Applications of Organic Bridged Polysilsesquioxane Xerogels to Nonlinear Optical Materials by the Sol–Gel Method

Henry W. Oviatt, Jr. and Kenneth J. Shea*

Department of Chemistry, University of California, Irvine, Irvine, California 92717

Srinath Kalluri, Yongqiang Shi, and William H. Steier

Center for Photonic Technology, Department of Electrical Engineering,
University of Southern California, Los Angeles, California 90089

Larry R. Dalton

Department of Chemistry, University of Southern California, Los Angeles, California 90089

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Sol–gel precursors of α,ω-bis(triethoxysilyl)-bridged polysilsesquioxanes containing a side-chain chromophore with known second-order nonlinear optical properties were synthesized. Thin films were formed from these precursors without the addition of other sol–gel forming components. The films were poled while curing at elevated temperatures. Poled films derived from 4-nitroaniline or 2,4-dinitroaniline chromophores resulted in sol–gel based materials with d_{33} coefficients of 35–37 and 9–10 pm/V, respectively. Electrooptic coefficients r_{33} (1.3 μm) extrapolated from d_{33} were calculated to be 9–10 and 2–2.5 pm/V, respectively.

Introduction

The use of sol–gel materials for optical applications is of interest for a number of reasons.[1,2] These include the excellent optical quality of sol–gel derived materials, the ability to add secondary components to the sol that are then trapped in the gel, low-temperature processing capability, high thermal stability, refractive index control of films, and ease of fabrication of devices from sol–gel derived films.[3,4] We are interested in systems utilizing silicon functionalized chromophores which possess large molecular hyperpolarizabilities. The resulting materials are therefore capable of producing a nonlinear optical (NLO) response. For convenience, chromophores capable of producing an NLO response are hereafter referred to as "optiphores." A number of investigators have incorporated *N*-[(3-triethoxysilyl)-propyl]-2,4-dinitroaniline into tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) gels. After orienting by electric field (EF) poling, these materials exhibit a second order NLO response.[5-10] Other investigators have utilized the similar *N*-[(3-triethoxysilyl)propyl]-4-nitroaniline derivative as the optiphore.[7,8,11] Previous studies utilizing sol–gel matrices with reactive optiphores have in common an optiphore linked to a single trifunctional silane in the silicate matrix. The presence of a single trifunctional silane precludes formation of a highly cross-linked sol–gel network without additional sol–gel forming components such as TEOS or TMOS. Addition of secondary components to the sol reduces the mole fraction of optiphores in the matrix, thereby limiting the magnitude of NLO response.

We have been involved in the synthesis and characterization of organic-bridged polysilsesquioxane xerogels formed by the sol–gel method.[12-19] We have synthesized monomers containing at least two trifunctional silane groups which, upon hydrolysis, condensation and drying, form a highly cross-linked three-dimensional xerogel. Simple aryl and alkyl derivation of these materials show thermal stability up to 500 °C in air, an improvement over conventional organic polymers.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

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These highly cross-linked organic–inorganic materials are good candidates for incorporating optiphores as the organic spacers. The resulting xerogels may possess increased thermal stability over NLO materials derived from pure organic polymer systems. Furthermore, hexafunctional sol–gel monomers have the capability of forming hybrid organic–inorganic sol–gel materials from low concentration solutions *without* the addition of secondary sol–gel forming components. Formation of sol–gel films solely from pure monomer containing optiphores, compared to doped systems, has the advantage of maximized loading of the optiphore in the film without phase separation. We describe here the results obtained with sol–gel films produced from novel hexafunctional silane monomers. The films are assembled from a building block that contains a known optiphore and two trifunctional silane groups.

Experimental Section

Instrumental Methods. ^{1}H and ^{13}C NMR spectra were taken on a GE QE 300 spectrometer at 300 and 75.5 MHz, respectively, using either $CDCl_3$(7.25 ppm) or TMS (0.00 ppm) as internal standard. Thermal analysis was performed with a DuPont TA 910 DSC. DSC samples were prepared by evaporation of a solution used for sol–gel film formation into an aluminum DSC analysis pan.

Reactions monitored by GC employed an HP 5710 gas chromatograph using a 6 ft Supelcoport packed column with 3% SP 2100, 100/120, 2.5 m × $^1/_8$ in. A temperature program from 80 to 250 °C at 16 °C/minute was typically employed, using He as the carrier gas at 30 mL/min and FID detection. Neat injections using a 1 μL syringe and an injection volume of 0.05 mL were used.

