

Effect of Processing Parameters and Polymerization Behavior on the Nonlinear Optical Response of Sol-Gel Materials

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The effect of processing parameters on the nonlinear optical response of thin films formed using TEOS-TDP (*N*-[3-(triethoxysilyl)propyl]-2,4-dinitrophenylamine) mixtures was studied. The optical response was found to be strongly dependent upon the poling voltage, the poling temperature, the substrate resistivity, and the extent of polymerization. Due to the limited thermal stability of the films, ²⁹Si NMR was used to investigate the initial stages of the polymerization. TDP was shown to polymerize very slowly with minimal cross-linking. Even when mixed with TEOS, the degree of cross-linking between TDP and TEOS was limited.

Introduction

Over the past few years, there has been increasing interest in sol-gel technology due to its potential for developing a wide variety of materials¹⁻⁵ with unique properties. The sol-gel process is a method for producing a three-dimensional inorganic network by chemical reaction at low temperature. The usual starting materials for this process are metal alkoxides such as tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS). These alkoxides are hydrolyzed to generate intermediate species of the metal hydroxides. These species then undergo a stepwise polycondensation reaction to form a three-dimensional network.⁶⁻⁹

New hybrid materials can be made by the incorporation of organic components inside the gel network or by the polymerization of organic containing metal alkoxides.¹⁰⁻¹⁴ The organic group in the oxide network can give the structure flexibility by reducing the amount of cross-linking but can also give additional functional properties. Many organic dyes such as laser-active dyes, photochromic dyes, and optically nonlinear dyes have been incorporated in sol-gel matrices to make optically active materials.¹⁵

Thin films of organic or polymeric materials with large second-order nonlinear optical (NLO) properties are of

interest for their potential use in optical communication and data storage.^{16,17} Large second-order NLO responses in materials are achieved only for noncentrosymmetric structures because of symmetry constraints on electric-dipole processes in second-order NLO events. To break centrosymmetry, NLO chromophores inside the polymer network are oriented by poling techniques; most commonly an applied electric field.¹⁸⁻²¹

Recently the sol-gel process has been applied to fabricate NLO materials.²²⁻²⁷ The authors have been developing nonlinear sol-gel films in which nonlinear chromophores are chemically bound to a silicon atom.^{25,26} Nonlinear chromophores were incorporated into the silica network by polymerizing chromophore containing organosilanes such as *N*-[3-(triethoxysilyl)propyl]-2,4-dinitrophenylamine (TDP) and [3-(4-formylphenoxy)propyl]trimethoxysilane (FPT). Transparent sol-gel films with large coefficients for second harmonic generation (SHG) were obtained after corona poling.²⁶ By mixing the organosilane

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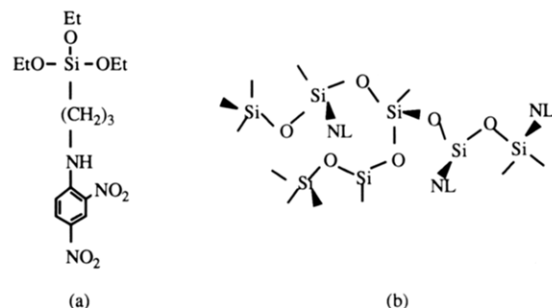


Figure 1. (a) Structure of the TDP monomer. (b) Structure of the polymerized organosilane.

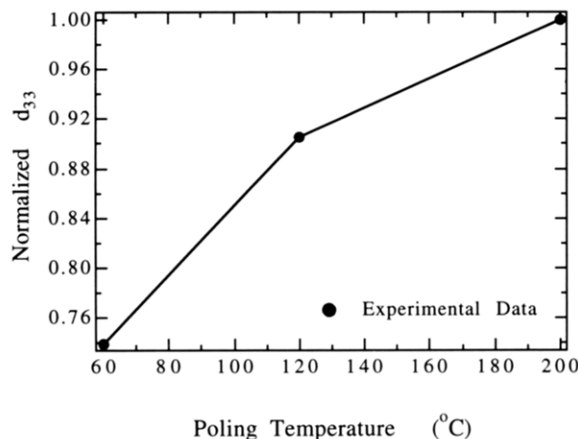


Figure 2. Variation in second harmonic intensity (relative to quartz) as a function of the poling temperature.

