Zero Dispersion Nonlinear Optical Polymeric Materials Containing Stilbene and Naphthalocyanine Dyes

James R. Sounik,*[1] Garo Khanarian,* Jacquelyn Popolo, and Steven Meyer

Hoechst Celanese Corporation, Robert L. Mitchell Technical Center, 86 Morris Ave., Summit, New Jersey 07901

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We report the synthesis of terpolymers containing anomalous and normal dispersive dyes, silicon naphthalocyanine and oxynitrostilbene, respectively. It is shown by refractive index measurements that the indexes at the wavelengths 0.63 and 1.3 μm can be made equal by adjusting the concentration of the anomalous dispersive dyes. However, the absorption coefficient at 0.63 μm is too high for these materials to be useful for phase-matched second harmonic generation.

Efficient frequency doubling has recently received great attention because of the need to generate shorter wavelengths in the range 400–500 nm.[2] Polymeric-based nonlinear optical (NLO) materials have also been studied, especially in waveguide configurations.[3] These materials require extensive device development in order to match the indexes at the fundamental and harmonic wavelengths, which is necessary for efficient frequency doubling. One approach to simplified device designs is to use anomalous dispersion of the refractive index near an absorption band of a second order $\chi^{(2)}$ nonlinear optical material to make the indexes equal at the fundamental and harmonic wavelengths.[4] However, since phase matching is a critical process, only a certain concentration of NLO dye will satisfy that condition. A better approach is to separate the two functions (i.e., NLO activity and anomalous dispersion). The Phillips group proposed dissolving an anomalously dispersive dye in a $\chi^{(2)}$ side-chain poled polymer.[5] An important issue with the use of anomalously dispersive dyes is the transparency of the material on the high-energy side of the absorption band where the second harmonic will be propagated. This will depend critically on the concentration and line width of the dye in the NLO material.

In this paper we propose a multifunctional polymer approach to the problem by covalently attaching the NLO and anomalously dispersive dye to the same polymer backbone. This approach has two distinct advantages. The poled polymer dye system will be stable temporally and the line widths of the anomalously dispersive dye will be narrower than in a comparable guest host system.[6] This should result in greater transparency at the second harmonic. We also report refractive indexes at a fundamental (1.3 μm) and its harmonic wavelengths which show that the indexes are matched. To test this approach, a silicon naphthalocyanine, oxynitrostilbene, and methyl methacrylate (SINC/ONS/MMA) terpolymer and a silicon phthalocyanine, oxynitrostilbene, and methyl methacrylate (SIPC/ONS/MMA) terpolymer were synthesized and characterized. Both terpolymers were synthesized as a 5 wt % anomalous dispersive dye using a 50/50 ONS/MMA mole ratio. A copolymer of oxynitrostilbene and methyl methacrylate (ONS/MMA) of a 50/50 mole ratio was previously used to fabricate frequency-doubling waveguides.[3]

We have previously described the preparation, characterization and thin film-fabrication of a series of methyl methacrylate copolymers of monomethyl methacrylate and dimethyl methacrylate functionalized silicon phthalocyanine monomers.[7,8] These studies have shown that copolymers of the phthalocyanine monomers and methyl methacrylate show little broadening of the Q band at 670 nm at concentrations below 4 mol %, whereas guest host materials show extensive band broadening. This has been shown to be due to the molecular association of the dye molecules in the solid-state thin film. This directly relates to the transparency of these materials at the second harmonic frequency and the need to covalently link the anomalous dispersive dye to the polymer backbone.

The synthesis of the 5% SIPC/ONS/MMA (0.0014/50.7/49.3 mole ratio) terpolymer follows directly from the free-radical polymerization of {[3-(methacryloxy)propyl]dimethylsiloxy}(tri-*n*-hexylsiloxy)phthalocyaninatosilicon 4-[(methacryloxy)hexyloxy]-4′-nitrostilbene, and methyl methacrylate (Figure 1).[7,9] The polymerization is done using 2,2′-azobis(isobutyronitrile) (AIBN) as the radical initiator in chlorobenzene at 60 °C. The terpolymer is precipitated from solution using methanol. The 5% SINC/ONS/MMA (0.001/50.7/49.3 mole ratio) terpolymer is synthesized in a similar manner using bis[(3-(methacryloxy)propyl)dimethylsiloxy]naphthalocyaninatosilicon (Figure 2). Molecular weight and DSC data for the two terpolymers used in this study are given in Table I. The molecular weights for these terpolymers are similar to those found for the ONS/MMA copolymers (150 000–

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[1] Current address: Hoechst Celanese Corp., Corpus Christi Technical Center, P.O. Box 9077, Corpus Christi, TX 78469.

