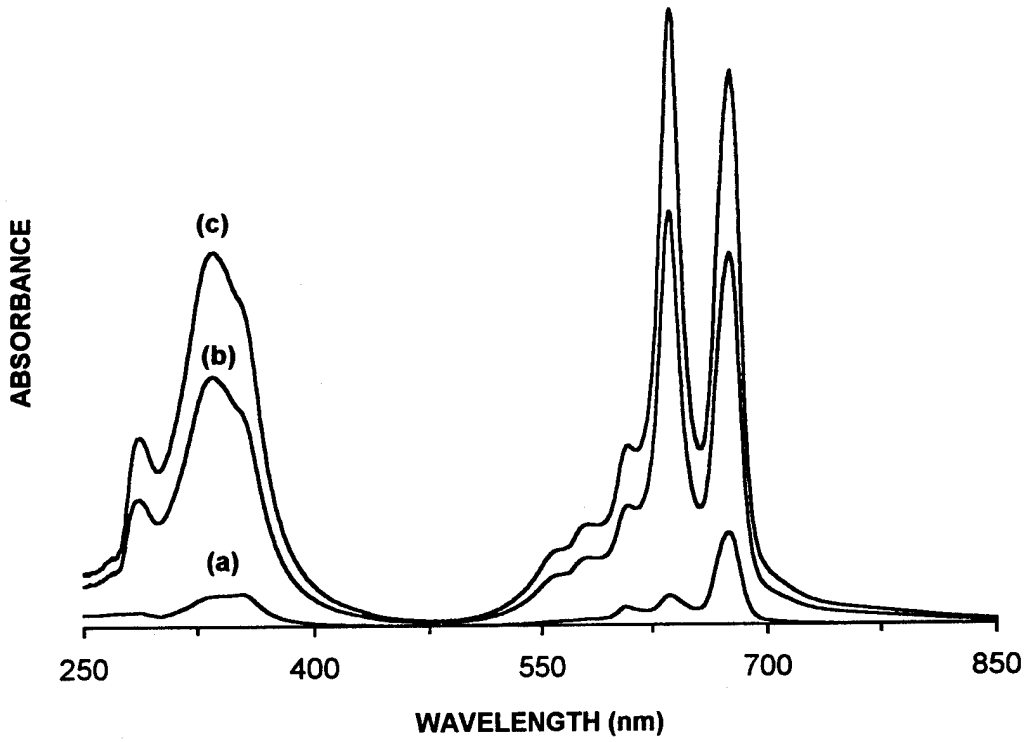

Figure 3 of 5 Mandal et al.

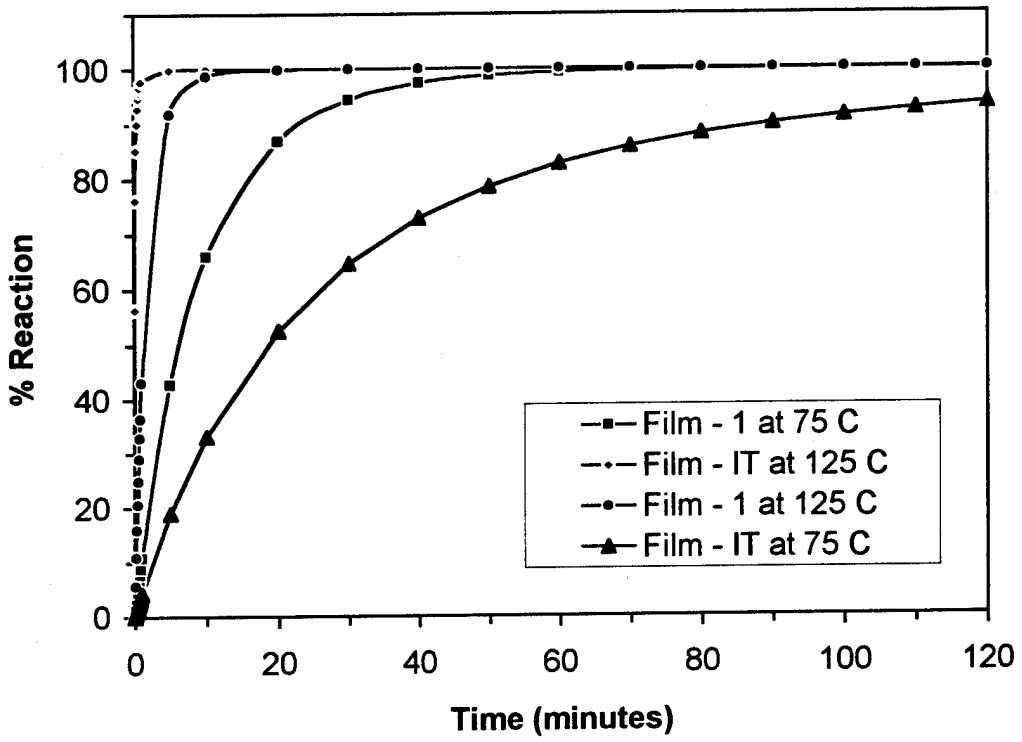

Figure 4 of 5 Mandal et al

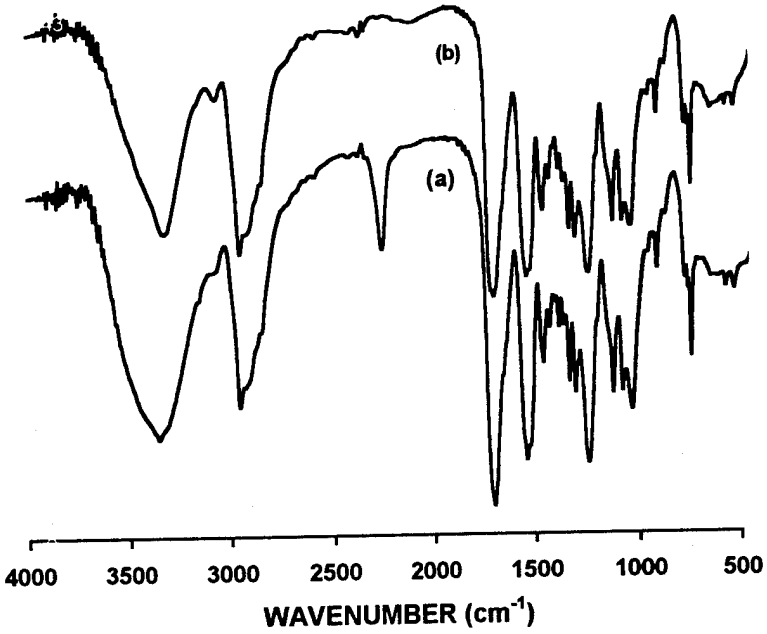

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Table I. Analytical Data of PHPc Derivatives

Compound	Yield	Analysis				^{1}H-NMR ($CDCl_3$)	FAB-MS
	%		C, %	H, %	N, %	δ, ppm	m/z
1	75	exp	63.51	4.98	16.69	-2.02 (t, 4H), -0.22 (t, 4H), 0.85 (t, 8H), 1.99 (t, 8H), 8.37 (m, 8H), 9.68 (m, 8H)	837, 688, 557
		calc	63.14	5.30	16.73		
2	80	exp	62.90	4.01	15.42	-1.97 (m, 4H), -0.90 (t, 2H), 0.83 (d, 4H), 8.39 (m, 8H), 9.66 (m, 8H)	- - -
		calc	63.15	4.18	15.50		
3	84	exp	63.33	5.03	13.12	-1.89 (t, 4H), 0.49 (t, 4H), 2.43 (m, 8H), 2.95 (t, 4H), 3.32 (t, 4H), 8.36 (m, 8H), 9.66 (m, 8H)	839, 689, 556
		calc	62.99	5.05	13.36		
4	76	exp	64.96	4.05	16.69	-2.00 (t, 4H), -1.63 (t, 4H), 8.37 (m, 8H), 9.64 (m, 8H)	- - -
		calc	65.25	3.95	16.91		
5	70	exp	64.97	4.55	17.58	-2.0 (t, 4H), -1.71 (t, 4H), 0.52 (t, 4H), 1.27 (t, 4H), 8.39 (m, 8H), 8.66 (m, 4H) 9.04 (m, 4H), 9.67 (m, 8H)	959, 854, 749 556
		calc	65.12	4.41	17.52		
6	64	exp	65.12	5.47	18.99	-1.93 (t, 4H), -0.52 (t, 4H), 0.27 (bs, 8H), 0.86 (bs, 4H), 2.08 (t, 8H), 2.55 (t, 4H), 8.34 (m, 8H), 9.67 (m, 8H)	887, 714, 557
		calc	64.99	5.68	18.95		

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Table II. Electronic Spectra[a] and Solubilities of PHPc Derivatives

Compound	Wavelength, nm (10^{-4} ε, mol^{-1} cm^{-1})			Solubility, gm/L[b]
1	677 (21.1084)	649 (2.9795)	610 (3.3731)	121.5 (0.145)
	356 (6.9402)	288 (2.1438)		
2	676 (25.3336)	647 (3.3094)	608 (3.8432)	- - -
	353 (7.8756)	334 (5.9061)	290 (2.4333)	
3	674 (17.9275)	645 (2.3412)	607 (2.7461)	64.0 (0.076)
	353 (5.3799)	280 (1.7930)		
4	675 (26.1700)	645 (3.3264)	607 (3.9199)	- - -
	356 (7.8762)	336 (6.0800)	290 (2.4169)	
5	677 (12.8583)	638 (4.5367)	610 (2.7112)	143.0 (0.149)
	355 (5.4310)	289 (2.2720)		
6	674 (10.1752)	636 (11.3527)	608 (3.3635)	35.9 (0.040)
	583 (1.8878)	563 (1.4319)	333 (6.9410)	
	285 (3.6462)			

[a] The electronic spectra of Pc derivatives were recorded in chloroform.

