Silicon Phthalocyanine/Methyl Methacrylate Copolymer Slab Directional Couplers for All-Optical Switching

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SYNOPSIS

Slab waveguide directional couplers were fabricated from the third-order nonlinear optical polymer silicon phthalocyanine/methyl methacrylate 2/98 copolymer as the active material and poly(methyl methacrylate) as the cladding layer. The monomethacrylate copolymer was synthesized, device fabrication conditions determined, and five-layer slab directional couplers fabricated. Completed couplers demonstrated waveguide loss on the order of 5 dB/cm and coupling lengths of 0.5 mm at 1.29 μm. These vertically coupled devices may be useful for all-optical switching. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Side-chain copolymers are a class of materials that provide the opportunity for incorporating specific functionalities into polymers, such as nonlinear optical properties. This is achieved by attaching functional groups to the main copolymer chain in a pendant fashion. This strategy has been successfully applied to making polymers for second-order nonlinear optics, and recent interest has developed on their applicability to third-order nonlinear optics, via which light can be switched with light (no electronics involved). There have been a number of reports in the literature on the third-order nonlinear optical activity of porphyrin derivatives, namely, tetrabenzporphyrins, phthalocyanines, and naphthalocyanines, that show relatively high third-order nonlinear optical responses. These molecules are planar π-conjugated systems that have sharp absorption bands in the visible and near-infrared and exhibit excellent thermal and chemical stabilities. Most studies have examined these dyes in solution,[1-3] sublimed thin films,[4,5] or in Langmuir–Blodgett thin films.[6,7] Some silicon phthalocyanines have been made into siloxane copolymers that show high third-order susceptibilities.[8,9] More recently, side-chain copolymers containing silicon phthalo-

cyanine have been synthesized and have demonstrated large resonant nonlinearities.[10] Furthermore, these materials are processible enough to be easily spin-coated, by which means multilayer nonlinear mirrors were constructed.[11] Here, we present the chemical synthesis of silicon phthalocyanine side-chain methyl methacrylate (SiPc/MMA) copolymers and a device design that is aimed at producing an all-optical switch.

DEVICE DESIGN

Figure 1 shows the proposed structure that consists of five layers: (1) lower cladding layer, (2) lower waveguide layer, (3) separation layer, (4) upper waveguide layer, and (5) upper cladding layer. Coupling will occur between the two waveguide layers once light is launched into one of the layers. If the waveguides are identical so that their propagation constants match ($\Delta\beta = 0$), complete coupling of energy from one waveguide to the other will occur after a distance called the coupling length. If the waveguiding material has an index of refraction that is a function of light intensity, this coupling length can be changed by changing the incident light intensity, thereby changing how much light emerges from the two waveguides at the end of the device. In the present design, this switching could be achieved in at least three ways: In one case, the incident light beam would act on itself, and as its own
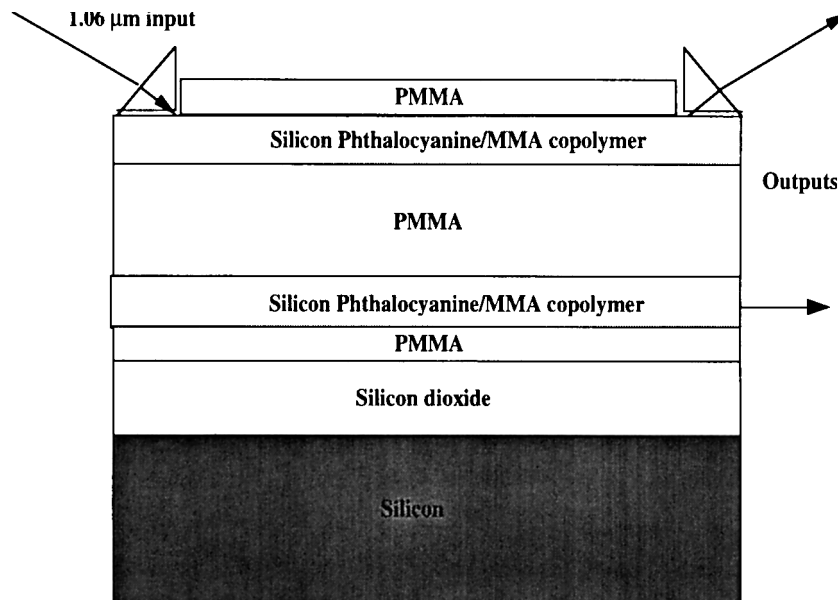
Figure 1   Slab directional coupler design using SiPc/MMA copolymer; active layer, 1.3 μm; center PMMA, 2.5 μm; top and bottom PMMA layer, 2.0 μm.