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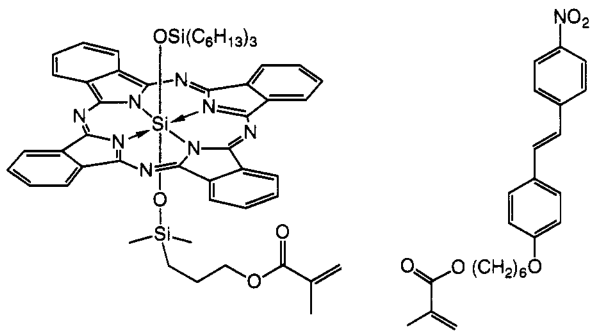

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Figure 1. Structures of {[3-(methacryloxy)propyl]dimethylsiloxy}(tri-*n*-hexylsiloxy)phthalocyaninatosilicon (I) and 4-[(methacryloxy)hexoxy]-4′-nitrostilbene (II).

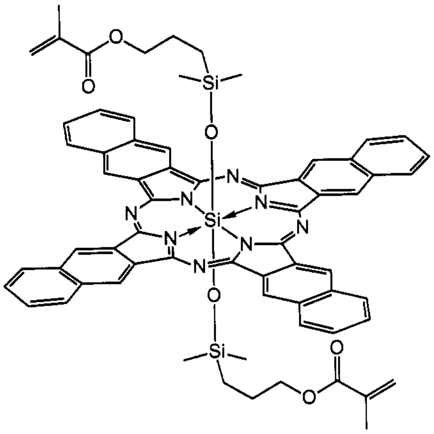

Figure 2. Structure of bis[[3-(methacryloxy)propyl]dimethylsiloxy}naphthalocyaninatosilicon.

Table I. Molecular Weight and Glass Transition Temperatures for 5% SIPC/ONS/MMA and 5% SINC/ONS/MMA Terpolymers

material	M_w	M_n	M_w/M_n	T_g (°C)
5% SIPC/ONS/MMA	166 000	147 000	1.5	60
5% SINC/ONS/MMA	575 000	27 000	21	69

500 000). Also, the glass transition temperatures are similar to those observed for the ONS/MMA 50/50 mole ratio copolymer and are lower then those seen for the SIPC/MMA copolymers. These observations are related to the relatively low concentration of the silicon phthalocyanine or naphthalocyanine monomer in each terpolymer. It is interesting to note that the SIPC monomer will give terpolymers that are not cross-linked, whereas the SINC monomer will react as a cross-linking agent. Thin films of the terpolymers were made on glass substrates by spin coating a 20 wt % solution of the material in cyclohexanone and were dried under nitrogen at 140 °C for 3 h. The optical absorption spectra of these thin films are shown in Figures 3 and 4. Analysis of the 5% SIPC/ONS/MMA terpolymer spectrum shows the Q-band of the phthalocyanine at 673 nm with a full width at half-maximum (fwhm) of 19 nm, which is similar to that seen for the SIPC/MMA copolymer systems. The 5% SINC/ONS/MMA terpolymer shows the Q-band of the naphthalocyanine at 784 nm with a fwhm of 27 nm. Both terpolymers also show a large absorption at 380 nm due to the oxynitrostilbene chromophore.

The terpolymer SINC/ONS/MMA with 5% SINC dye content was dissolved in cyclohexanone (20% wt/wt) and spun coated onto silicon wafers to give uniform thin films of about 2-μm thickness. We also prepared guest host films of the SINC dye dissolved in ONS/MMA 50/50 copolymers where the concentration of the SINC dye was comparable to that in the terpolymer (Table II).[10] The index of the base copolymer ONS/MMA 50/50 was also measured. Measurements were performed with a Metricon prism coupler (Model 2010) at 633 and 1289 nm. Note that 633 nm is almost the second harmonic wavelength of 1289 nm. The dispersion results are shown in Figure 5. The results show that the base polymer has a dispersion of 0.044 and that this dispersion decreases with increasing amount of the SINC dye. For the guest–host film there is a linear decrease in dispersion, and one finds zero dispersion at about 9.2% (wt/wt) of the SINC dye in the