Monomer Synthesis. *N,N-Bis[3-(triethoxysilyl)propyl]amine (**1**).* This starting material was prepared by the method of Dinh and Lo.[20] To a 250 mL three-neck flask containing a magnetic stir bar and N_2 inlet was added palladium oxide (PdO or Pd black, 0.32 g, 2.6 mmol, Aldrich), followed by freshly distilled (from CaH_2) 3-(triethoxysilyl)propylamine (TESPA, 177 g, 0.800 mol). The flask was fitted with a reflux condenser and sampling valve, and the contents heated in an oil bath at 240 °C. The reaction mixture was monitored at 20 to 30 min intervals by GC as described above. The heating was stopped after 3 h when GC analysis showed the desired product to be 50% of the mixture. Removal of PdO by filtration under N_2 followed by high vacuum distillation of the reaction mixture resulted in two fractions containing a total of 61.6 g (36%) of the desired compound in 85% purity, with approximately 5% starting material and 5% *N,N,N*-tris-[3-(triethoxysilyl)propyl]amine. bp 129–137 °C/0.15 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.65 (q + shoulder, 13H), 2.43 (t, 4H), 1.42 (m, 4H), 1.05 (t, 18H), 0.46 (t, 4H). ^{13}C NMR (75.48 MHz, $CDCl_3$) δ 58.11, 52.51, 23.23, 18.11, 7.83; HRMS (CI, isobutane) *m/e* calcd for $C_{18}H_{43}NO_6Si_2$ + H 426.2707, found 426.2695. This compound will readily polymerize if exposed to atmospheric moisture.

*4-Nitro-N,N-bis[(3-triethoxysilyl)propyl]aniline (**2**).* To a 100 mL round-bottomed flask containing a magnetic stir bar was added 1-chloro-4-nitrobenzene (1.57 g, 10 mmol), followed by 20 mL of dry DMSO (CaH_2 distilled), pyridine (20 mL), and **1** (4.67 g, 11 mmol). The flask was fitted with a reflux condenser and N_2 purge, and the contents heated at 150 °C for 36 h. The solvent was evaporated in vacuo and the remaining liquid was rapidly filtered through a plug of silica gel with CH_2Cl_2. The colored fraction was collected, CH_2Cl_2 removed in vacuo, and the residual DMSO pumped off under high vacuum. The remaining liquid was chromatographed from silica gel using diethyl ether as the eluent and the solvent evaporated. A light red-to-orange liquid was recovered, in which crystals of chloronitrobenzene (starting material) were obtained after standing overnight. The product was dissolved in hexanes and again chromatographed from silica gel by gradient elution from hexanes to CH_2Cl_2. The desired product was isolated in 9% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, 2H), 6.60 (d, 2H), 3.82 (q, 12H), 3.36(t, 4H), 1.71 (m, 4H), 1.22 (t, 18H), 0.62 (t, 4H). ^{13}C NMR (75.48 MHz, $CDCl_3$) δ 152.50, 136.20, 126.44, 110.02, 58.53, 53.47, 20.36, 18.33, 7.42; HRMS (CI, isobutane) *m/e* calcd for $C_{24}H_{46}N_2O_8Si_2$ + H: 547.2807, found 547.2854.

*2,4-Dinitro-N,N-bis[3-(triethoxysilyl)propyl] aniline (**3**).* To a 50 mL round-bottomed flask containing a magnetic stir bar was added 1-chloro-2,4-dinitrobenzene (2.02 g, 10 mmol), followed by triethylamine (10 mL, 72 mmol) and bis-[(3-triethoxysilyl)propyl]amine (4.25 g, 10 mmol). The mixture was heated to 70 °C for 20 min, during which the mixture darkens and a precipitate forms. After cooling, dry diethyl ether (30 mL) was added and the mixture rapidly filtered through silica gel (30 g) with diethyl ether as eluent. The yellow band was collected and the solvent evaporated to yield 4.81 g (81%) of a clear, viscous red liquid. The liquid appears to be stable in air without polymerization. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.10 (d, 1H), 7.05 (d, 1H), 3.75 (q, 12H), 3.25 (t, 4H), 1.67 (m, 4H), 1.21 (t, 18H), 0.50 (t, 4H). ^{13}C NMR (75.48 MHz, $CDCl_3$) δ 148.59, 137.33, 136.50, 127.37, 123.83, 118.95, 58.37, 54.30, 20.86, 18.18, 7.23; HRMS (CI, isobutane) *m/e* calcd for $C_{24}H_{45}N_3O_{10}Si_2$ + H 592.2722, found 592.2722.