[b] Measured from a saturated solution at 25°C, where c = A/εl and l = 1 cm.

Figures in the parentheses represent molarity of corresponding saturated solutions in mol/L.

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Table III. Kinetics of Curing and Thermal Properties[a] of Polyurethane Films

Film[b]	Pc content	DSC[c]			TGA[c]			
		ΔE^d	ΔH	n^d	PDT[e]	Isothermal Heating[f]		
	%	KJ/mol	J/g		°C	125°C	150°C	175°C
1	21.9	37.4	39.5	1.11	268	1.2	1.8	3.4
3	23.2	48.0	57.9	0.98	375	0.9	2.9	6.7
5	23.1	37.5	19.4	0.78	250	2.0	8.9	- - -
6	23.3	50.6	43.5	0.76	369	1.9	4.8	5.6
IT	0	129.4	60.9	1.64	306	4.8	9.8	14.9

[a] All experiments were performed under nitrogen. [b] All films are named after the PHPc compound number given in Figure 1 except film-IT which was made by heating a mixture of x mole of IDI and 3x/2 mole of TEA.

[c] Heating rate, 10°C/min. [d] Anticipated error is within ±6%. [e] Temperature for 5% weight loss.

[f] Weight loss in % after 15 h of heating.

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New Reactive Tetraphenylporphyrin Derivative for Nonlinear Optical Polymeric Films

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ABSTRACT: A new tetraphenylporphyrin (TPP) derivative containing four triethoxysilane groups has been synthesized to be processable with a commercially available reactive polysiloxane. Optical quality films displaying high thermal stability and containing 25% (w/w) of the TPP derivative have been made. The synthesis and properties of the TPP derivative are described.

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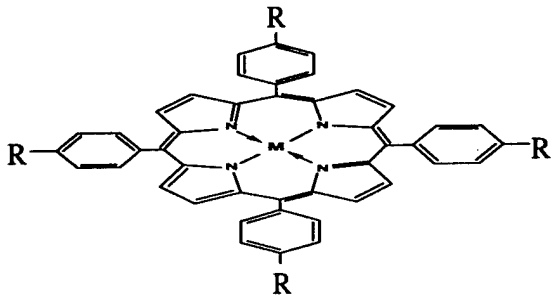
Introduction

There is currently a great interest in polymeric thin films containing high concentrations of cyclic π-conjugated systems in the areas of laser-pumped electro-optical devices,[1] sensors,[2] and optical limiters for the protection against short and intense laser pulses.[3] It is predicted that polymeric films containing high concentrations of π-conjugated chromophores will lead to useful properties such as high nonlinear optical susceptibility.[4] Although the tetraphenylporphyrin (TPP) system which contains extended cyclic π-conjugation has been the subject of numerous research investigations in past decades, only a few accounts of TPP polymeric films have been reported.[5] Most TPP polymers were made by derivatization through the para positions of the phenyl rings, and thin film processing often proved problematic due to the poor solubility of these derivatives in common organic solvents. To our knowledge, there has yet to be reported a TPP derivative soluble in concentrations of over 20% (w/w) in organic solvents. Moreover, little effort has been made to incorporate high concentrations of covalently linked TPP rings into a polymer that is processable into thin films. Covalent attachment of TPP rings with the polymer matrix is essentially required to avoid phase-segregation and formation of micro-crystals which result in polymeric films unsuitable for practical applications.

Spin-on-glass (SOG),[6] a reactive polysiloxane, has been used by several research groups for electronic applications.[7] The polymer contains pendant reactive ethoxy groups which undergo crosslinking on heating, leading to a glass-like, hard, amorphous film. Since most TPP derivatives containing reactive functional groups (e.g., hydroxyl or carboxyl groups) are sparingly soluble in common organic solvents, we decided to make a reactive TPP derivative that will be compatible with SOG. We postulated that the presence of several reactive ethoxysilane groups on a TPP ring will not only take part in the crosslinking process but also will improve solubility in the SOG solution.[8] Here we describe a convenient synthetic route to obtain a highly soluble TPP derivative (**1**) that is processable into optical quality thin films with SOG.

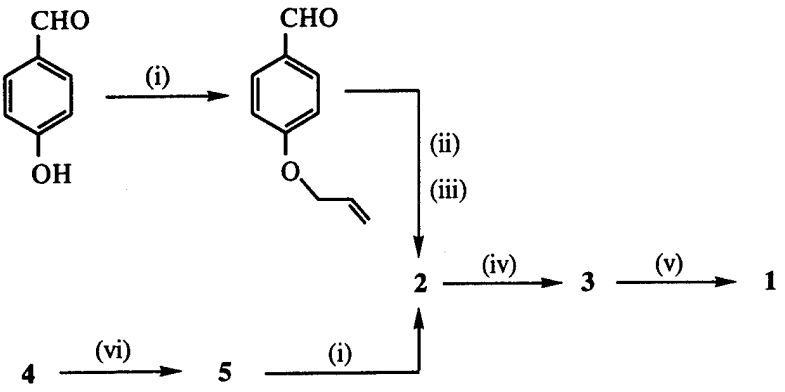


	M	R
1	Zn	$OCH_2CH_2CH_2Si(OEt)_3$
2	2H	$OCH_2CH{=}CH_2$
3	Zn	$OCH_2CH{=}CH_2$
4	2H	OMe
5	2H	OH

Results and Discussion

The TPP derivative **1** which contains four reactive triethoxysilane groups was prepared by hydrosilylation of allyloxy TPP derivative **2** using triethoxysilane in the presence of a catalytic amount of chloroplatinic acid.[9] Compound **2** was prepared by two routes (Scheme 1). In one method the cyclization of 4-allyloxybenzaldehyde[10] (synthesized by allylation of 4-hydroxybenzaldehyde with allyl bromide) and pyrrole was performed to construct a TPP ring following a standard procedure described elsewhere.[11] Due to low yield of cyclization (ca. 13%), we developed another route using a commercially available TPP derivative **4**. The two-step process, demethylation[12] and allylation, produces **2** in an overall yield of 60%. Preparation of zinc complex **3** was necessary prior to hydrosilylation since the hydrosilylation of metal-free porphyrin **2** was not successful due to the formation of an insoluble, green colored complex salt in the presence of chloroplatinic acid. The metallation was carried out by treatment of **2** with zinc acetate in DMF.[13] The assigned structures of all TPP derivatives were supported by the analytical data.

Scheme 1



(i) CH_2=$CHCH_2Br$, K_2CO_3, Acetone; (ii) Pyrrole, Butyric acid; (iii) DDQ; (iv) $Zn(OAc)_2$, DMF; (v) $HSi(OEt)_3$; H_2PtCl_6; (vi) BBr_3, $CHCl_3$, -78°C.

The TPP derivative **1** was found highly soluble in common organic halogenated solvents and in SOG solution. For instance, the solubility of **1** was measured in chloroform at 23% by weight.[14] An optical quality film containing 25% of **1** (w/w) was conveniently prepared by casting a solution of **1** in SOG, followed by curing at 200°C for 30 min under nitrogen. While the electronic spectra of all TPP derivatives showed an intense soret-band at ca. 422 nm, the Q-bands of metal-free compound **2** differed from zinc derivatives **1** and **3**. The Q-bands of **2** appeared at 519, 556, 592 and 650 nm while that of the zinc derivatives **1** and **3** showed complete disappearance of the bands at 519 and 650 nm.[15] The cured polysiloxane film containing **1** exhibits similar optical absorption characteristics to that of **1** in solution. The cured film was found highly thermostable as indicated by thermogravimetric analysis (Figure 1). High thermostability is desirable in optical limiting applications where the film experiences heat gain due to absorption of laser light. The cured polymer film was also found resistant to solvent attack as indicated by the absence of surface damage upon immersing the film in chloroform for several hours. Recently, our group has published the nonlinear optical properties of similar SOG composite films incorporating over 20% (w/w) of an axially modified phthalocyanine derivative.[16] Multilayered films without any interlayer phase separation were produced. Multilayered films of **1** are currently under investigation.

INSERT Figure 1

Experimental Part

4-allyloxybenzaldehyde. A 250 mL three-neck round bottom flask equipped with a magnetic stirring bar and a reflux condenser was charged with 4-hydroxybenzaldehyde (48.84 g, 0.40 mol), anhydrous K_2CO_3 (57 g, 0.413 mol) and acetone (200 mL), and stirred for 15 min. Allylbromide (50 g, 0.413 mol) in 25 mL acetone was added slowly over a period of 15 min and the mixture was refluxed for 24 h under nitrogen. The resulting solution was then poured into water, extracted with ether (50 mL x 3) and dried over anhydrous Na_2SO_4. The solvent was evaporated to obtain a pale yellow oil. Yield: 59.19 g (91%). The product was used in the next step without further purification. For purpose of analysis, a small amount of the compound was chromatographed over silica gel (benzene). Anal. Calcd for $C_{10}H_{10}O_2$: C, 70.06; H, 6.21. Found: C, 69.87; H, 6.06. FT-IR (neat, cm^{-1}): 3374 w, 2924 vs, 2855 vs, 2730 m, 1697 vs, 1601 vs, 1579 s, 1509 s, 1459 s, 1377 m, 1311 m, 1257 vs, 1161 s, 1111 m, 966 m, 929 m, 857 m, 832 vs, 2730 m, 1697 vs, 763 w, 722 m, 657 m, 597 m. ^{1}H-NMR ($CDCl_3$, δ): 4.61 (m, 2H, C=CH_2), 5.38 (m, 2H, OCH_2), 6.04 (m, 1H, C=CH), 6.99, 7.82 (dd, 4H, C_6H_4).