with tetrafunctional silanes such as TEOS, better thermal and chemical stability could be obtained.²⁵

Many process parameters are involved in fabricating NLO sol-gel films. A systematic investigation of process parameters affecting the optical and physical properties of these films is necessary to optimize processing. In the present study, we investigated those parameters involved in film preparation and poling. SHG intensities were measured against a quartz standard and chromophore thermal relaxations were studied. The polymerization behavior of the TDP and TEOS as single components or binary systems was studied using nuclear magnetic resonance spectroscopy (NMR), and results were compared with the thermal relaxation of the sol-gel films.

Experimental Procedures

Materials and Film Preparation. The SHG response of TDP-derived sol-gel films are larger than those derived from FPT.^{25,26} TDP was subsequently used as the monomer for the current work. Figure 1 shows the structure of the TDP monomer and the organosilicate gel derived from a mixture of TDP and TEOS. TDP and TEOS were purchased from Huls America Inc. and used as received. The coating solutions were prepared by mixing the silane, water, and acetone in a polyethylene beaker. Stoichiometric amounts of water were employed and the molar ratio of solvent to silane was held at 20:1. HCl was used as the catalyst in a molar ratio to the silane of 0.01:1. After several hours of aging at 30 °C, the sol was spun onto a microscope slide. The chromophore containing sol-gel film was further polymerized and poled by the corona discharge technique at high temperature. After several hours of poling the film temperature was reduced to room temperature and the electric field was removed. To investigate the effect of processing parameters on the optical nonlinearity of the film, different aging times, substrates, poling temperatures, and poling voltages were used.

SHG Measurements. SHG measurements of the sol-gel films at 532 nm were performed, immediately after poling, using a

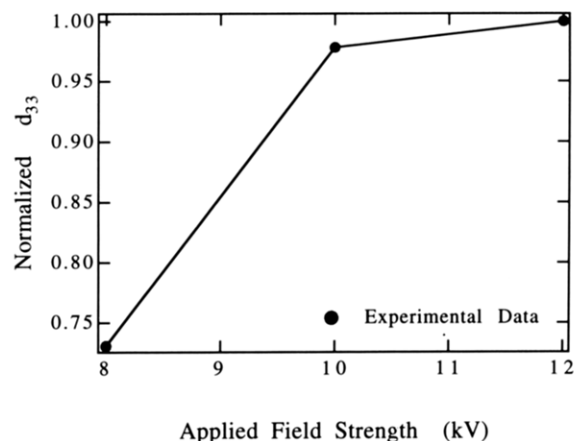


Figure 3. Variation in second harmonic intensity as a function of poling voltage.

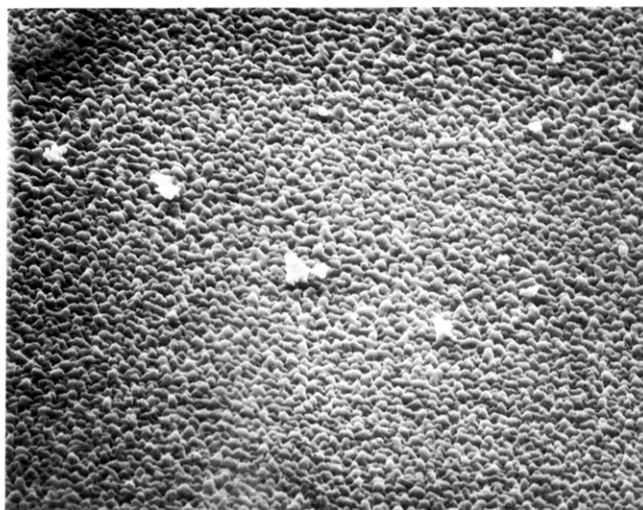


Figure 4. SEM photograph of the surface of a polycrystalline film formed during corona poling.

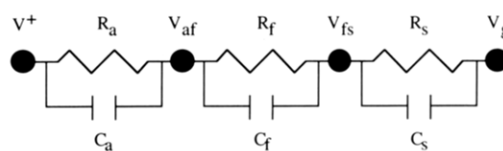


Figure 5. Electrical analogy for film-substrate system. C_a , R_a : air capacitance and resistance. C_f , R_f : film capacitance and resistance. C_s , R_s : substrate capacitance and resistance.