N′,N′-Bis[(3-triethoxysilyl)propyl]dansyl Sulfonamide. To a 25 mL round-bottomed flask under N_2 and containing a magnetic stir bar was added dansylsulfonyl chloride (1.0 g, 3.7 mmol, Aldrich), dry pyridine (5 mL, 61 mmol), and **1** (1.57 g, 4.07 mmol). The reaction mixture was heated to 85–90 °C for 30 min and allowed to cool to room temperature overnight. The solution changes from orange to red during the heating period. The solvent was evaporated and the residue chromatographed from silica gel (THF) yielding 1.25g (52%) of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (d, 1H), 8.26 (d, 1H), 8.13 (d, 1H), 7.49 (d–d, 2H), 7.13 (d, 1H), 3.71 (q, 12H), 3.24 (t, 4H), 2.86 (s, 6H), 1.85 (m, 4H), 1.21 (t, 18H), 0.43 (t, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.62, 135.58, 130.10, 130.00, 129.46, 127.80, 123.13, 123.04, 119.64, 115.05, 98.32 (impurity), 67.29 (impurity), 58.31, 49.34, 45.36, 33.20 (impurity), 23.40, 21.54 (impurity),18.23, 7.42; HRMS (EI) *m/e* calcd for $C_{30}H_{54}N_2O_8SSi_2$: 658.3139, found 658.3153.

Sol–Gel Film Formulations. Solutions were prepared in 0.25–1 mL volumes for thin-film spinning. The formulation was arrived at by calculating the volume of precursor, solvent, and formic acid solution required to form a solution with a monomer concentration of 0.4 M. The density of the precursor was assumed to be 1.0. The density for 90% formic acid (Fisher) used was 1.29. For films catalyzed with concentrated ammonia, a density of 0.90 for 33% w/v ammonia was used.[21] Volumes of dimethylformamide (DMF), tetrahydrofuran (THF), or 1-butanol (BuOH) were calculated by difference and added to bring the total volume of solution to 0.25 mL. All solutions were prepared volumetrically.

Example 1: 4-Nitro-N,N-bis[(3-triethoxysilyl)propyl]aniline Sol–Gel Film. To a 5 mL test tube was added **2** (0.055 mL) followed by 1-butanol (ACS grade, 0.140 mL) and the solution gently agitated until homogenous. Catalyst (formic acid 90%), 0.056 mL, 4 equiv of H_2O to precursor was added and the mixture again agitated. Solutions were aged 5–10 min prior to spin coating. A 50 μL volume of solution was placed on 1 × 1 in. indium tin-oxide (ITO) coated glass (Thin Film Devices, Anaheim, CA) surface for spin coating. Films were spun from this solution with a commercial thin-film spinning apparatus (Headway Research). A spin rate between 800 and 1000 rpm for 20 s was used, and films were cast between 5 and 20 min after the addition of catalyst.

Example 2: 2,4-Dinitro-N,N-bis[(3-triethoxysilyl)propyl]aniline Sol–Gel Film. To a 5 mL test tube was added **3** (0.059 mL) followed by 1-butanol (ACS grade, 0.140 mL), and the solution gently agitated until mixed. Catalyst (formic acid 90%) 0.056 mL, 4 equiv of H_2O to precursor was added and the mixture again agitated. Solutions were aged 5–10 min prior to spin coating as described in example 1 above.

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[20] Dihn, P. C.; Lo, Y. K. U.S. Patent 5,101,055.

[21] *CRC Handbook of Chemistry and Physics*, 52nd ed.; Weast, R. C., Ed.; 1971.

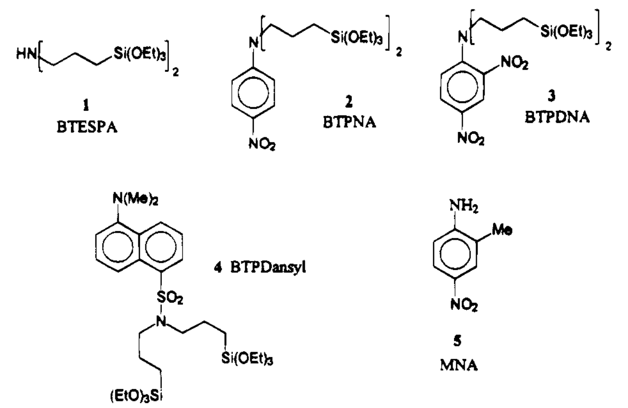

Figure 1. Structure and abbreviations for the optiphores in this study .