Meso-tetrakis-(4-allyloxyphenyl)porphyrin (2). Method (a): 4-Allyloxybenzaldehyde (53.53 g, 0.33 mol) in butyric acid (500 mL) was brought to reflux under nitrogen. Pyrrole (22.14 g, 0.33 mol) was then added and reflux continued for 3 h. The reaction mixture was allowed to cool to room temperature and kept overnight in a refrigerator. The solid was filtered, washed with hot water (70 mL x 3) to remove traces of butyric acid and dried at 60°C in a vacuum oven. The solid was further treated with dichlorodicyanoquinone (DDQ) (3 g, 0.013 mol) in 100 mL methanol and the solution was refluxed for 1 h. The crude product was filtered from the cooled solution and purified by soxhlet extractions with acetonitrile (fraction discarded) and dichloromethane (fraction collected and evaporated). Further purification was done by column chromatography over silica gel (dichloromethane). Yield: 9.1 g (13%). Anal. Calcd for $C_{56}H_{46}N_4O_4$: C, 80.16; H, 5.53; N, 6.68. Found: C, 79.76; H, 5.49; N, 6.48. FT-IR (KBr, cm^{-1}): 3435 br, 3082 w, 3027 w, 2927 w, 2706 w, 1605 s, 1506 vs, 1473 s, 1350 m, 1291 s, 1241 vs, 1175 vs, 1120 w, 1024 m, 966 m, 926 m, 804 vs, 740 m. ^{1}H-NMR ($CDCl_3$, δ): -2.75 (s, 2H, NH), 4.78 (m, 8H, C=CH_2), 5.57 (m, 8H, OCH_2), 6.24 (m, 4H, C=CH), 7.25, 8.09 (dd, 16H, C_6H_4), 8.85 (s, 8H, β-pyrrole). UV-Vis ($CHCl_3$, nm): 422, 519, 556, 592, 650.

Method (b): **Meso-tetrakis-(4-hydroxyphenyl)porphyrin (5). 4** (7.5 g, 0.0102 mol, Aldrich) dissolved in 40 mL of dichloromethane was added dropwise into BBr_3 (9 mL, 0.095 mol) in dry dichloromethane (15 mL) at -78°C over a period of 1.5 h. The mixture was warmed slowly to room temperature and stirred overnight. The reaction mixture was then cooled to 0°C, poured slowly into ice water (500 mL) to hydrolyze unchanged BBr_3, and neutralized with triethylamine. The crude product was filtered, washed with hot water and dried. Further purification was performed by soxhlet extractions with dichloromethane (fraction discarded) and acetone (fraction collected and evaporated). Yield: 6.06 g (88%). Anal. Calcd for $C_{44}H_{30}N_4O_4$: C, 77.86; H, 4.45; N, 8.25. Found: C, 77.46; H, 4.61; N, 7.98. FT-IR (KBr, cm^{-1}): 3457 br, 1614 vs, 1516 vs, 1481 w, 1473 w, 1433 m, 1399 m, 1359 m, 1352 vs, 1276 vs, 1183 s, 1111 m, 1075 m, 983 m, 968 m, 811vs, 730 w. ^{1}H-NMR (DMSO-d^6/$CDCl_3$, 4:1, δ): -2.88 (s, 2H, NH), 7.18, 7.96 (dd, 16, C_6H_4), 8.86 (s, 8 H, β-pyrrole), 9.88 (s, 4H, -OH). UV-Vis ($CHCl_3$, nm): 418, 518, 555, 593, 650.

Compound **2** was obtained by refluxing a mixture of compound **5** (4 g, 0.006 mol), allylbromide (11.6 g, 0.048 mol) and anhydrous K_2CO_3 (66.4 g, 0.048 mol) in acetone (200 mL) under nitrogen for 24 h. The reaction mixture was filtered, washed throughly with dichloromethane and the filtrate was evaporated in a rotavap. The residue was washed with water, extracted with ether, dried over anhydrous Na_2SO_4 and the solvent was evaporated. The solid product was purified by the same procedure described above. Yield: 3.4 g, (70%). The analytical data were found similar to the product obtained by method (a).

Meso-tetrakis-(4-allyloxyphenyl)zinc porphyrin (3). A mixture of metal free porphyrin **2** (3 g, 0.0036 mol) and $Zn(OAc)_2.2H_2O$ (2 g, 0.009 mol) was refluxed in DMF (40 mL) for 20 min. The solution was cooled, poured into cold water, and the solid was filtered, washed with water and dried. The product was purified by column chromatography over silica gel (dichloromethane). Yield: 2.9 g (91%). Anal. Calcd for $C_{56}H_{44}N_4O_4Zn$: C, 74.54; H, 4.90; N, 6.21. Found: C, 74.11; H, 4.66; N, 6.38. FT-IR (KBr, cm^{-1}): 3448 br, 2929 w, 1656 s, 1608 s, 1512 s, 1463 w, 1385 vs, 1342, 1240 vs, 1180 s, 1113 w, 1065 m, 999 vs, 933 m, 806 m, 727 w. ^{1}H-NMR ($CDCl_3$, δ): 4.83 (m, 8H, $C=CH_2$), 5.64 (m, 8H, OCH_2), 6.29 (m, 4H, C=CH), 7.29 , 8.26 (dd, 16H, C_6H_4), 8.98 (s, 8H, β-pyrrole). UV-Vis ($CHCl_3$, nm): 423, 553, 596.

Meso-tetrakis-(4-triethoxysilylpropyloxyphenyl)zinc porphyrin (1). In a 50 mL flask equipped with a reflux condenser, **3** (1.5 g, 0.0017 mol), triethoxysilane (1.1 g, 0.0068 mol) and dichloromethane (20 mL) were placed under nitrogen. Chloroplatinic acid (2.6 mg) was dissolved in 5 mL of dry THF and added dropwise. The reaction mixture was refluxed for 10 h after which triethoxysilane (0.05 g, 0.0034 mole) and chloroplatinic acid (1.3 mg) were added and reflux was continued for a further 10 h. The solvent was removed in a rotavap, the residue redissolved in chloroform, filtered over silica gel and the solvent was evaporated. The product was further purified by dissolving in ethylacetate and precipitated in hexane to obtain a purple solid. Yield: 1.73 g (67 %). Anal. Calcd for $C_{80}H_{108}N_4Si_4O_{16}Zn$: C, 61.61; H, 6.98; N, 3.61. Found: C, 61.12; H, 6.67; N, 3.46 . FT-IR (KBr, cm^{-1}): 3447 br, 2928 w, 1614 s, 1512 s, 1439 w, 1390 vs, 1342 m, 1252 vs, 1173 vs, 1107 w, 1077 vs, 992 s, 963 w, 799 m, 715 w. ^{1}H-NMR ($CDCl_3$, δ): 1.30 (m, 36H,CH_2Si), 1.39 (t, 36H, OCH_2CH_3), 3.94 (q, 24H, OCH_2CH_3), 4.23 (m, 8H, CH_2), 4.41 (m, 8H, OCH_2), 7.25 , 8.09 (dd, 16H, C_6H_4), 8.97 (s, 8 H, β- pyrrole). UV-Vis ($CHCl_3$, nm): 423 (ε = 375249 $mol^{-1}cm^{-1}$), 553 (ε = 17181), 595 (ε = 7530).

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(6) SOG solution used in this study was obtained from Allied Signal. The solution contained about 9.4 wt.% of reactive phenyl siloxane polymer (M_w = 500 - 10,000) in alcohol solution.

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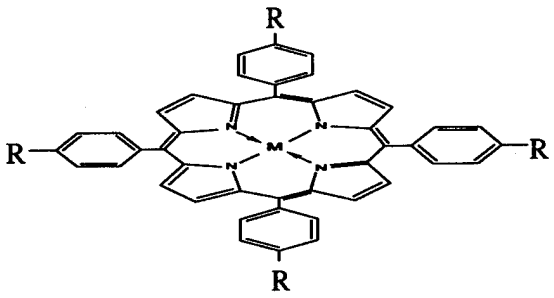
LEGEND TO THE FIGURE

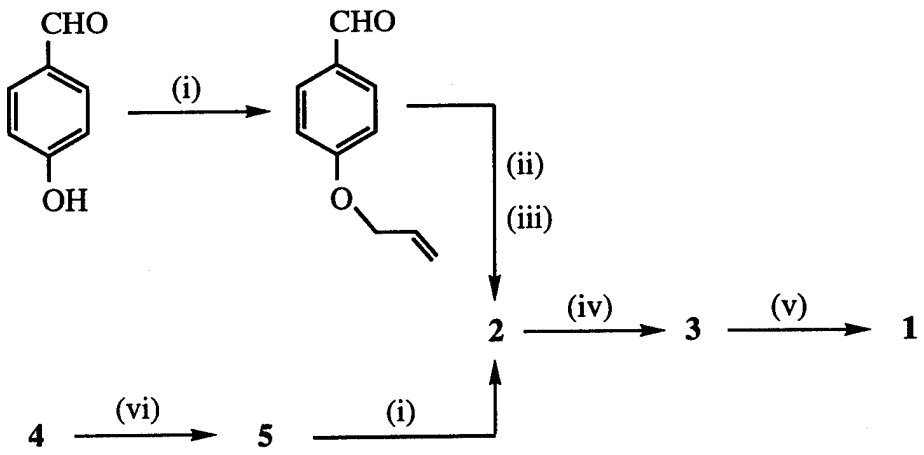
Figure 1. TGA trace of cured polymer film.