Q-switched Nd:YAG laser in the p-polarized geometry. A 0.5-mm-thick, Y-cut quartz crystal was used as a reference NLO material. The experimental setup for SHG measurements was based on a standard configuration described elsewhere.²⁵ The relaxation behavior of the second-order optical nonlinearity, at 60 °C, was studied by monitoring the SHG signal decay as a function of time.

²⁹Si NMR. Polymerization of the silanes was monitored by ²⁹Si nuclear magnetic resonance spectroscopy (NMR) using a Varian Unity-500 spectrometer operating at 500 MHz. Deuterated acetone containing a small amount of TMS (tetramethylsilane) as a reference was used as a solvent. The starting materials and a trace of chromium acetylacetonate, a spin relaxation agent, were mixed in a test tube maintained at 30 °C. After 5 min of mixing, about 3.5 mL of the sol was placed in a 10-mm NMR sample tube and inserted into the magnet. The acquisition time was set to 2 s with a relaxation delay of 4 s. Spectra were monitored every 30 min using a preacquisition delay.

Results and Discussion

Four processing parameters involved in NLO film fabrication were investigated: substrate type, sol aging

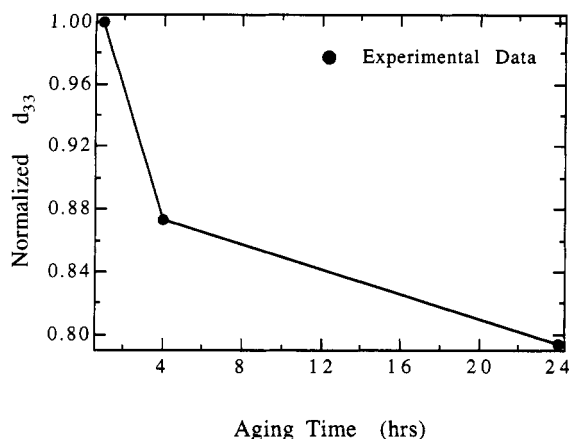


Figure 6. Variation in second harmonic intensity as a function of sol aging time.

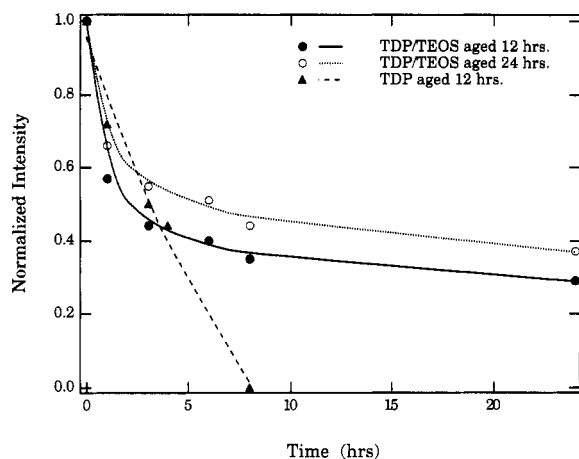


Figure 7. Relaxation behavior of the SHG signal for pure TDP and 50:50 TDP/TEOS mixtures at 60 °C.

time (extent of sol reaction), poling temperature, and poling voltage. Nominal values for these process variables were: substrate, Fisher Brand microscope slide; reaction temperature, 30 °C; aging time, 4 h; poling voltage, 10 kV; poling time, 3 h; poling temperature, 120 °C.

Effect of Poling Parameters. The second harmonic intensity, generated by the film (referenced to the quartz standard), is shown in Figure 2. The poling temperature was varied between 60 and 200 °C in these experiments. Higher poling temperatures were not feasible because the organo-silane decomposes near 230 °C.²⁶ As expected, the NLO response of the film increased with the poling temperature. At higher poling temperatures, the film is more mobile and easier to align with the field.²⁸ No falloff in ability to orient the film structure was observed at these temperatures. As in other step polymerizations, the sol-gel polymerization route produces a wide, molecular weight distribution film with a broad glass transition temperature.^{29,30} Unlike hydrocarbon-based polymers, we are unable to raise the film to a temperature high enough to overcome the aligning force produced by the electric field. The sol-gel film also tends to polymerize further upon heating and application of the field, and so the glass transition temperature rises during the poling procedure.