intensity increased or decreased, the coupling between the two waveguides would change. Another approach would be to have a low-intensity probe beam propagating through the waveguide structure whose coupling ratio would be controlled by the imposition of an intense pumping beam. This pump beam could be at nearly the same wavelength as the probe and copropagating with the probe, being wavelength-filtered out of the network at the end of the device. On the other hand, the pump could be imposed from above the waveguide and could change the coupling between the waveguides if its wavelength were such that the majority of the pump light was absorbed in the upper waveguide. Since the proposed device is all-optical, isolation of the coupling region through the use of waveguide bends is not critical. However, for the electrooptic case, this problem could be solved if, e.g., a photobleachable material were used for the center layer, in which case a graded index structure could be formed that would act like a bend, since it would allow the adjustment of the waveguide coupling. Furthermore, a structure such as that in Figure 1 could be readily turned into a channel waveguide device by direct photolithography or by photobleaching.

A directional coupler's characteristics depend critically on the wavelength of light used, the refractive indices of the materials, and the dimensions of the waveguides and their separation. In the present case, the layer thicknesses were determined by considering three basic principles:

(a) According to coupled mode theory,[12] the single mode cutoff condition (for TE modes)

$$\Delta n = \frac{\lambda_0^2}{4t_g^2(n_1 + n_0)} \tag{1}$$

depends on the active layer thickness t_g; λ_0, the wavelength of light; and the refractive indices of the active layer n_1 and the cladding layer n_0; $\Delta_n = n_1 - n_0$. A Metricon prism coupler was used to measure the refractive indices of the active layer SiPc/MMA 2/98 (mol/mol) (1.520 at 1.289 μm) and that of the cladding layer poly(methyl methacrylate) (1.483 at 1.289 μm). The actual operating wavelength for the directional coupler in a single-beam configuration was then designed for 1.064 μm radiation to avoid the presence of two-photon absorption, which has been measured to be very large in the SiPc/MMA copolymer at 1.3 μm.[13] The above information suggests that the thickness of SiPc should be approximately 1.3 μm to be below the multimode cutoff and, therefore, single mode for 1.064 μm light. This calculation ignores the effect of refractive index dispersion from 1.3 to 1.064 μm, which will be small for the PMMA layer, but may be appreciable for the SiPc layer.

(b) The cladding (passive) layers should be thick enough to prevent light from reaching the substrate. For TE light, the attenuation of the exponentially decaying wave in the cladding layer is given by

$$I = I_0 e^{-2px} \qquad (2)$$

where

$$p = (N_{eff}^2 - n_{PMMA}^2)^{1/2} \left(\frac{2\pi}{\lambda_0} \right) \qquad (3)$$

N_{eff} is the effective index of the waveguide, and x, the cladding layer thickness. Application of (2) and (3) suggests that x should be much larger than $2/2p(x \gg 2/2p)$ and for the present materials determines an upper and lower cladding PMMA layer thickness of approximately 2 μm.

(c) The coupling length is related to the thickness of the middle PMMA layer by

$$L = \frac{\pi}{2\kappa_{12}} \qquad (4)$$

where L is the coupling length, and κ_{12}, the amplitude coupling coefficient. For the designed device operating at 1.06 μm, κ_{12} may be expressed as $\kappa_{12} = \kappa_0 e^{-3.46d}$, where $2d$ is the center-to-center guide separation and $\kappa_0 = 0.590$ μm^{-1}. Therefore, $L = [\pi/(2\kappa_0)e^{3.46d}] = 2.67$ $e^{3.46d}$ μm. To obtain a coupling length of a few millimeters at 1.06 μm, we need a central PMMA layer thickness of approximately 2.5 μm. The coupling length is exponentially varying with the waveguide parameters so that small changes in thickness, wavelength, or refractive index give large changes in the coupling length. As demonstrated below, this was manifested by a significantly shorter coupling length than the design length being observed at 1.29 μm.