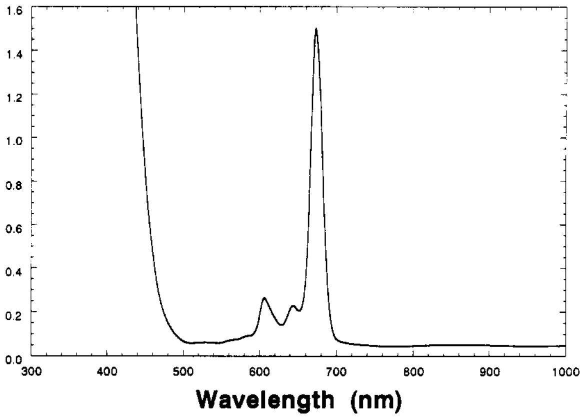

Figure 3. Optical absorption of a 0.92-μm thin film of 5% SIPC/ONS/MMA terpolymer on glass.

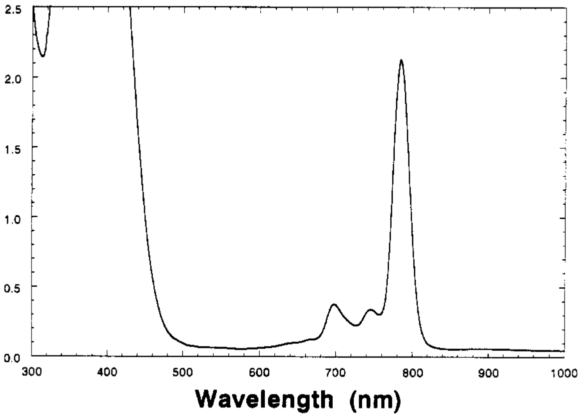

Figure 4. Optical absorption of a 1.92 μm thin film of 5% SINC/ONS/MMA terpolymer on glass.

Table II. Molar Concentration, Index of Reflection *n*,[a] and Disperson Δ*n* = *n*(633 nm) − *n*(1289 nm) of ONS/MMA Copolymer,[b] 5 and 10% SINC–ONS/MMA Guest–Host (G/H), 5% SIPC/ONS/MMA, and SINC/ONS/MMA Terpolymer Thin Films

		n		
material	M^c (m/L)	1289 nm	633 nm	Δ*n*
ONS/MMA		1.6019	1.6457	0.044
5% SINC–ONS/MMA(G/H)	4.11×10^{-2}	1.615	1.6336	0.019
10% SINC–ONS/MMA(G/H)	8.22×10^{-2}	1.6294	1.621	−0.008
5% SIPC/ONS/MMA	6.65×10^{-2}	1.5975	1.6312	0.034
5% SINC/ONS/MMA	5.02×10^{-2}	1.607	1.619	0.012

[a] Transverse electric component (TE). [b] 50/50 mole ratio. [c] Molar concentration of the dispersive dye.

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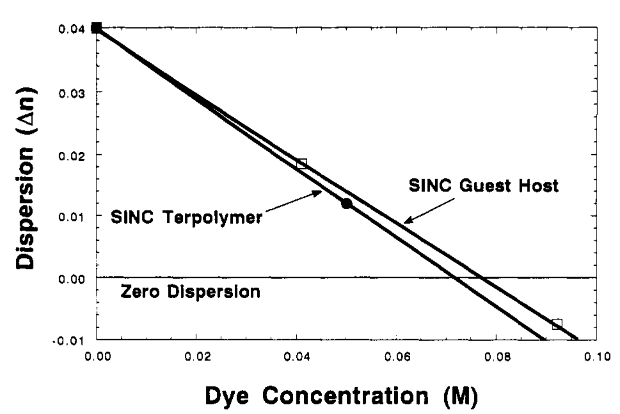

Figure 5. Dispersion of index for a 5% and 10% SINC/ONS/MMA guest–host and 5% SINC/ONS/MMA terpolymer thin films measured at 1289 and 633 nm.

NLO copolymer. For the terpolymer the extrapolated zero dispersion concentration is about 7.5% (wt/wt). Micron-thick thin films of the 5% SIPC/ONS/MMA terpolymer were fabricated in a similar manner. Index measurements show a dispersion of 0.034 which is higher than that seen for the 5% SINC/ONS/MMA terpolymer. This is due to the vibrational overtones of the SIPC chromophore at 606 and 642 nm being close to the measurement wavelength at 633 nm.