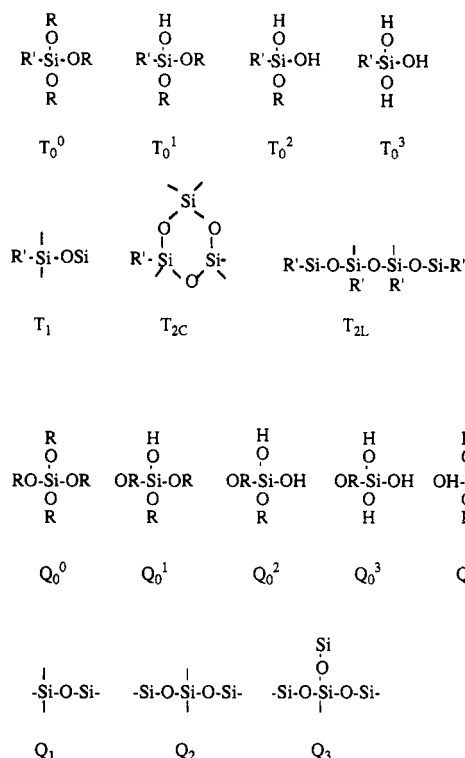


Figure 8. "T" and "Q" silicate species occurring during the polymerization of TDP and TEOS monomers.

These results suggest that the best NLO response is obtained when the poling temperature is at its highest possible value.

Figure 3 shows the effect of the electric field intensity on the NLO response of the films. Poling voltage was varied from 8 to 12 kV. As the poling voltage increased, the optical response increased, but beyond 10 kV, dielectric breakdown occurred. The high currents passing through the film and strong field force resulted in reorientation of low molecular weight components and possibly bond breakage so that the resulting film lost its transparency. The opaque regions were observed to be polycrystalline. Figure 4 shows a scanning electron micrograph of the surface of one of the polycrystalline films formed during the poling operation. The turbid area disappeared once the poling voltage was decreased, which indicated that the intensity of the electric field could be controlled to maximize the NLO response. A feedback loop continually adjusting the poling voltage as a function of the film turbidity is required. All subsequent experiments were run by controlling the poling voltage manually.

Seeking to reduce the current flowing through the film, we investigated using a high- and low-resistivity glass as the film substrate. The high resistivity glass was Corning 7059 whose resistivity at 100 °C is $10^{13.1} \Omega/\text{cm}$. The low-resistivity glass was the conventional microscope slide whose resistivity at 100 °C is $10^{6.4} \Omega/\text{cm}$. Using a high electric field, 12 kV, we found that the turbidity of our films and the optical response of the films depended on the resistivity of the substrate and the amount of catalyst used in the polymerization. High-resistivity substrates enabled very high fields (>15 kV) to be applied without causing film turbidity. Unfortunately, the NLO response was essentially nonexistent at all applied fields. Lower resistivity substrates showed larger NLO responses but with increasing film turbidity. Clearly the same forces involved in orienting the chromophores are also responsible