MATERIALS

The synthesis of the monoacrylate silicon phthalocyanine monomer (Fig. 2) requires the synthesis first of the symmetrically substituted silicon phthalocyanine followed by the hydrolysis of one of the monoreactive groups to give the hydroxy silicon phthalocyanine. This compound can then be reacted to give the unsymmetrically substituted monoacrylate. Radical polymerization can be used to obtain copolymers of the monoacrylate with methyl methacrylate.

Synthesis

Dichlorosilicon Phthalocyanine

A mixture of 1,3-diiminoisoindoline (0.517 mol = 75.00 g) and distilled dried quinoline (450 mL)

was stirred at room temperature for 10 min. Silicon(IV) chloride (0.255 mol = 43.40 g) was added, and the mixture was refluxed for 1.5 h under argon. The solution was added slowly to a mixture of hydrogen chloride (400 mL) and distilled water (600 mL). The solution crystallized overnight and the solid was filtered, washed with methanol, vacuum-dried (RT, 20 h), and weighed (75.34 g, 95%).

Bis(tri-n-hexylsiloxy)silicon Phthalocyanine

A mixture of tri-n-hexylsilanol (0.108 mol = 32.64 g), sodium methoxide (0.094 mol = 5.08 g), and absolute ethanol (165 mL) was reduced to an oil under vacuum. This oil was added to a mixture of dichlorosilicon phthalocyanine (0.123 mol = 75.34 g) and distilled dried pseudocumene (300 mL). The resulting suspension was refluxed for 2 h and filtered hot. The filtrate was allowed to cool (12 h) and was diluted with methanol. The solid was isolated by filtration, washed with methanol, dried (20 h), and weighed (33.98 g). The product was recrystallized by addition of hexane (112.5 mL). The suspension was heated to boil and filtered hot, and the filtrate was allowed to cool overnight and was diluted with hexane. The solid was isolated by filtration, washed with hexane, dried under vacuum (RT, 20 h), and weighed (26.37 g, 19%).

Hydroxy(tri-n-hexylsiloxy)silicon Phthalocyanine

A mixture of bis(tri-n-hexyloxy)silicon phthalocyanine (0.0231 mol = 26.37 g), trichloroacetic acid (0.058 mol = 9.45 g), and distilled dried toluene (350 mL) was refluxed for 1 h. The resulting solution was concentrated under vacuum and added to a mixture of 5 : 1 pyridine/water (195 mL) that was stirred for 2 h at 64°C. The suspension formed was concentrated under vacuum and diluted with methanol (400 mL). The solid was isolated by filtration, washed with methanol, dried under vacuum (RT, 20 h), and weighed (18.82 g, 95%).