Example 3: N′,N′-Bis[(3-triethoxysilyl)propyl]dansyl Sulfonamide Sol–Gel Film. To a 5 mL test tube was added N′,N′-bis[(3-triethoxysilyl)propyl]dansyl sulfonamide (0.065 mL) followed by 1-butanol (ACS grade, 0.140 mL) and the solution gently agitated. Catalyst (formic acid 90%) 0.056 mL, 4 equiv of H_2O to precursor was added, and the mixture again agitated. Solutions were aged 5–10 min prior to spin coating as described in example 1 above.

Sol–Gel Film Formation. The structures of precursors used in this work appear in Figure 1. A number of attributes for the conditions of sol–gel formation with the monomeric precursors was desired. A reasonable working time before gelation (hours rather than days) was sought, yet it was desired that the final material be formed with a high degree of condensation. Transparent films were sought that were not completely polymerized at room temperature but that would cure further upon poling and heating. Catalyst systems were also desired that would not leave residual ions within the films.

It is well-known that under conditions of acid catalysis, alkoxysilane sol–gel precursors form predominately linear polymers before cross-linking, while base catalyzed systems tend to form colloidal particulate systems.[22] Previous work by our group has shown that base catalysis, such as NaOH, tends to form mesoporous materials from alkylene bridged monomers. Porosity may be undesirable in films for optical use due to possible scattering by the voids within the film. The focus was therefore placed primarily on acid catalyzed systems for film formation.

Formic acid (90%, aqueous solution) was found to be an excellent catalyst for these systems. Acetic acid fails to yield gels, most probably because the pK_a is an order of magnitude lower than formic acid. Three solvents were found to be acceptable in conjunction with formic acid catalysis; DMF, THF, and BuOH.

Thin films were formed using a monomer concentration of 0.4 M in the solvent–catalyst mixture. The system contained four to six equivalents of water from 90% formic acid. Four equivalents of water (produced by lowering the catalyst concentration) gives a more acceptable pot life for the solutions than 6 equiv, usually of the order of 30–40 min. It was necessary to age the solution for 5–10 min before high-quality films could be formed by spin casting. This "induction period" allows the preliminary hydrolysis and condensation to occur. After aging the solutions, films were prepared by spin casting onto indium tin oxide (ITO) coated glass slides on the ITO surface. Solutions of precursors must be filtered through 0.45 μm nylon filters prior to spinning to remove particulate matter for high-quality films. After spinning at 1000 rpm for 20 s, the majority of the solvent and catalyst evaporates, leaving a slightly tacky to hard sol–gel film, depending on the aging time of the coating solution prior to spin casting. Immediately after spin coating the films may be dry to the touch; however, they are readily soluble in acetone.

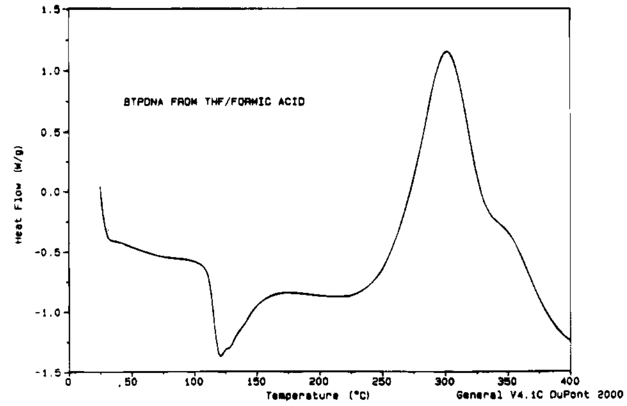

Figure 2. DSC thermogram of 0.4 M **3** formed in the THF–formic acid system.

Films cast from DMF tend to be very thin and less uniform than those from the other solvents. Films cast from THF were usually of high optical quality. However, THF solutions had more of a tendency to cloud during spin casting than DMF or butanol solutions. Films cast from butanol performed best. This solvent allows solutions to be spread onto the ITO coated slide without rapid solvent evaporation prior to spin coating. Prevention of rapid solvent evaporation aids in forming uniform films.

Curing of Spin Cast Films and Electric Field Poling. Heating films formed in DMF, butanol, or THF with formic acid catalysis to 180 °C in air induces further condensation of the matrix, rendering the film insoluble in acetone or other organic solvents. With this technique, sol–gel films can be prepared using bis-silane-functionalized optiphores *without any additional sol–gel forming components*. Spin cast films were typically cured by heating at 10 °C/min to 180 °C in air, holding at 180 °C for 30 min, cooling at 10 °C/min to 100 °C, then continued cooling without temperature control to room temperature, typically another 20 min. This temperature program was used to cure spin cast films during the poling process. Several films were cured at elevated temperatures for longer times without noticeable effect. Poling was accomplished using a needle-and-plane configuration with a 5 kV field and an approximate needle-to-plane distance of 1 cm.