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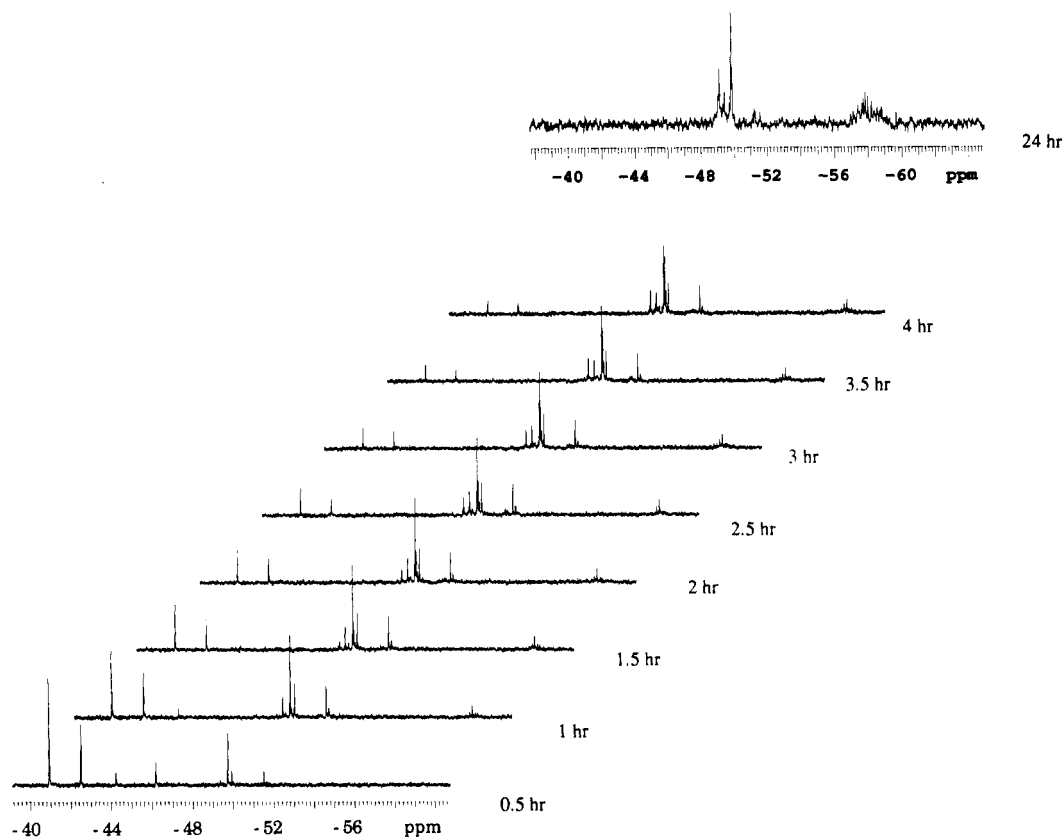


Figure 9. ^{29}Si NMR analysis of the early stages of TDP polymerization.

for main-chain movement. The use of low resistivity substrates also showed that film turbidity and process current increased with increasing catalyst concentration. Results indicate that film and substrate resistivities are important and that they must be optimized for any given sol-substrate combination.

The corona poling system accumulates charge on the surface of the film which, for a given overall voltage, produces a current through the material on the order of 1–10 μA . The film-substrate system acts as a voltage divider-capacitor network (Figure 5), and the current observed is the leakage current of the composite capacitor. If the substrate resistivity is very high, leakage currents are low, but very little voltage drop can be sustained across the film and poling is weak. Thus using high-resistivity glasses, very clear films are formed but they exhibit no, or very small, NLO response. Using lower resistivity glasses yields films with increased NLO response but also increased film turbidity because of increased current flow through the composite capacitor. Correlating the NLO response with the overall poling voltage is not accurate. The true voltage drop across the film, and the effective orientational force may be much lower than thought.

Effect of Reaction Extent. The sol-gel process is a step polymerization and so the average molecular weight and degree of crosslinking both increase geometrically with time. The extent of polymerization should play an important role in determining the optical response of the material and its environmental stability. We expect better environmental stability as the polymerization proceeds and poorer NLO response because of random addition of polymeric chains cross-linking chromophores in all possible orientations. Figure 6 shows how aging time, or the extent of polymerization, affects the NLO response of the films. Here the sols were aged at 30 °C for periods ranging from

1 to 24 h. As expected the longer the sol is aged, the lower the optical response. The falloff in response appears to stabilize after about 12 h. For increased mechanical and thermal stability, long aging times would appear to be beneficial. Unfortunately, the higher the degree of cross-linking, the more non-Newtonian the sol becomes. At long aging times, spin casting to produce thin films becomes unfeasible and another film formation technique is required.

Chromophore Relaxation. To investigate the effect of cross-linking on the thermal stability of the chromophore orientation, tetrafunctional TEOS was mixed with TDP and the partially copolymerized sol was used for film casting. The SHG signals from these films were compared with a film formed from pure TDP. Figure 7 shows the relaxation of the SHG signal of the films at 60 °C. The SHG signal from the pure TDP film disappeared after 6 h, while films formed by copolymerization with TEOS showed relatively better stability. Over 24 h at 60 °C, the SHG signal from the 50:50 TDP-TEOS film aged for 12 h decreased by 71%, while that from the film aged for 24 h decreased to 62%.