3-Methacryloxypropyldimethylsiloxy(tri-n-hexylsiloxy)silicon Phthalocyanine

A mixture of hydroxy(tri-n-hexylsiloxy)silicon phthalocyanine (0.022 mol = 18.82 g), 3-methacryloxypropydimethylchlorosilane (0.088 mol = 19.41 g), tri-n-butylamine (0.088 mol = 16.29 g), and distilled dried toluene (560 mL) was stirred at room temperature for 48 h. The tri-n-butylamine was dried through an aluminum oxide (I) column prior to use. The solution was concentrated under vacuum and was diluted with methanol. The solid was iso-
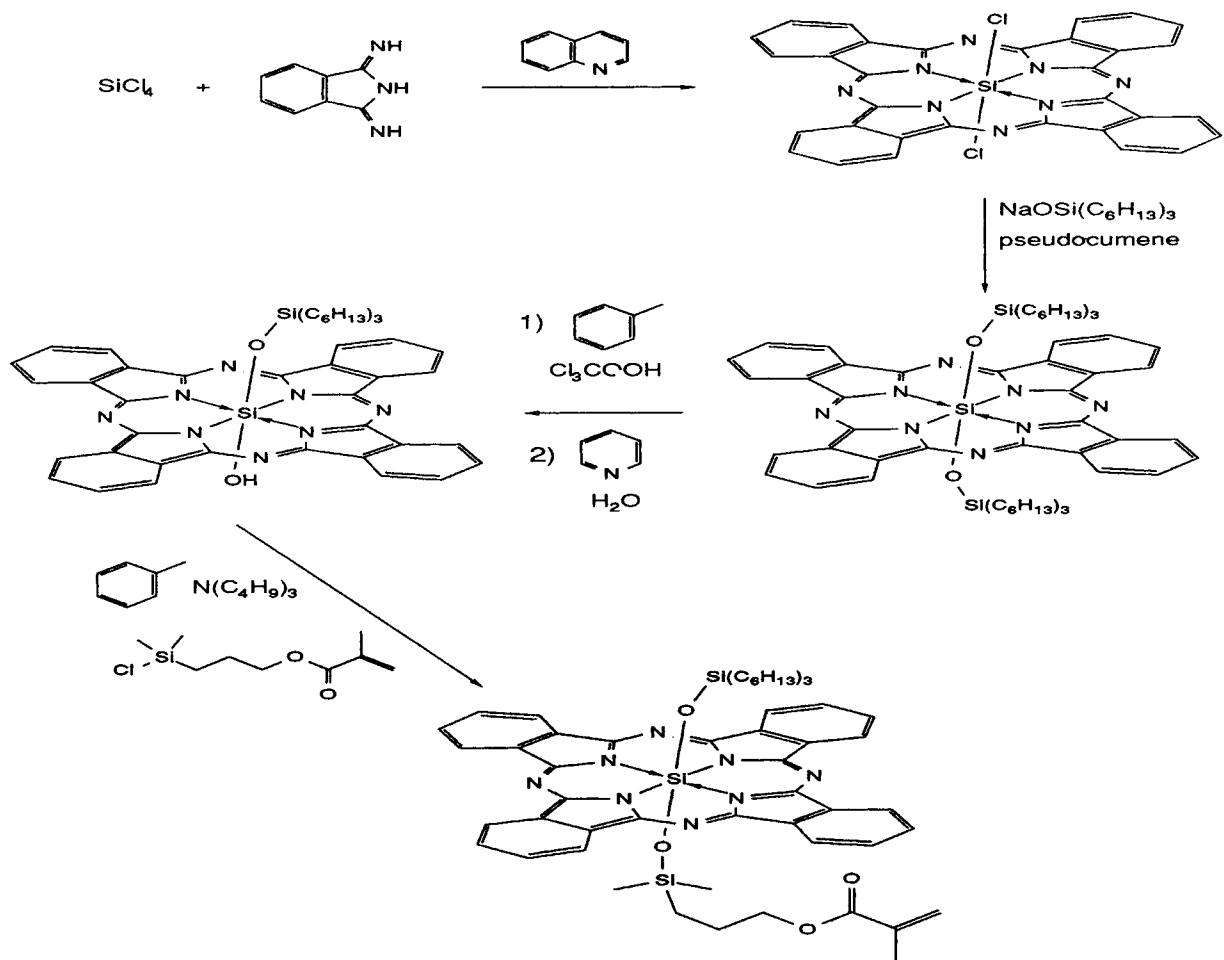
Figure 2 Synthesis of silicon phthalocyanine monomethacrylate copolymers.

lated by filtration, dried under vacuum (RT, 20 h), and weighed (21.71 g). The product was recrystallized by addition of 2-propanol (426 mL) to the solid. The suspension was heated to boil and filtered hot. The filtrate was allowed to cool overnight, then filtered, washed with 2-propanol, dried under vacuum (RT, 20 h), and weighed (11.20 g, 51%): mp 127–130°C; ^{1}H-NMR δ 9.66 (m, Pc–H), 8.34 (m, Pc–H), 5.75 (s, C=CH$_2$), 5.41 (s, C=CH$_2$), 2.74 (t, γ-CH$_2$, C3 chain), 1.74 (s, CH$_2$), 0.79 (m, ε-CH$_2$), 0.67 (t, CH$_3$), 0.36 (m, δ-CH$_2$), −0.02 (m, γ-CH$_2$, C6 chain), −0.99 (m, β-CH$_2$, C3 chain), −1.27 (m, β-CH$_2$, C6 chain), −2.27 (m, α-CH$_2$, C3 chain), −2.43 (m, α-CH$_2$, C6 chain), −2.84 (s, SiCH$_3$).