Thermal Analysis of Sol–Gel Films. Figure 2 shows the DSC thermogram of a gel formed from **3** in the THF–formic acid solvent–catalyst system after air-drying for 2–3 h. The endotherm occurring between 100 and 150 °C is thought to be due to both solvent evaporation and further condensation reactions in the film. A similar thermogram was obtained for a sample aged at room temperature for 5 days, only the magnitude of the endotherm was smaller. A similar endotherm was observed in phenylene- and ethylene-bridged xerogels prepared with HCl as the catalyst and, to a lesser extent, in NaOH catalyzed xerogels. The endotherm is believed to be due to condensation of free silanols and is not observed in the pure monomer. The large exotherm above 225 °C is due to decomposition of the monomer, as verified by thermal gravimetric analysis (TGA).

An experiment was conducted to explore the effect of temperature on films formed in THF with formic acid catalysis. Six identical samples were prepared by spin coating a THF–formic acid solution of **3** on 1 × 1 in. borosilicate glass microscope slides at the same spin rate. All samples appeared dry to the touch before heating. One sample was not heated as a control, and the other samples were heated in air to 50 °C for 30 min. After 30 min, one sample was removed, and the temperature was increased at the rate of 1 °C/min. Samples were then removed at 50 min (50 °C) intervals and tested for solubility in acetone. The last sample was heated at 200 °C for an additional 50 min. Solubility was tested by vigorously rubbing the film with a cotton swab soaked in acetone. Absorbance measurements were also performed on each film in the range 300–600 nm. The results are summarized in Table 1. Films heated to at least 150 °C became insoluble in acetone. Although the acetone solubility test does not quantitatively evaluate the degree of cross-linking, it

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[22] Brinker, J. C.; Scherer, G. W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*; Academic: San Diego, CA; 1990; Chapter 3.

Table 1. Curing Data for Films Cast from 3 in THF/Formic Acid

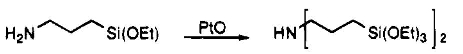
sample	temp/°C	total heating time/h	solubility	λ_{max}
1	control	0	soluble	390
2	50	0.50	soluble	388
3	100	1.33	slightly soluble	386
4	150	2.17	insoluble	384
5	200	3.00	insoluble	378
6	200	3.83	insoluble	376

serves as a useful qualitative guide. (Because the heating time for each sample is the sum of the prior heating times, the samples heated to the highest temperature also experienced the longest heating time.) The films also exhibit a decrease in the λ_{max} with increasing temperature.

Second Harmonic Generation from Sol–Gel Films. Second harmonic generation experiments were performed at the Center for Photonic Technology, Department of Electrical Engineering, University of Southern California. The experimental apparatus and experimental details for measuring the second harmonic intensity has been described recently.[23]

Results and Discussion

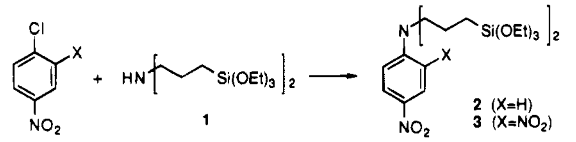
Synthesis of Sol–Gel Precursors. Compound **1** was prepared from 3-(triethoxysilyl)propylamine by refluxing with palladium black catalyst by the method of Dinh and Lo[20] (eq 1). This procedure avoids isomeric



(1)

mixtures of silyl amines that are produced upon hydrosilation of diallylamine.

A successful synthesis was developed which utilized direct nucleophilic aromatic substitution with **1**. The syntheses of **2** and **3** using this alternative method are shown in eqs 2 and 3.



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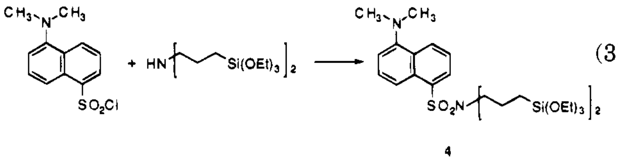

(3)

Thin-Film Formation. Although previous studies involving sol–gel-based nonlinear optical materials have employed aqueous acid catalysts,[4] phase separation was found to be a problem with **3** upon thin-film spinning when using aqueous HCl catalysts. Formic acid was found to suitable for promoting hydrolysis and condensation of the alkoxysilyl groups. Thin films could be formed from monomers **2–4** without addition of TEOS or related gel-forming monomers. In contrast, precursors containing a single triethoxysilyl group would not form uniform films from solutions even at concentrations as high as 0.8 M. Above this concentration, single phase solutions of precursor, catalyst, and solvent could not be formed.