	M	R
1	Zn	$OCH_2CH_2CH_2Si(OEt)_3$
2	2H	$OCH_2CH{=}CH_2$
3	Zn	$OCH_2CH{=}CH_2$
4	2H	OMe
5	2H	OH

Sinha & Mondal

Scheme 1



(i) $CH_2=CHCH_2Br$, K_2CO_3, Acetone; (ii) Pyrrole, Butyric acid; (iii) DDQ; (iv) $Zn(OAc)_2$, DMF; (v) $HSi(OEt)_3$; H_2PtCl_6; (vi) BBr_3, $CHCl_3$, -78°C.

Sinha & Mandal

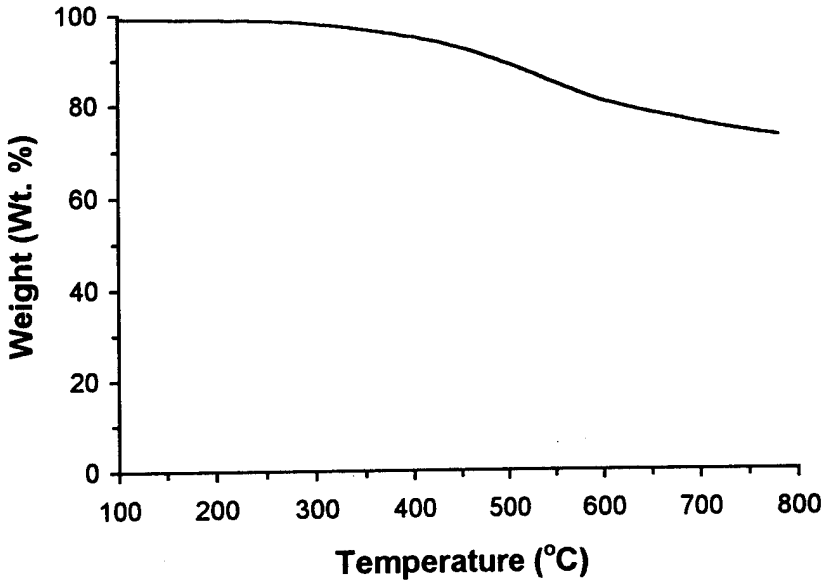

100
80
60
40
20
0
Weight (Wt. %)
100
200
300
400
500
600
700
800
Temperature (°C)

Figure 1

CROSSLINKED COPOLYMERS OF CYANOETHYLATED CELLULOSE

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Illinois 60616, U.S.A.

Abstract -- Two new cellulose copolymers have been developed by crosslinking cyanoethylated cellulose with reactive monomers or prepolymers of step-growth polymers such as polyurethane and polysiloxane. Both copolymers formed compatible transparent films at 50% loading of step-growth polymers. The films possess high impact resistance, water repellency and thermostability at 150°C for over 15 h without weight loss. The kinetic parameters of crosslinking such as conversion versus time and temperature, heat of reaction (ΔH), activation energy (ΔE), and reaction order (n) have been investigated. The morphology of the fractured surfaces of the films as revealed by SEM is also discussed.

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INTRODUCTION

Recently, there has been great interest in making new and useful products by combining (physically or chemically) cellulose or its derivatives with vinyl or step-growth polymers. The resulting products exhibit better moisture resistance and better mechanical properties over cellulose alone. As a result, a number of cellulose derivatives are now commercially available. However, a majority of the applications found to date have been described in patent literature. These include development of (i) conductive membranes by reacting cellulose with polyoxyethylene diisocyanate and subsequent impregnation with $LiClO_4$ (ii) hemodialysis membranes by surface treatment of regenerated cellulose membrane with tolylene diisocyanate (iii) formation of hydrogels by reacting the sodium salt of carboxymethyl cellulose with 1,6-hexamethylene diisocyanate (iv) heat and sound insulating coatings by heating hydroxyethyl cellulose with acrylic resins and polyisocyanates (v) solvent, abrasion, heat and stain resistant coatings by reacting cellulose acetate butyrate with isophorone diisocyanate (vi) miscible polymer blends of cellulose esters (namely, cellulose acetate butyrate and cellulose acetate propionate) with condensation polyesters such as poly(hydroxybutyrate-co-valerate) and poly(tetramethylene glutarate) [1-6] (vii) grafted copolymers by chemical modification of cellulose with common vinyl monomers [7] and (viii) biological composites by forming semi-interpenetrating polymer networks of cellulose esters with crosslinked polyacrylamide [8,9]. In a recent paper, we reported a series of interpenetrating polymer networks of a new cellulose derivative, allyl cellulose cinnamate, with crosslinked vinyl polymers [10].

Cyanoethylated cellulose (CEC), a commercially available cellulose derivative, is known for its stability towards air-oxidation, water repellency and solution processability [11-13]. CEC has been used to develop a number of useful products such as: (i) crosslinked products by reacting with formaldehyde [11] (ii) electrophotographic photoreceptors for high quality images [14] and (iii) new dielectric materials by treating CEC with propylene oxide [15]. However, no systematic report has been published on crosslinked copolymers of CEC with reactive polyurethanes or polysiloxanes. In this paper we describe their synthesis, thermal properties and morphological characteristics.

EXPERIMENTAL

Materials

Cyanoethylated cellulose (CEC), isophorone diisocyanate (IDI), 2,4-tolylene diisocyanate (TDI) were purchased from Aldrich and used as received. Triethylene glycol (TEG) obtained from Eastman Kodak, was freshly distilled under reduced pressure. Acetonitrile (Aldrich) was dried over molecular sieves and distilled under nitrogen prior use. Spin-on-glass (SOG) solution which contains about 9% by weight reactive polysiloxane in an alcohol mixture was obtained from Allied Signal.

Instrumentation

Thermal analysis was performed on a Perkin-Elmer Thermal analyzer Series 7 instrument. Elemental analysis was carried out on a Perkin-Elmer 2400 elemental analyzer. SEM photographs were obtained with a digital scanning microscope (Jeol T-300).

Preparation of Crosslinked Copolymer Films

A stock solution of cyanoethylated cellulose made by stirring overnight 30 g of CEC in 600 ml of acetonitrile was divided into three equal volumes. Each part was thoroughly mixed with the components shown in Table 1 in an ultrasonicator for 10 min and then solution cast into films. The films used for thermal analysis were cured at 125°C for 1 h. For DSC kinetics studies, uncured films were dried at room temperature overnight under mild vacuum and peeled off from the glass slide into a hermetically sealed pan to ensure no significant mass loss during reaction.

Table 1. Composition of crosslinked copolymers

Film	CEC (g)	IDI (g)	TDI (g)	TEG (g)	SOG (g)	CEC Content (%)
I	10.0	7.6	---	2.4	---	50
II	10.0	---	7.4	2.6	---	50
III	10.0	---	---	---	111*	50

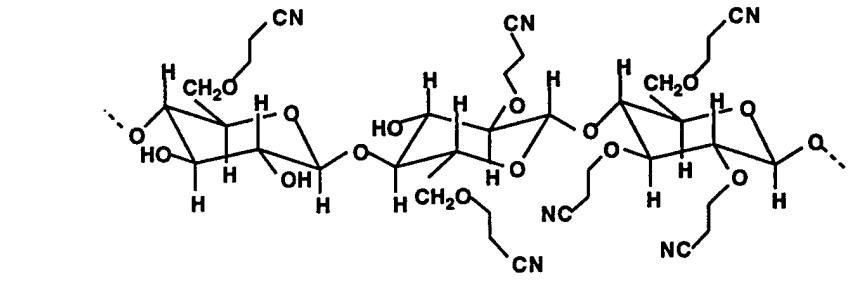
* contains about 10 g of reactive polysiloxane.

RESULTS AND DISCUSSION

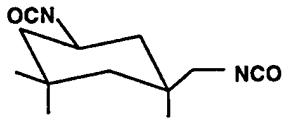
In this study two reactive polymer matrices in which one contains a polyurethane backbone (organic matrix) and the other containing a polysiloxane backbone (inorganic matrix) were used to react with CEC to produce potentially useful products. Polyurethane was chosen because of the high reactivity of the isocyanate group with hydroxyl groups and the insignificant formation of reaction by-products, while a commercially available spin-on-glass (SOG), a reactive

polysiloxane, was chosen to improve the thermal stability of the resulting matrix. In both cases a crosslinked copolymer of CEC was formed due to the presence of a large number of unsubstituted hydroxyl groups in CEC. The degree of substitution of CEC was determined at 2.7 by comparing the nitrogen content in the sample.

The polyurethane matrix was generated by reacting mole excess of an appropriate diisocyanate derivative with triethylene glycol (TEG). Two well known diisocyanate derivatives, isophorone diisocyanate (IDI) and tolylene diisocyanate (TDI), were compared to appraise which copolymer exhibits better compatibility and thermal properties. The structures of each component are shown in Fig. 1. Intimate mixing of CEC with the reactive components was performed by mixing the component(s) into a solution of CEC in acetonitrile (about 5% by weight) followed by solution casting into thin films.