An important issue in using anomalously dispersive dyes is the transparency on the high energy side of the absorption maximum. Waveguide loss measurements were carried out on slab waveguides of thin films made from the 5% SINC/ONS/MMA terpolymer. Light was coupled into the film by means of a prism, and the scattered light from the film was measured as a function of distance from the prism.[11] The change in scattered light is a measure of attenuation in the film. Measurements were attempted at 633 and 540 nm, which correspond to the transparency window on the high-energy side of the SINC molecule (see Figure 4). Nevertheless, we found a high attenuation over a distance of less than 1 mm, which suggests that the waveguides were highly absorbing the 633- and 540-nm radiation. Even though the SINC dye has a narrow absorption band in the terpolymer, the residual tail appears to be large enough to cause excess absorption. Other workers have also referred to the difficulty of finding anomalously dispersive dyes that have a sufficiently low absorption to make waveguiding of the second harmonic possible.[4,5]

In conclusion we have demonstrated a covalently bonded terpolymer system consisting of an NLO dye and anomalously dispersive dye based on a phthalocyanine and naphthalocyanine ring system that results in a zero dispersion material. However the observed losses at the second harmonic frequencies of 540 and 633 nm are too high to be used in waveguide type applications. It seems that we need narrower line width dyes with resultant lower losses at the second harmonic wavelength, in order to make transparent zero dispersion polymers for frequency doubling.

Experimental Section

Methods of Analysis. NMR spectra were obtained on a Bruker MSL300 spectrometer and chemical shifts were reported in ppm relative to tetramethylsilane. Polymer molecular weights were determined on a Waters 201 GPC equipped with a Waters 401 RI and a Viscotek Model 100 differential viscosity detector using tetrahydrofuran as the mobile phase. Molecular weights were calculated from a universal calibration curve. Thermal analysis was done using a du Pont 9900-910 thermal analyzer. Melting points were obtained on a Melt-Temp II capillary melting point apparatus and are uncorrected.

Synthesis of 5% Silicon Phthalocyanine/Oxynitrostilbene/Methyl Methacrylate Terpolymers. *Bis(tri-n-hexylsiloxy)phthalocyaninatosilicon.*[12] A mixture of tri-*n*-hexylsilanol (14.9 g), sodium methoxide (2.67 g), and absolute ethanol (50 mL) was reduced to an oil under vacuum. This oil was added to a mixture of dichlorosilicon phthalocyanine (15.10 g) and distilled dried 1,2,4-trimethylbenzene (70 mL). The resulting suspension was refluxed for 1 h and was filtered hot to remove any organic insoluble material. The filtrate was allowed to cool (12 h) and was diluted with methanol (350 mL). The solid was isolated by filtration, washed with methanol (100 mL), vacuum dried (room temperature, 12 h), and weighed (22.06 g, 79%): mp 175 °C; IR (Nujol) 1525 (s), 1325 (s), 1125 (s), 1080 (s), 1038 (s, Si–O–Si), 725 (s).

Hydroxy(tri-n-hexylsiloxy)phthalocyaninatosilicon.[13] A mixture of bis(tri-*n*-hexylsiloxy)phthalocyaninatosilicon (15.05 g), trichloroacetic acid (6.27 g), and distilled dried toluene (120 mL) was refluxed for 1 h. The resulting solution was concentrated under vacuum. The remaining oil was then added to a mixture of 5:1 pyridine/water (60 mL) and was stirred for 2 h at 62 °C. The suspension formed was concentrated under vacuum and diluted with methanol (100 mL). The solid was isolated by filtration, washed with methanol (100 mL), dried under vacuum (room temperature, 12 h) and weighed (9.45 g, 84%): IR (Nujol) 3500 (w, OH), 1340 (s), 1125 (s), 1037 (m, Si–O–Si), 740 (s).