Acidic catalysts can protonate the amine nitrogen in **2** or **3**. Protonation of the optiphore would result in charges within the film, lowering the breakdown voltage of the film and producing a change in the absorption characteristics of the film. For example, the UV absorption maxima of **3** in ethanol changes from 374 to 388 nm upon addition of HCl (Figure 3). Under conditions of thin film formation (**3**, THF, formic acid), the absorption maxima starts at 390 nm then exhibits a hipsochromic shift upon curing and heating (Table 1). This can be attributed in part to loss of formic acid (and deprotonation of **3**) as well as a reduction in the overall dielectric of the environment of the chromophore that takes place upon drying and condensation of the film.

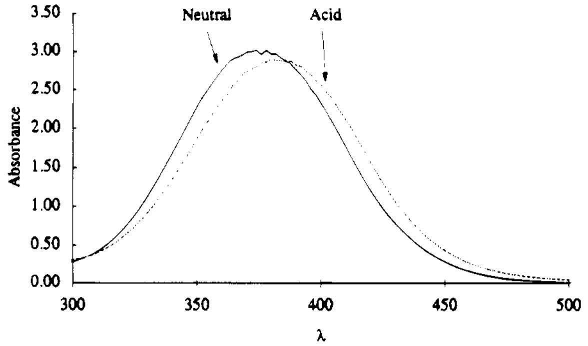

Figure 3. Absorbance spectrum of **3** in ethanol with and without added HCl.

Second Harmonic Generation. Of the three bis(triethoxysilyl) precursors that were synthesized (**2–4**) only **2** and **3** showed a significant SHG response. As a result, d_{33} coefficients are reported only for thin films prepared from these materials.

EF poling of thin films was attempted before significant cross-linking of the sol–gel matrix occurred. Thin films were prepared immediately prior to EF poling and concurrent with thermal curing of the samples. Poling was conducted while monitoring the second harmonic signal. A second harmonic signal typically was not observed until the temperature of the films reached 45–50 °C in the curing profile while poling. At this temperature an increase in signal intensity began to appear, which leveled off at 180 °C and then continued to increase upon cooling to about 100 °C. Below 100 °C and without the applied field the signal usually decreased to approximately 50% of the peak value. For samples in which d_{33} values are reported, the signal used for calculations was measured after the poling voltage had been removed for at least an hour at room temperature to allow initial randomization and charge dissipation to occur.

The bulk second-order nonlinear susceptibility d_{33} was calculated from the intensity data referenced to a Y-cut quartz crystal using the Maker fringe technique.[23,24] The electrooptic coefficients r_{33} at $\lambda = 1.3\ \mu m$ are calculated by extrapolation from the d_{33} values.[25] This method of calculation of the electrooptic coefficient for organic materials is valid because the second harmonic arises only from electronic contributions of the chromophore. Table 2 shows the calculated d_{33} and r_{33} coefficients of sol–gel materials from **2** and **3**. d_{33} coefficients for other sol–gel based-NLO materials with similar optiphores from the literature are listed for comparison. The results show that the sol–gel precursors used in this work are competitive with previous studies when pre-

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Table 2. d_{33} Coefficients of Films from 2 and 3 and Previously Published Values Utilizing Similar Optiphores

optiphore	matrix	catalyst	d_{33}/pm/V	r_{33}/pm/V	ref
3	$R(SiO_{1.5})_2$	formic acid	9–10	2–2.5	this work
2,4-dinitroaniline	SiO_2	HCl	9.1–11.7		5
2,4-dinitroaniline	$MeSiO_{1.5}ZrO_2$	H_2O	0.35–1.6		9
N-(4-nitrophenyl)-1-prolinol	$MeSiO_{1.5}ZrO_2$	H_2O	0.08		9
N-(4-nitrophenyl)-l-prolinol	SiO_2-TiO_2	unknown	10.9		11
2	$R(SiO_{1.5})_2$	formic acid	35–37	9–10	this work
lithium niobate	$LiNbO_3$		44		

cursor **3** was used. The sol–gel films formed from precursor **2** exceed previously reported values of a similar optiphore by a factor of 4.