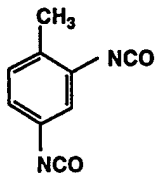


CEC



IDI

TEG



TDI

$$\left[SiO_a(C_6H_5)_b(OC_2H_5)_c(OH)_d\right]_n$$

a : ≥ 1; b, c, d : ≤ 0.5
n = 5 -100

SOG

Fig. 1. Components of crosslinked CEC copolymer films.

Initially, an effort was made to crosslink CEC with IDI alone. Although crosslinking was very fast (as evident from DSC conversion kinetics ; curve a in Fig. 2) the resulting film became brittle after curing at 125°C for 1 h. This is probably due to high rigidity of the matrix after crosslinking. In view of this, we used TEG as a co-monomer with the diisocyanate derivative. This allowed the diisocyanate derivative to undergo two parallel reactions, one with CEC hydroxyl groups and the other with TEG hydroxyl groups. DSC kinetics study of 2:1 mole proportion of IDI and TEG indicates that IDI reacts much slower with TEG (curve b in Fig. 2) than with CEC. Further studies on the nature of crosslinks were made by two-stage reactions. First, an isocyanate group terminated polyurethane was made by heating a mixture of IDI and TEG (2:1 mole proportion) at 125°C for 1 h and then this functionalized polyurethane which showed a T_g of 176°C was processed with CEC followed by curing at 125°C for 1 h. However, the crosslinking reactions were rapid in the presence CEC as observed in the curing curve of the CEC, IDI and TEG mixture (curve c), and CEC and diisocyanate terminated polyurethane (curve d). The curing times of films-II and III that involve TDI and SOG respectively were found slightly longer than that of film-I which contains IDI. Although all reactions require curing times ranging from 1 to 30 min (as evident from DSC kinetics curves) an optimum cure time of 1 h was chosen to ensure complete curing. DSC studies were also performed to detect the segmental motions of the crosslinked polyurethane or polysiloxane chains. No CEC crosslinked copolymers exhibited a T_g.

Insert Fig. 2

The activation energy (ΔE) of curing, heat of reaction (ΔH) and order of reaction (n) of the above reactions were also determined and are presented in Table 2. The parameters of the reaction involving IDI (film-I) were found much higher compared to the reaction involving TDI

(film-II). However, the highest value of the order of reaction, n, was found in the case of the reaction involving SOG (film-III).

Insert Table 2

The thermal stability of the films was measured by thermogravimetric analysis (TGA). The product decomposition temperature (PDT) values obtained from the TGA thermograms indicate that film-III has distinct stability (ca. 50°C) over films-II and III (Fig. 3). We also ran TGA thermograms of CEC (film-IV) and polyurethane (film-V) independently in order to investigate the decomposition kinetics of CEC crosslinked copolymers. TGA thermograms indicate that the decomposition of polyurethane film occurs at 295°C compared to CEC at 324°C (Table 2). The results of isothermal heating at 125°C of all CEC films indicate resistance to thermal breakdown for up to 15 h. However, CEC films containing polyurethane segments (films-I and II) showed over 20% weight loss at 200°C. This is primarily due to the breakdown of polyurethane linkages since it (film-V) shows more weight loss than CEC (film-IV) under similar conditions. On the other hand, film-III which contains polysiloxane crosslinks showed a weight loss of only 7% after heating at 200°C for 15 h (Table 2).

Insert Fig. 3.

All CEC copolymer films appeared transparent and homogeneous, and exhibit strong adhesion with glass substrates. SEM micrographs of fracture surfaces of the films indicate that the morphology of film-I (polyurethane based) is very different from film-III (polysiloxane based). The former produced uniform microcrystallite morphology under mechanical stress

(Fig. 4a), typical for cellulose grafted copolymers [16], while the later showed single phase homogeneous amorphous morphology (Fig. 4b). Higher magnification of the later revealed layered fracture surfaces, typical for glassy materials [17].

Insert Fig. 4.

Acknowledgements - The authors wish to thank Bob Zechman for obtaining SEM micrographs. This work is supported by the U. S. Army (Natick, Massachusetts) under contract # DAAK60-93-C-0086. Acknowledgment is also made to AFOSR (# F49620-93-1-0583) for providing funds for instruments used in this study.

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LEGEND TO THE FIGURES

Fig. 1. Components of crosslinked CEC copolymer films.

Fig. 2. Curing of characteristics of mixtures: (a) IDI and CEC; (b) IDI and TEG; (c) IDI, TEG and CEC; (d) isocyanate groups terminated polyurethane and CEC.

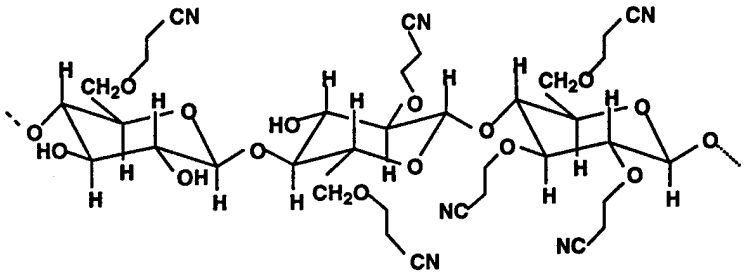
Fig. 3. TGA thermograms of CEC copolymer films.

Fig. 4. SEM micrographs of (a) film-I; (b) film-III and (c) same as b, but with a higher magnification.

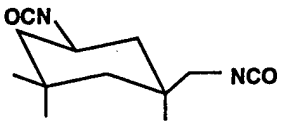
LEGEND TO THE TABLES

Table 1. Composition of crosslinked copolymers

Table 2. Kinetics of curing and thermal properties[a] of CEC copolymer films

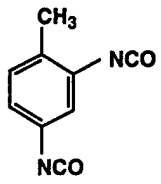


CEC



IDI

TEG



TDI

$$\left[SiO_a(C_6H_5)_b(OC_2H_5)_c(OH)_d\right]_n$$

a : ≥ 1; b, c, d : ≤ 0.5
n = 5 -100

SOG

Fig. 1. Kamath et al.

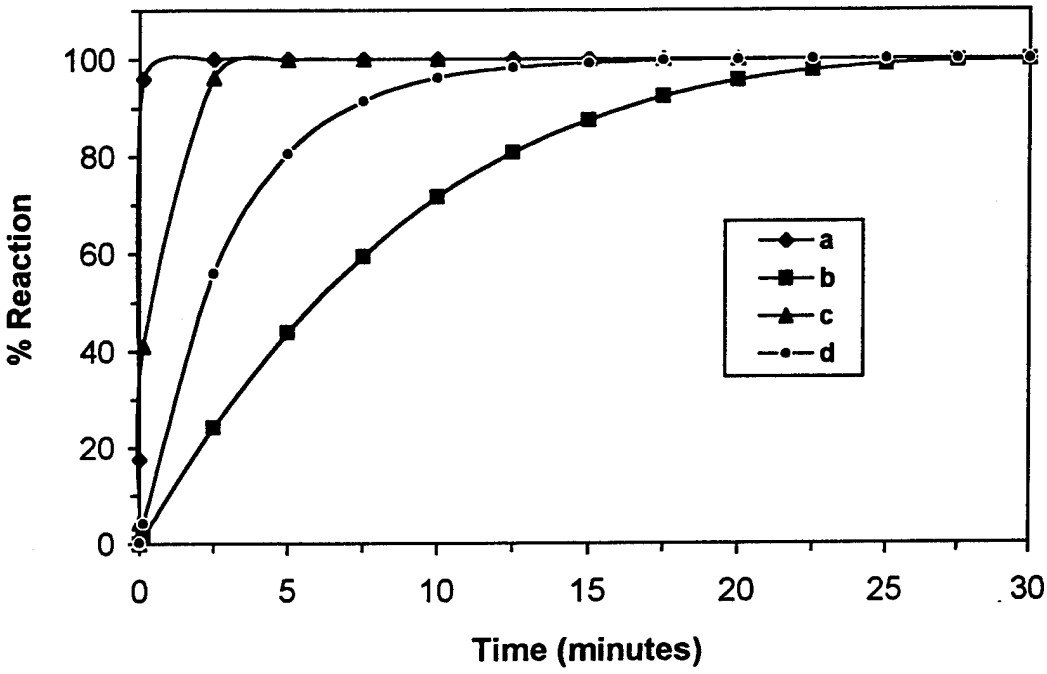


Fig. 2. Kawaoka et al.