Monomethacrylate Silicon Phthalocyanine/ Methyl Methacrylate Copolymer (2 : 98)

A mixture of 3-methacryloxypropyldimethylsiloxy(tri-n-hexylsiloxy)silicon phthalocyanine (0.01 mol = 10.00 g), methyl methacrylate (0.40 mol

= 40.00 g), and distilled dried chlorobenzene (500 mL) was stirred for 45 min under an inert atmosphere. AIBN (2.02 g) was added to the mixture and then it was heated (60°C) for 48 h under inert atmosphere. Precipitation of the product was done in methanol (400 mL) and the solid was isolated by filtration, washed with methanol, dried under vacuum (RT, 20 h), and weighed (34.42 g): ^{1}H-NMR δ 9.63 (s, Pc–H), 8.34 (s, Pc–H), 3.58 (m, OCH$_3$), 2.74 (t, γ-CH$_2$, C3 chain), 1.74 (s, CH$_3$), 0.79 (m, ε-CH$_2$), 0.67 (t, CH$_3$), 0.36 (m, δ-CH$_2$), −0.02 (m, γ-CH$_2$, C6 chain), −0.99 (m, β-CH$_2$, C3 chain), −1.27 (m, β-CH$_2$, C6 chain), −2.27 (m, α-CH$_2$, C3 chain), −2.43 (m, α-CH$_2$), C6 chain), −2.84 (s, SiCH$_3$).

Characterization

Figures 3 and 4 are the NMR of the monomer and the copolymer, respectively, where Figure 3 shows
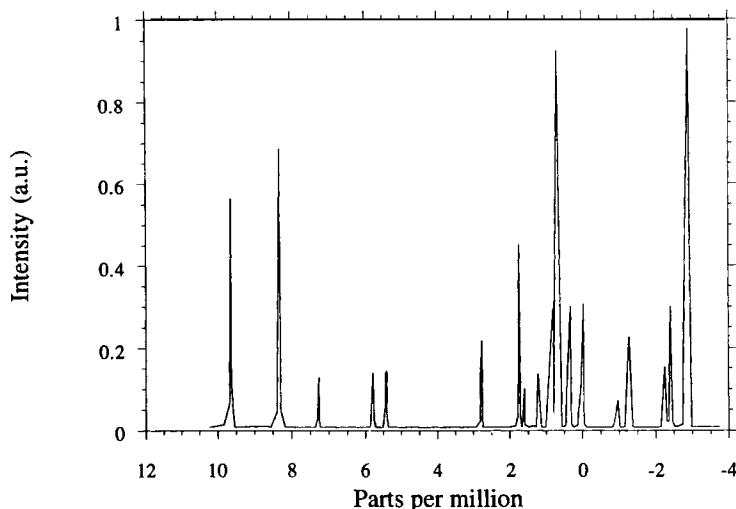
Figure 3   NMR spectrum of methacryloxypropyldimethyl(tri-n-hexylsiloxy)silicon phthalocyanine monomer.

both $OSi(CH_3)_2CH_2$ and $OSiCH_2$ peaks at -2 to -3 ppm for the methacrylate and Figure 3 shows peaks for both the PMMA backbone as well as the $Si(CH_3)_2CH_2$ and $OSiCH_2$ peaks at -2 to -3 ppm with no olefinic protons.

Figure 5 shows UV-VIS spectra at various drying temperatures (90, 120, 140, and 180°C), where there is no shift observed at different temperatures. This confirms that no damage was done to the chromophore at high drying temperatures and also that increased agglomeration did not occur. The latter has been observed in guest/host samples of similar loadings.

UV-VIS spectra of SiPc copolymers compared to comparable loading guest/hosts show the limited solubility of the dye in the polymer, resulting in shifts and broadening of the absorption bands owing to interactions between neighboring silicon phthalocyanine chromophores.[10] These copolymers show low absorption at wavelengths higher than 800 nm and can give films that may be used for waveguide devices at these wavelengths.