{[3-(Methacryloxy)propyl]dimethylsiloxy}(tri-n-hexylsiloxy)phthalocyaninatosilicon. A mixture of hydroxy(tri-*n*-hexylsiloxy)phthalocyaninatosilicon (4.43 g), 3-methacryloxypropyldimethylchlorosilane (3.43 g), tri-*n*-butylamine (2.88 g), and distilled dried toluene (100 mL) was stirred at room temperature for 48 h. The solution was concentrated under vacuum and was diluted with methanol. The solid was isolated by filtration, dried under vacuum (room temperature, 12 h) and weighed (4.30 g, 80%). The solid is recrystallized from isopropyl alcohol: 120 °C; IR (Nujol) 1714 (s, C=O), 1336 (s), 1250 (m, $SiCH_3$), 1158 (s), 1123 (s), 1081 (s), 1044 (s, Si–O–Si), 736 (s); FAB-MS *m/z* (rel intensity) 1040 [M^+, 93], 839 [$M^+ - C_9H_{17}O_3Si$, 69], 741 [$M^+ - C_{18}H_{39}OSi$, 100]; ^1H 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_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, $SiCH_3$).

5% Phthalocyaninatosilicon/Oxynitrostilbene/Methyl Methacrylate Terpolymer. A mixture of recrystallized {[3-(methacryloxy)propyl]dimethylsiloxy}(tri-*n*-hexylsiloxy)phthalocyaninatosilicon (I) (0.65 g), methyl methacrylate (2.44 g), 4-[(methacryloxy)hexyloxy]-4′-nitrostilbene (II) (10.00 g) and dry distilled chlorobenzene (120 mL) was purged with argon for 2 h while being heated. AIBN (0.24 g) was added, and the reaction was heated for 72 h under an inert atmosphere (argon). Precipitation of the product was done in methanol (10:1, methanol:solution) and the solid was isolated by filtration, dried (vacuum, 50 °C, 12 h), and weighed (12.59 g, 96%); T_g 60 °C; M_w (THF, ultrastyragel columns) 166 000; M_w/M_n 1.5; ^1H NMR δ 9.66 (m, Pc-H), 8.34 (m, Pc-H), –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, $SiCH_3$).

5% Naphthalocyaninatosilicon/Oxynitrostilbene/Methyl Methacrylate Terpolymers. *Bis{[3-(methacryloxy)propyl]-dimethylsiloxy)}naphthalocyaninatosilicon.* A mixture of dihydroxynaphthalocyaninatosilicon (2.10 g), (3-(methacryloxy)-propyl)dimethylchlorosilane (3.09 g), and distilled dried pyridine (75 mL) was stirred at 50 °C for 48 h. The chlorosilane was distilled under vacuum prior to use. The mixture was filtered, and the filtrate was diluted with a 1:1 ethanol/water solution

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(100 mL). The solid was isolated, washed with methanol (50 mL), vacuum dried (room temperature, 12 h) and weighed (2.96 g, 86%). The solid is recrystallized from toluene: mp 170–172 °C; IR (Nujol) 1714 (s, C=O), 1336 (s), 1250 (m, $SiCH_3$), 1158 (s), 1123 (s), 1081 (s), 1044 (s, Si–O–Si), 7.36 (s); FAB-MS *m/x* (rel intensity) 1142 [M^+, 75], 942 [$M^+ - C_9H_{17}O_3Si$, 54]; ^{1}H NMR δ 10.11 (s, Nc-H), 8.66 (m, Nc-H), 7.96 (m, Nc-H), 5.48 (s, C=CH), 5.09 (s, C=CH), 2.83 (t, γ-CH_2), 1.49 (s, CH_3), –0.66 (m, β-CH_2), –1.95 (m, α-CH_2), –2.46 (s, $SiCH_3$).

5% Naphthalocyaninatosilicon/Oxynitrostilbene/Methyl Methacrylate Terpolymer. A mixture of recrystallized bis{[3-(methacryloxy)propyl]dimethylsiloxy)naphthalocyaninatosilicon (III) (0.65 g), methyl methacrylate (2.44 g), 4-[(methacryloxy)hexyloxy]-4′-nitrostilbene (II) (10.00 g), and dry distilled chlorobenzene (30 mL) was purged with argon for 2 h while being heated. AIBN (0.24 g) was added, and the reaction was heated for 96 h under an inert atmosphere (argon). Precipitation of the product was done in methanol (10:1, methanol:solution), and the solid was isolated by filtration, dried (vacuum, 50 °C, 12 h) and weighed (11.83 g, 90%); T_g 69 °C; M_w (THF, ultrastyragel columns) 575 000; M_w/M_n 21; ^{1}H NMR δ 10.11 (s, Nc-H), 8.66 (m, Nc-H), 7.96 (m, Nc-H), –0.66 (m, β-CH_2), –1.95 (m, α-CH_2), –2.46 (s, $SiCH_3$).