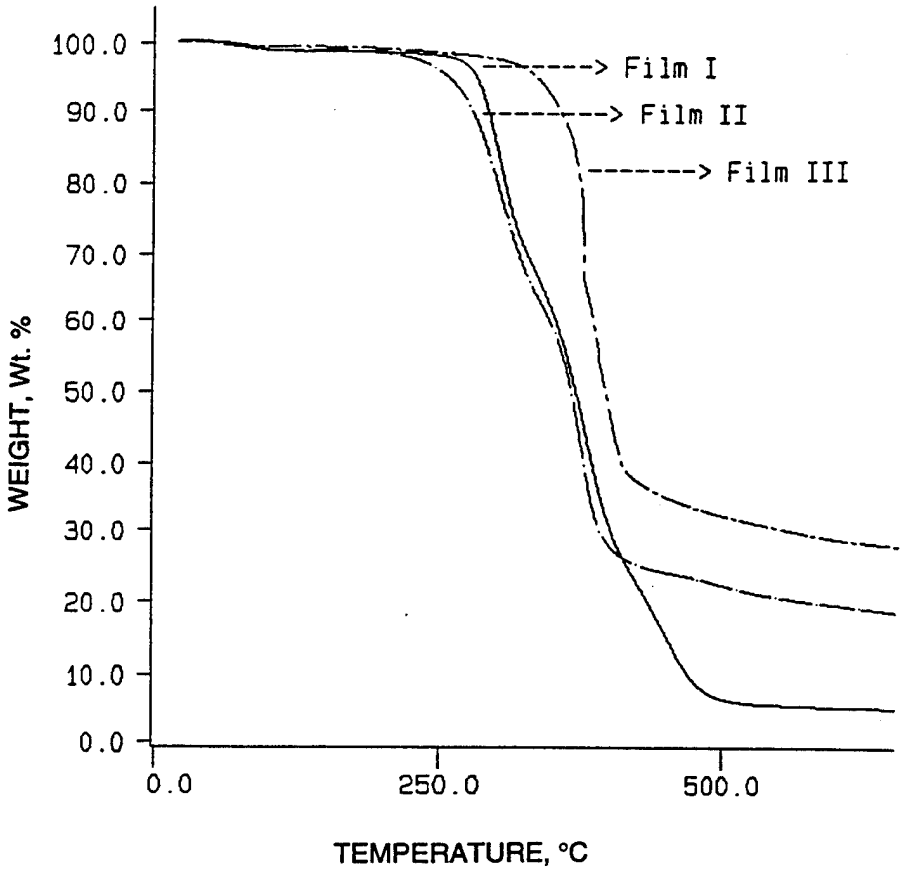


Fig. 3 Kamath et al.

Table 1. Composition of crosslinked copolymers

Film	CEC (g)	IDI (g)	TDI (g)	TEG (g)	SOG (g)	CEC Content (%)
I	10.0	7.6	---	2.4	---	50
II	10.0	---	7.4	2.6	---	50
III	10.0	---	---	---	111*	50

* contains about 10 g of reactive polysiloxane.

Table 1 Kimura et al

Table 2. Kinetics of curing and thermal properties[a] of CEC copolymer films

Film	CEC content %	DSC[c]			TGA[b]		
		ΔE[c] KJ/mol	ΔH J/g	n[c]	PDT °C	Isothermal Heating[d] 150°C	200°C
I	50	106.0	58.0	1.31	297	0.0	23.1
II	50	44.9	18.7	0.93	283	0.0	26.8
III	50	81.9	13.8	1.47	371	0.0	7.0
IV	100	---	---	---	324	0.0	15.5
V[e]	0	41.9	129	0.74	295	10.0	20.2

[a] All experiments were performed under nitrogen. [b] Heating rate, 20°C/min. [c] Anticipated error is within ±6%.

[d] Weight loss in % after 15 h of heating. [e] Film obtained from 2:1 IDI and TEG mixture.

INTERPENETRATING POLYMER NETWORKS OF PHOTOCROSSLINKABLE CELLULOSE DERIVATIVES

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SYNOPSIS

A series of interpenetrating polymer networks has been prepared from two cellulose derivatives, one of which contains cinnamate groups and the other containing randomly substituted cinnamate and allyl groups. The latter derivative forms a crosslinked network in less than five minutes on exposure to ultraviolet radiation and can be used to make amorphous interpenetrating polymer networks containing 50% by weight loading level of crosslinked vinyl polymers. The syntheses of both derivatives and the thermal properties and film morphologies of their interpenetrating polymer networks are discussed.

KEY WORDS: Interpenetrating polymer network, photocrosslinkable cellulose derivative, cellulose cinnamate, allyl cellulose cinnamate.

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* To whom all correspondence should be addressed.

INTRODUCTION

In past decades, interpenetrating polymer networks (IPNs) of "organic-organic" polymers such as poly(n-butyl acrylate) with polystyrene[1,2], styrene-butadiene with polystyrene[3,4] and polyurethane with epoxy or unsaturated polyesters[5], and "organic-inorganic" polymers such as polyurethane with polysiloxane[6] and polystyrene with polyphosphazene[7,8] have been extensively studied. In most cases, IPNs provide better physicochemical properties over the individual polymers used to make the IPNs. In spite of their potential for numerous applications, all IPN systems investigated thus far have been limited to synthetic polymers. Although extensive studies on grafting of cellulose[9] have been performed, there are surprisingly no reports on IPNs made from cellulose (especially surprising in light of its superior mechanical properties and ready availability from natural resources). Nevertheless, a number of synthetic hydrogels of cellulose esters constituting semi-interpenetrating polymer networks with polyacrylamide have recently been developed to mimic some aspects of the behavior of biological composites.[10,11] Cellulose IPNs have a distinct potential for yielding light weight and high strength materials. The mechanical properties of such systems are expected to be far superior to those obtained by grafting, since the former involves two intermeshed three-dimensional networks.

Years ago, due to insufficient knowledge of proper solvents to dissolve cellulose, cellulose derivatives were synthesized under heterogeneous conditions that produced non-uniform substitutions. Among these, cellulose derivatives containing photocrosslinkable group such as cinnamate were made.[12] Recently, McCormick et al.[13] discovered a solvent system, N,N-dimethylacetamide containing 9% LiCl , for cellulose dissolution. Consequently, a number of cellulose derivatives such as ethers, esters and carbamates have been prepared under homogeneous reaction conditions.[14] Degrees of substitution ranging from 2.5 to 3 have been

achieved by controlling reaction conditions. However, regioselective synthesis of cellulose derivatives containing cinnamate groups has not been attempted thus far. In this paper we present the properties of IPNs derived from photocrosslinkable cellulose derivatives and common vinyl monomers.

EXPERIMENTAL

Instrumentation

FT-IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrophotometer. Ultraviolet spectra were taken on a Perkin-Elmer Lambda-19 spectrophotometer. The thermogravimetric analyses were performed on a Perkin-Elmer Thermal analyzer Series 7 instrument. Elemental analysis was carried out on a Perkin-Elmer 2400 elemental analyzer. SEM photographs were obtained with a digital scanning microscope (Jeol T-300).

Materials

Cellulose was purchased from Aldrich and used directly after pre-treatment by a solvent-exchange technique.[13] Allyl bromide, cinnamoyl chloride, and lithium chloride were obtained from Aldrich and used without further purification. N,N-dimethylacetamide (DMAc), dioxane, triethylamine, pyridine, styrene, 1,4-divinylbenzene (DVB), methylmethacrylate (MMA), ethylene glycol dimethacrylate (EGDMA) and vinyl acetate (VA) were obtained from Aldrich and distilled under nitrogen before use. AIBN was purchased from Eastman Kodak and used as received.

Cellulose dissolution

Homogeneous solutions of cellulose were obtained following a procedure described by McCormick et al.[13] In a typical procedure, lithium chloride (18 g) was dissolved in 200 ml of DMAc at 100°C. The solvent was then allowed to cool to room temperature. 6.6 g of pre-treated cellulose (which contains about 4 g of dry cellulose) was then added under a nitrogen atmosphere. The mixture was stirred for approximately 2 h at room temperature to get a clear solution.

Synthesis of Cellulose Cinnamate (1)

To 100 ml of the above cellulose solution 11.1 g (0.11 mol) triethylamine in 25 ml DMAc was added. A solution of 18.3 g (0.11 mol) cinnamoyl chloride in 25 ml DMAc was then added dropwise over a period of 1 h. After stirring overnight at room temperature the product was precipitated by pouring the reaction mixture into water, washed with water and methanol and dried at 50°C under vacuum to constant weight (~6.3 g). Analysis: C, 63.95%; H, 4.73%; (degree of substitution = 2.9). IR (KBr): 1578 (aromatic C-C stretching), 1633 (C=C stretching) and 1702 (carbonyl stretching) cm^{-1}. Ultraviolet (λ_{max}): 284 nm (dioxane).

Synthesis of Allyl Cellulose Cinnamate (2)

To 100 ml of the cellulose solution 8.1 g (0.08 mol) of triethylamine in 25 ml DMAc was added. A solution of allyl bromide (9.7 g, 0.08 mol) in 25 ml DMAc was added dropwise under nitrogen over a period of 1 h. The stirring was continued overnight at room temperature, after which a solution of cinnamoyl chloride (13.3 g, 0.08 mol) and triethylamine (8.1 g, 0.08 mol) in 25 ml of DMAc was added slowly at 0°C. After stirring overnight at room temperature the product was precipitated by pouring the reaction mixture into water, washed with water and

methanol and dried at 50°C under vacuum to constant weight (~4.1 g). Analysis: C, 62.33%; H, 5.69%. IR (KBr): 1578 (aromatic C-C stretching), 1635 (C=C stretching) and 1715 (carbonyl stretching) cm^{-1}. Ultraviolet (λ_{max}) = 277 nm (dioxane); 287 nm (film).

Preparation of IPNs

IPNs were made by heating a mixture of one of the above photocrosslinkable cellulose derivatives, a monomer, a crosslinker and AIBN followed by exposure to ultraviolet light. The composition of each IPN is shown in Table I. In a typical procedure, monomer (1 g), crosslinker (0.3 g) and AIBN (0.03 g) were heated at 80°C for 20 min to obtain a viscous solution. The cellulose derivative (1.06 g) in 10 ml dioxane was added and the mixture sonicated for 10 min prior to film casting. The film was allowed to dry at room temperature overnight and then baked at 80°C for 10 h. The film was then photocrosslinked by irradiation at 254 nm for 15 min to obtain IPNs .