Estimated d_{33} Using the Oriented Gas Model. As a check of the d_{33} values determined from measured SHG data, the bulk susceptibility was calculated using the oriented gas model.[23] In this model, the bulk susceptibility is given as

$$d_{33} = {}^1/_2 N\beta f\langle\cos^3\theta\rangle$$

where N is the number density of chromophores in the material, β is the second order molecular hyperpolarizability, f is the local field factor due to both the fundamental and second harmonic frequencies, and the bracketed term is the average value of the cubed cos θ term describing the orientation of the chromophore with the applied poling field.

The number density (N) for **2** (1.62×10^{21}) and **3** (1.43×10^{21}) was calculated assuming a fully hydrolyzed and condensed network using a MW of 345 g/mol and a fractional mass of the chromophore of 45% in the silsesquioxane matrix. The density was estimated to be 2.0 g/cm^3 (fused SiO_2 is 2.2 g/cm^3).

The β value used for **2** (2.15×10^{-38} m^4/V) and **3** (8.8×10^{-39} m^4/V) were literature values for *N*,*N*-dimethyl-4-nitroanaline and 2,4-dinitroanaline, respectively.[27]

The local field factor f is calculated from the refractive indexes of the fundamental and second harmonic wavelength in the film. The refractive indexes at frequencies ω and 2ω were calculated from measured dispersion data at three separate wavelengths for films **2** cast on polished silicon wafers.

An approximate d_{33} value of 10 pm/V was calculated for the sol–gel film derived from **2**, about a fourth of the measured value. A d_{33} of 3.4 pm/V was calculated for the film derived from **3**. It is emphasized that this calculation was made to determine if the experimentally determined second-order nonlinear susceptibility was reasonable. The criteria is that the calculated value should be within an order of magnitude of the experimentally determined value. It appears from the calculated d_{33} coefficients that the experimentally determined quantities are reasonable.

Temperature Stability of Poled Sol–Gel Films. Temperature stability of these poled sol–gel films was monitored by heating a poled sample in the absence of a poling voltage and monitoring the loss of the second harmonic signal. In this experiment, linear polymer systems with an optiphore show a relatively stable signal until the temperature approaches the glass transition temperature (T_g) of the polymer host, followed by a abrupt loss of the second harmonic signal.[25] In contrast, the sol–gel films derived from **3** exhibit a gradual loss of signal over the temperature range 25–200 °C when heated at 10 °C/min, with the maximum loss occurring near 125 °C (Figure 4). The sol–gel-derived materials are analogous to highly cross-linked organic polymers possessing optiphores as short side chains. These side chains are oriented by poling and upon cooling exhibit thermal stability similar to doped, un-cross-linked NLO polymer systems after EF poling.

Figure 4. Second harmonic signal loss of poled sol–gel film derived from **3** vs temperature.

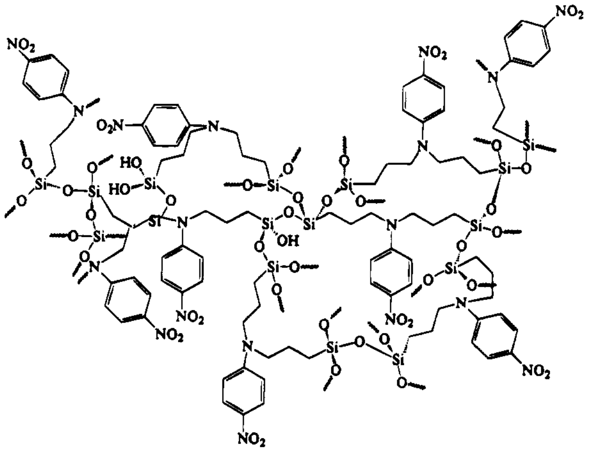

Figure 5. Conceptual sol–gel matrix composed of **2**.

The shape of the loss curve of the second harmonic signal vs temperature is indicative of a distribution of relaxation times of the oriented optiphores in the sol–gel matrix. Due to the extensive cross-linking in these systems, we do not expect a glass transition temperature within an observable experimental temperature range in these materials.