According to previous measurements using degenerate four-wave mixing,[14] the ratio of third-order nonlinear optical activity to absorption $\chi^{(3)}/\alpha$ is constant up to a composition of 2/98 SiPc/MMA.
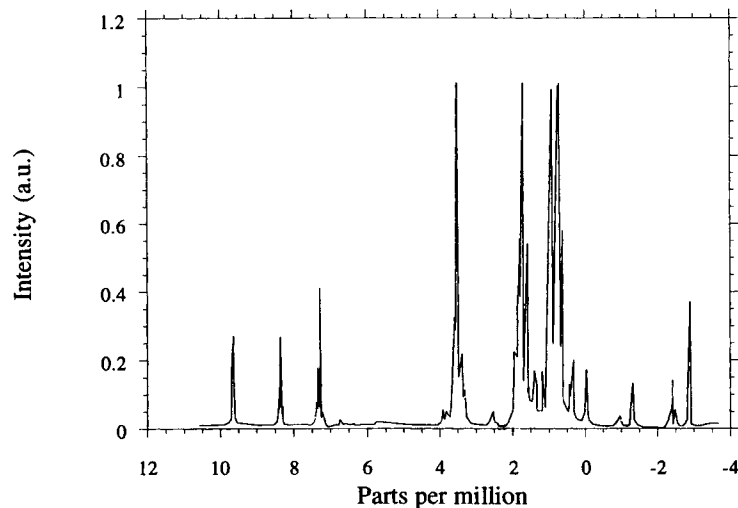

Figure 4   NMR spectrum of silicon phthalocyanine/methyl methacrylate 2/98 copolymer.
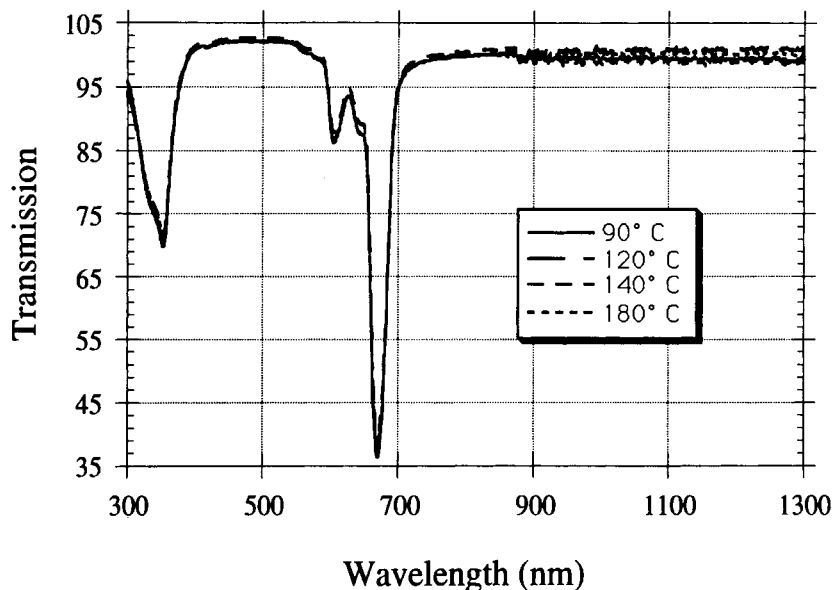
Figure 5 UV-VIS-NIR spectra of SiPc/MMA copolymer films dried at various temperatures.

Above 2% loading, the ratio of $\chi^{(3)}/\alpha$ begins to decrease, perhaps stemming from increased ground-state interactions between the SiPc chromophores. The larger $\chi^{(3)}$ is the shorter the device can be for a given input power, so we want to use the copolymer with the combination of the highest figure of merit and a large $\chi^{(3)}$. With these considerations in mind, the 2/98 copolymer was chosen as the candidate material.

DEVICE FABRICATION

Spin Coating

To achieve the desired thicknesses used in the five-layer device (Fig. 1), a series of spin-coating experiments were done. The correct spin speeds for desired thicknesses were determined by plotting spin speed vs. film thickness. The measured thicknesses differed from the design thickness by 4.9–7.6%. In all cases, the substrates were silicon dioxide-coated silicon wafers, the solvent was cyclohexanone, and films were dried at approximately 100°C for approximately 1 h. A key advantage of the copolymer approach is that it practically eliminates any diffusion between layers during drying, as opposed to what can occur in the guest/host case.