Table I Composition of IPNs

IPN	Cellulose Derivative		Monomer			Crosslinker		AIBN
	1	2	Styrene	MMA	VA	DVB	EGDMA	
I	X		X			X		X
II		X	X			X		X
III	X			X			X	X
IV		X		X			X	X
V	X				X		X	X
VI		X			X		X	X

RESULTS AND DISCUSSION

In this study two photocrosslinkable cellulose derivatives, **1** and **2**, were synthesized under homogeneous conditions (Figure 1). One derivative, cellulose cinnamate (**1**), which was previously synthesized in a heterogeneous condition[12], was prepared by reacting a homogeneous solution of cellulose with cinnamoyl chloride in the presence of a base such as triethylamine. The other derivative, allyl cellulose cinnamate (**2**), was made by reacting cellulose with allyl bromide followed by reaction with cinnamoyl chloride. Both products were isolated as pale yellow flakes. Elemental analysis was used for the determination of the degree of substitution and indicated a high degree of substitution, e.g., the value for **1** was calculated at 2.9. Although both derivatives were found soluble only in dioxane, derivative **2** showed greater solubility over derivative **1**.

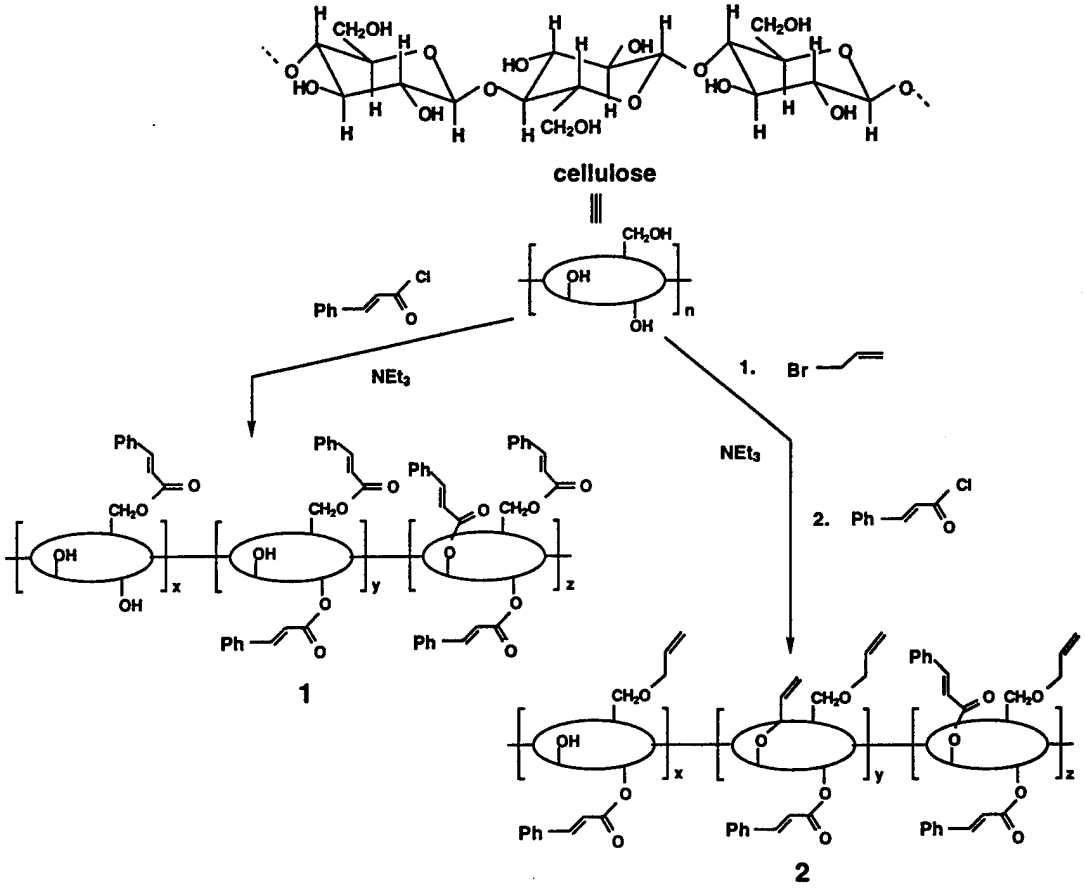

Figure 1 Synthesis of photocrosslinkable cellulose derivatives.

Thin films of the photocrosslinkable derivatives were made by either solution casting or by spin casting from solutions containing ~2% by weight of the derivative. Derivative **1** formed opaque crystalline or somewhat phase-segregated films after evaporation of the solvent. Similar behavior was reported by another group[15] which subsequently made an amorphous transparent film by co-derivatizing with trimethylsilyl chloride. In light of this, we partially derivatized cellulose with allyl groups prior to functionalization with cinnamate groups. Indeed, the co-derivatized product **2** formed transparent films which can be removed from a glass surface as tough, free-standing films.

Although the two derivatives possess similar chromophores they differ slightly in their infra-red and ultraviolet spectra. For instance, the C=O stretching in derivative **1** was observed at 1702 cm^{-1} and that of derivative **2** at 1715 cm^{-1}. Other absorption frequencies due to C=C stretching (1633 cm^{-1}) and the cellulose residue were found to be similar for both derivatives.[16] The absorption maximum (λ_{max}) due to the cinnamate groups of **1** and **2** appeared at 284 nm and 277 nm respectively in dioxane solution. A red-shift of 10 nm was observed when a thin film of **2** was measured.

Photoreactivity characteristics were studied with a film obtained from derivative **2**, since derivative **1** produced phase-segregated films. An ultraviolet lamp which emitted maximum intensity of light at 254 nm was used to irradiate the sample. 2+2 Photodimerization between two cinnamate double bonds was very rapid as indicated by a sharp decrease in absorption at 287 nm in less than 5 minutes due to depletion of double bonds leading to formation of cyclobutane rings (Figure 2).[17]

INSERT Figure 2

Both derivatives **1** and **2** were used to produce IPN films using vinyl monomers. Three common vinyl monomers: styrene, MMA and VA, and two well-known crosslinkers, DVB and EGDMA, were used to generate network polymers. Table I describes the combination of monomer and crosslinker used with the cellulose derivative. AIBN was used as an initiator to polymerize all vinyl monomers. Initially a semi-IPN film was made by polymerizing an appropriate monomer and crosslinker with a cellulose derivative. The film was converted into an IPN by irradiating at 254 nm for 15 min. The resulting films contained an equal composition (50:50) of cellulose derivative and crosslinked vinyl polymer. Derivative **2** forms compatible films with all three crosslinked vinyl polymers in both semi-IPN and IPN stages as indicated by their visual transparency. Derivative **1** , on the other hand, formed translucent to phase segregated films with the vinyl crosslinked polymers, quite similar to the film obtained from derivative **1** alone.

Thermal properties of both photocrosslinkable derivatives and their IPN films have been studied by thermogravimetric analysis. Derivative **2** showed much greater thermostability compared to derivative **1** (Figure 3a). The high thermostability of derivative **2** is probably due to facile thermal crosslinking and/or polymerization in contrast to derivative **1** which is more hindered due to the presence of a large number of bulky cinnamate groups. Thermal behavior of the IPN films is shown in Figure 3b. Higher thermal stability of IPN films prepared from derivative **2** was also observed.

INSERT Figure 3

SEM micrographs of fractured surfaces of all films derived from derivative **2** are shown in Figure 4. The IPN with polystyrene showed homogeneous single phase morphology (Figure 4a). This is more clearly revealed at higher magnification (shown in Figure 4b). The fractured

surfaces of IPNs obtained from polymethylmethacrylate and polyvinylacetate showed no significant crystalline domains but irregular stress propagation across the films.

INSERT Figure 4

CONCLUSION

A new processable cellulose derivative containing allyl and cinnamate groups has been synthesized. This derivative forms compatible IPNs with common crosslinked vinyl polymers at equal masses of each component. The compatibility and thermal stabilities of these IPNs are better in comparison to similar IPNs of cellulose cinnamate. Further investigation of the mechanical properties of the IPNs as well as of the composites fabricated with glass fiber are under progress.

The authors wish to thank Dr. Arun K. Sinha for technical assistance and Bob Zechman for obtaining SEM micrographs. This work is supported by the U. S. Army (Natick, Massachusetts) under contract # DAAK60-93-C-0086. Acknowledgment is also made to AFOSR (# F49620-93-1-0583) for providing funds for instruments used in this study.

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Legend to Figures

Figure 1 Synthesis of photocrosslinkable cellulose derivatives.

Figure 2 Change in absorption maximum due to cinnamate chromophores under exposure to ultraviolet light (wavelength of irradiation 254 nm; irradiation time (min): 1, 2, 3, 5, 7, 11).

Figure 3 TGA thermograms of (a) photocrosslinkable cellulose derivatives and (b) IPN films derived from photocrosslinkable cellulose derivatives (heating rate of 20° C/min under nitrogen).

Figure 4 SEM micrographs of (a) film-II; (b) same as a, but higher magnification; (c) film-IV and (d) film VI.