We found we could reversibly orient the optiphores within the sol–gel film that has been heated in the absence of a poling field by again heating the sample to 180 °C while poling. Figure 5 is a depiction of a sol–gel matrix from **2** with various degrees of condensation. Because the dipole of the optiphore does not lie along the axis of the repeat unit, these materials belong to the class of side-chain NLO systems. Upon inspection of the length of the repeat unit in Figure 5 in comparison to the size of the optiphore, we postulate that in these sol–gel films the free volume present between op-

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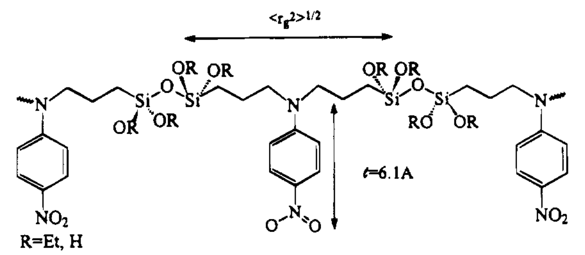
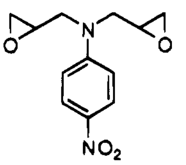


Figure 6. Mean distance between chromophores $(\langle rg^2\rangle^{1/2})$ in a sol−gel matrix, with $T1$ as the degree of condensation. The estimated length of the chromophore is also shown.

tiphores in the matrix is of sufficient size to allow some mobility of the optiphore even after curing. This mobility is due to both the large size of the siloxane linkage and the propyl chain used as a tether between the silicon and the optiphore. We suspect that optiphores larger than the free volume of the network should have improved thermal stability with respect to the poled configuration. Evidence for increased thermal stability of larger optiphores in a silicate matrix (where the free volume would be expected to be smaller than in a matrix made from the present polysilsesquioxane sol−gel precursors) has appeared in the literature.[27,28] Additionally, a system utilizing *N,N*-diglycidyl-2,4-dinitroaniline (**5**), which differs from the sol−gel precursors by a slightly shorter distance between chromophores and lack of the siloxane linkage, was shown to have reasonable temperature stability at 80 °C.[30]



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As a crude "back of the envelope" calculation, the mean distance between chromophores in our sol−gel materials can be estimated using the equation for the radius of gyration of a freely rotating chain. For a chain with tetrahedral bond angles the mean squared radius is given as

$$\langle r_g^{\,2}\rangle = 2nl^2$$

where n is the number of bonds and l the bond length when the bond angle is fixed at 109°. For the case with T^1 as the degree of condensation, the chain would appear as shown in Figure 6.

Using a bond length of 1.54 Å for the carbon sp^3 bond, 1.47 Å for the carbon−nitrogen sp^3 bond, 1.40 for the aromatic sp^2 bond,[31] 1.88 Å for the carbon silicon bond, and 1.63 for the silicon oxygen sp^3 bond,[32] the root-mean-square radius between siloxane linkages in the sol−gel network is calculated to be 7.2 Å. This calculation reflects the *mean* distance between siloxane linkages using the freely rotating chain model. A similar calculation for the epoxide based material from reference 38 is calculated to be 6 Å. The size of the 4-nitroaniline chromophore is calculated to be approximately 6.1 Å in length along the dipole axis shown in Figure 6. It is expected that as the material is heated, chain expansion should occur concurrent with increasing kinetic energy of the side chain optiphores. Higher degrees of condensation would be expected to decrease the distance between chromophores. The point of this calculation is to add weight to the postulate that the lack of thermal stability in the sol−gel materials investigated here is due to the free volume in the matrix with respect to the size of the chromophore.

Conclusions

We have demonstrated the concept of using bis(triethoxysilyl) functionalized chromophores with known second order nonlinear susceptibilities to form thin films by the sol−gel process. Formation of these films was accomplished without the addition of secondary network forming components although the films prepared from precursors **2** and **3** (Figure 1) were shown to exhibit second harmonic generation after electric field poling of the sol−gel films. The second order bulk nonlinear susceptibility (d_{33}) and electrooptic coefficient (r_{33}) were found to be 9−10 and 2−2.5 pm/V, respectively, for films prepared from precursor **3**. Respective d_{33} and r_{33} values of 35−37 and 9−10 pm/V were found for films prepared from precursor **2**. Films from precursor **2** exhibit a comparable magnitude of second order nonlinear susceptibility as lithium niobate.

We did not achieve the desired effect of increased thermal (and consequently temporal) stability of the electric field poled optiphores at temperatures in excess of 100 °C. Increasing the size of the optiphore or decreasing the alkyl chain length between the optiphore and the silane moiety both should contribute to increased thermal stability of the poled materials. It would also seem likely that the current catalyst can be modified to ensure a high degree of cross-linking. Increased thermal stability of NLO materials using main-chain NLO chromophores, formed by cross-linking across the chromophore dipole, have recently been reported.[33,34] Sol−gel precursor optiphores possessing triethoxysilyl groups at opposite ends of the dipole should yield highly cross-linked main chain NLO systems with high thermal stability. These systems have recently been evaluated.[35]

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