Upper PMMA Layer Removal

As shown in Figure 1, prism coupling is to be attempted into the upper SiPc layer for selective excitation of a single waveguide. To accomplish this, the upper PMMA layer was removed from the device surface by taping a piece of Scotch tape on the upper SiPc layer, spinning on a layer of PMMA, and immediately removing the tape from the surface. The only observed defect is a transition line produced by the tape while spinning the upper PMMA layer. The transition line width is approximately 1.5 mm. This provides a convenient way to remove upper cladding layers for the purpose of characterization of guide layers, deposition of electrodes, etc.

RESULTS

A number of five-layer devices were made for investigation of waveguide loss, coupling, and reproducibility of the fabrication techniques. Also, since the coupling characteristics are highly dependent on the center-layer thickness and optical wavelength, a number of devices with differing center-layer thicknesses were made. The center-to-center waveguide separation and resulting coupling lengths calculated are given in Table I for 1.289 and 1.064 μm wavelengths; dispersion in the copolymer refractive index was taken into account with a two-level model.

Table I Coupling Length as a Function of Guide Separation for 1.289 and 1.064 μm Wavelengths

Center-to-center Guide Separation (μm)	Coupling Length (at 1.289 μm) (mm)	Coupling Length (at 1.064 μm) (mm)
3.80	0.548	1.908
3.54	0.409	1.217
3.30	0.304	0.804
3.04	0.227	0.513

Since there are no electronic absorptions in silicon phthalocyanine in the near-infrared, the loss of the material should be only weakly dependent on wavelength. Although the design wavelength was 1.06 μm for reasons of increasing $\chi^{(3)}$ and avoiding two-photon absorption, it is reasonable to use 1.289 μm light for assessing waveguide loss. This was done using a standard setup based on the detection of light scattering from the guiding layer for light launched by prism coupling (made possible by the lift-off technique) into the guide layer. Figure 6 shows the loss of a three-layer waveguide (PMMA/ SiPc:MMA/PMMA) as measured with the 1.289 μm loss apparatus for the TE mode. The loss is estimated to be 5–7 dB/cm, which is not prohibitively large if the device is only a few millimeters long. The origin of loss may be absorption but could also

be scattering caused by partial alignment of the SiPc copolymers. Figure 7 demonstrates evidence for a modulation with a 1 mm periodicity in the loss of a five-layer device. This represents coupling between the two waveguides since the top guide will scatter considerably more than the bottom guide. This modulation should have a periodicity of twice the coupling length, which is consistent with the calculated coupling length of 500 μm for this five-layer device at 1.289 μm (see Table I). The "extinction ratio" cannot be accurately determined from these data since the bottom guide will still exhibit some scattering.

Waveguiding was also observed using endfire optical fiber coupling into the waveguides and an infrared camera and beam scanning system to image the output. A 1.06 μm-diode-pumped Nd:YAG laser was used, and slab waveguiding in both waveguides was clearly observed, as shown in Figure 8. Detailed measurements indicate that the top waveguide confines light more strongly. This comes from the inherent asymmetry in the structure shown in Figure 1, since the top waveguide sees an air "substrate," while the bottom sees an Si/SiO$_2$ substrate.