Legend to Table

Table I Composition of IPNs

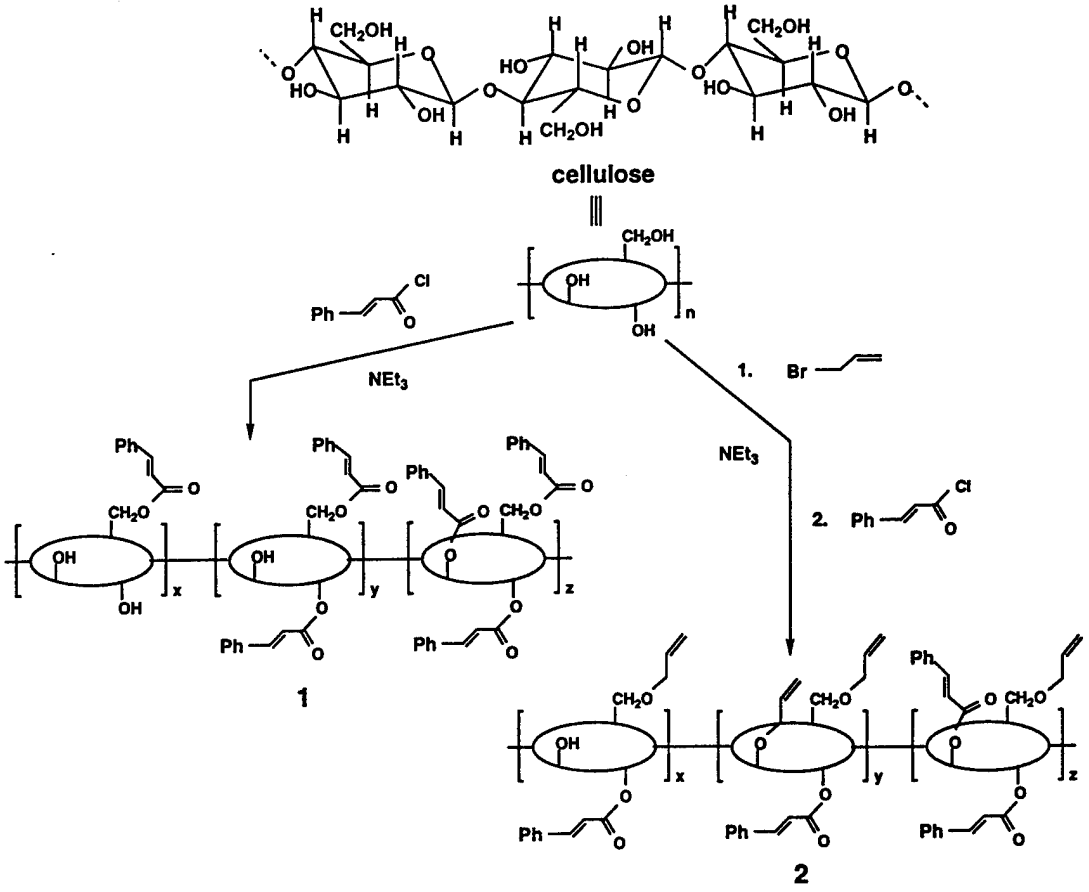
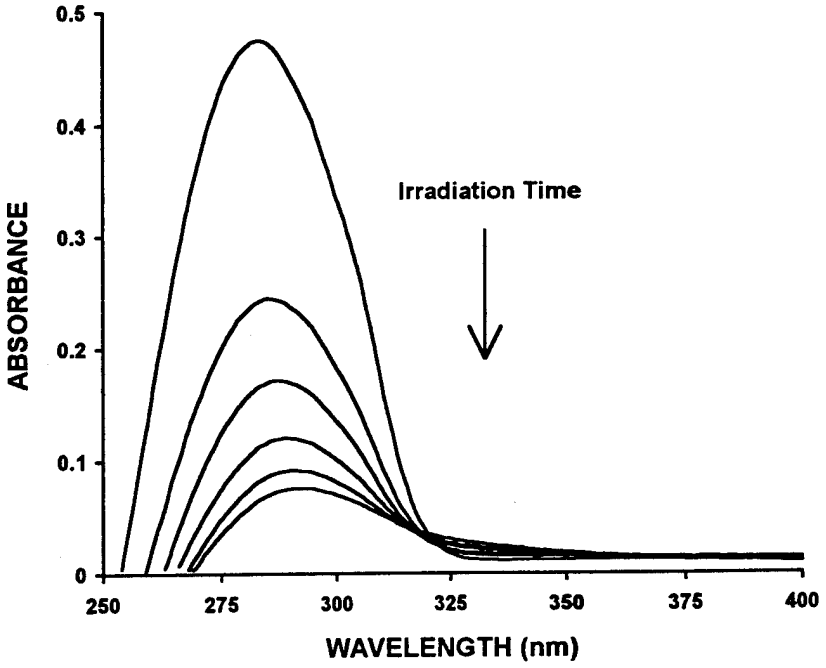


Fig. 1 Kamath et al.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0.4
0.3
0.2
0.1
0
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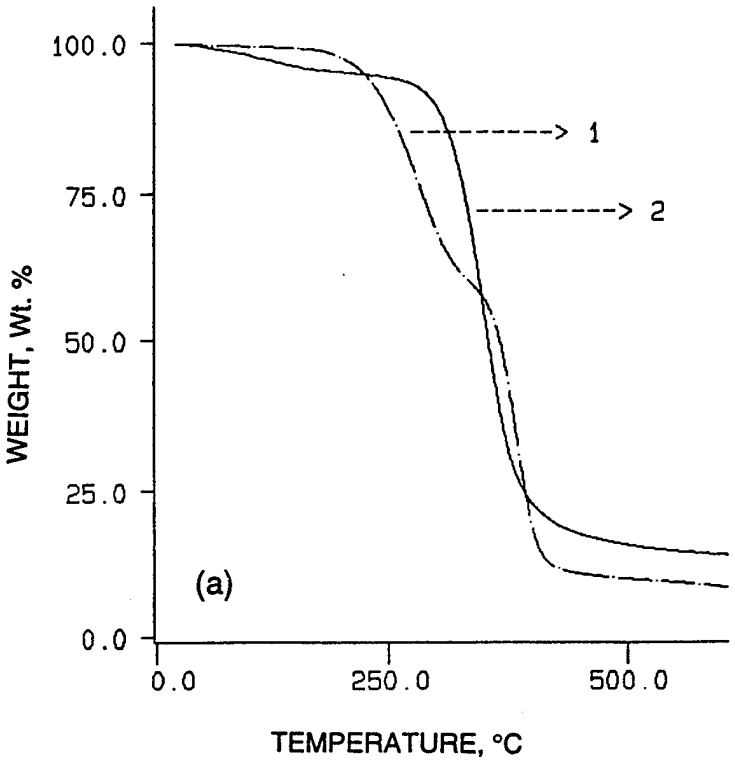
275
300
325
350
375
400
WAVELENGTH (nm)



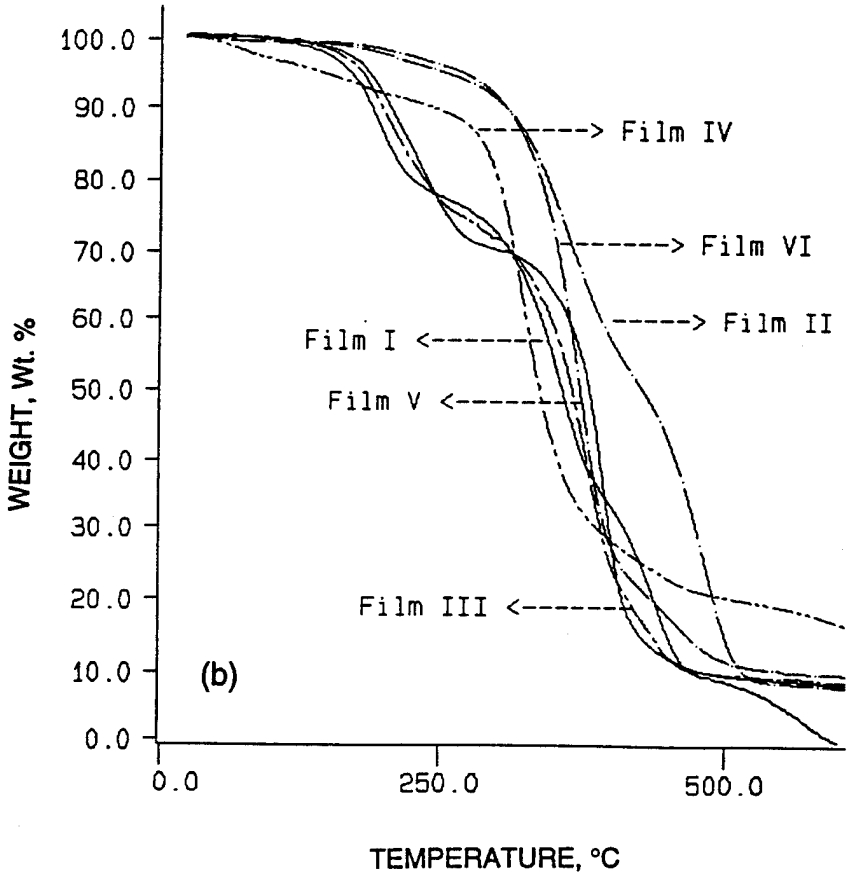


Fig. 3. Kamath et al.

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III	X			X			X	X
IV		X		X			X	X
V	X				X		X	X
VI		X			X		X	X

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