These experiments demonstrate that relatively low loss waveguiding can be achieved at 1.06 μm and that both SiPc layers can simultaneously support waveguiding modes. The silicon phthalocyanine/ methyl methacrylate copolymer is a processible third-order nonlinear optical polymer that appears to have some of the properties desired for all-optical
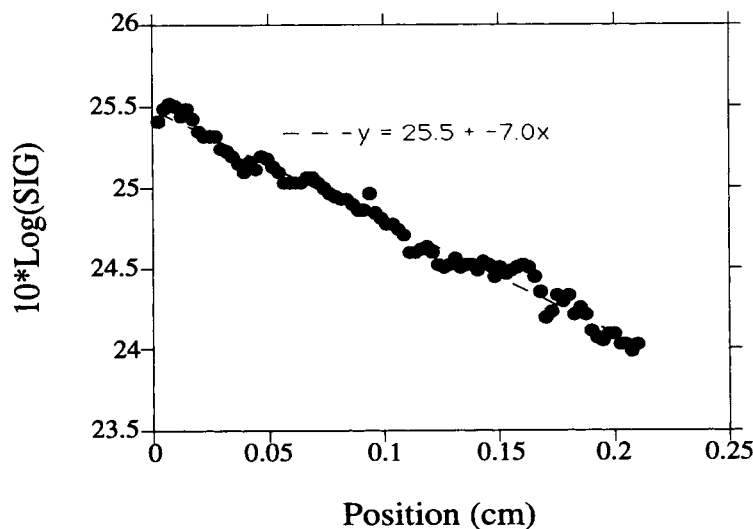
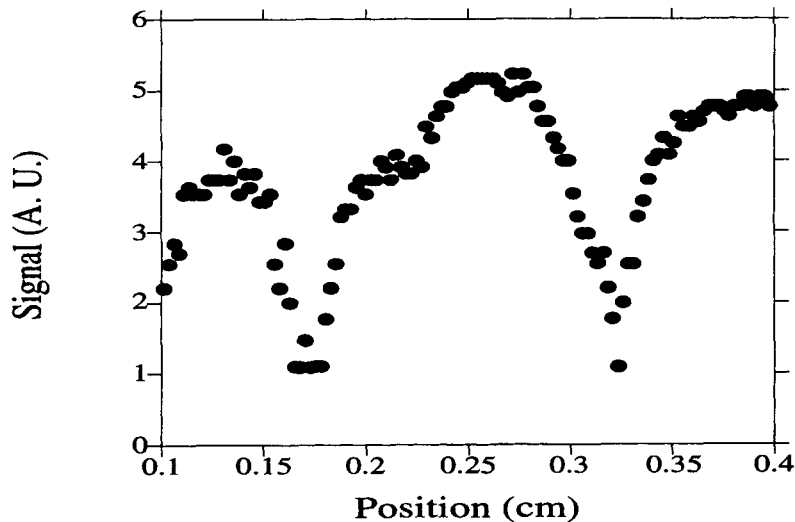**Figure 6** Loss of a three-layer waveguide as measured by the scattering technique at 1.289 μm.

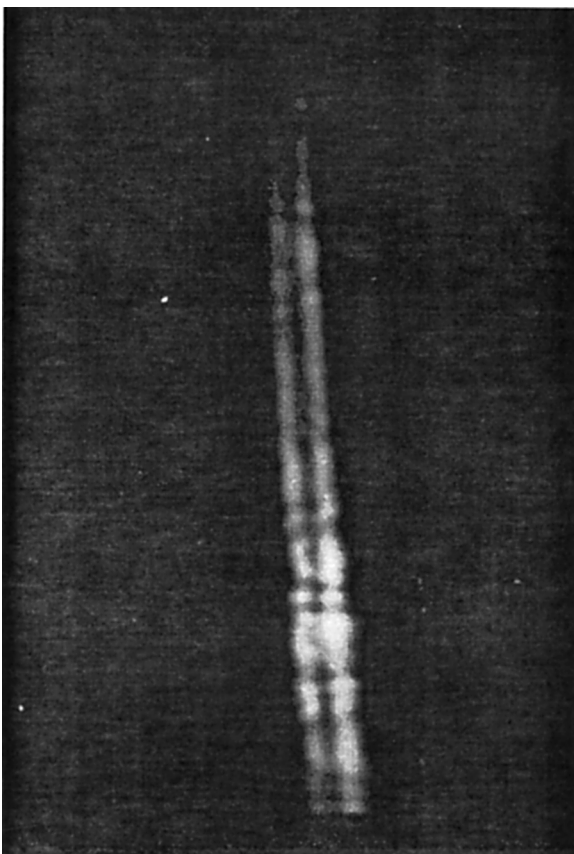**Figure 7** Coupling between SiPc/MMA waveguides as measured with the scattering technique.

Figure 8 Photograph of both waveguides waveguiding in a five-layer sample at 1.06 μm as obtained with an infrared camera.

switching. For specific applications, similar chemistry can be applied to other macrocyclic dye systems. Future work will concentrate on demonstrating switching between the two waveguides, either through the imposition of a resonant optical pump incident perpendicular to the plane of the slab waveguide or a nonresonant optical pump along the waveguide.

This work is dedicated to the memory of Dr. Alan Buckley and his vision of a new world through polymer chemistry and physics.

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