The stability of the NLO response is very dependent on the glass transition temperature (T_g) of the polymer, and the glass transition temperature depends on the degree of cross-linking.²¹ The above result shows that the extent of cross-linking for any of the TDP-based films was not high enough to maintain chromophore orientation. Better stability was obtained by copolymerizing with TEOS, but the overall stability was not satisfactory. The T_g of the pure TDP derived film was measured as 54 °C, while that of the 50:50 TDP-TEOS film was 85 °C. Higher fractions of TEOS would increase the glass transition temperature, but since both materials were polyfunctional, a 50:50 mixture should have yielded much higher T_g 's.

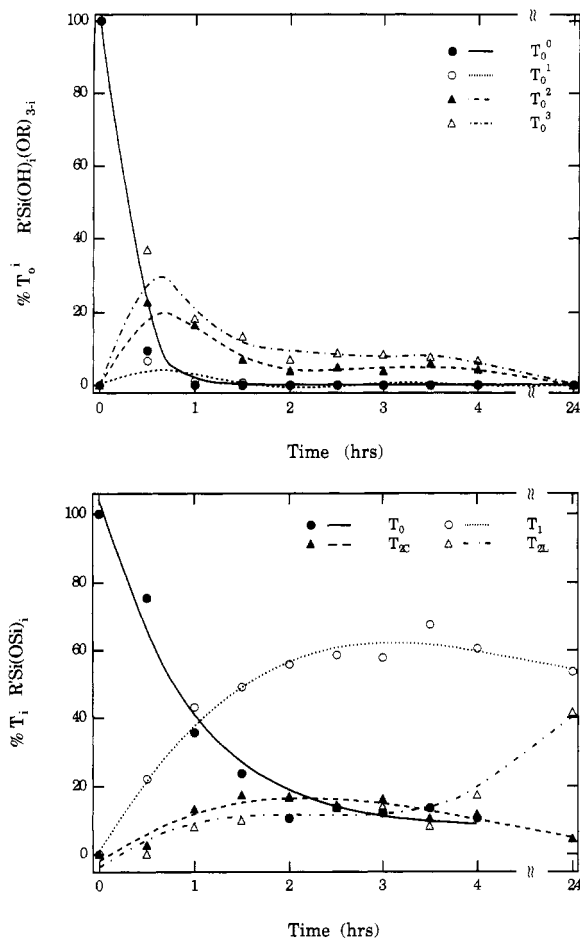


Figure 10. (a, top) Hydrolysis of the TDP monomer during the initial stages of polymerization at 30 °C [$R'Si(OR)_3:H_2O:HCl$: solvent 1:1.5:0.01:20]. (b, bottom) Evolution of condensed TDP species during the initial stages of polymerization at 30 °C [$R'Si(OR)_3:H_2O:HCl$: solvent 1:1.5:0.01:20].

The results of Figures 6 and 7 show that the degree of orientation of the nonlinear chromophore and its thermal stability are dependent on the network structure. Information on the polymerization kinetics and the siloxane bond distribution is necessary to determine the optimal reaction extent (aging time) prior to film formation.

Polymerization Behavior of TDP and TEOS. To understand the NLO response of the sol-gel polymer and its thermal stability in terms of the network structure and siloxane bond distribution, ^{29}Si NMR was used to monitor the condensation reactions of TDP and TEOS. We use conventional "T" and "Q" notations for TDP- and TEOS-derived silicate structures, respectively.³¹ The numerical subscripts for both T and Q represent the number of bridging oxygens attached to a silicon and the superscripts represent the number of OH groups attached to a silicon. Figure 8 shows, schematically, the different types of silicate structures and the symbols used to designate each species.

Figure 9 shows the ^{29}Si spectra of an acid-catalyzed sol-gel solution of TDP during the first 24 h of the reaction. TMS was used as an internal standard. The peak at -46.2 ppm corresponds to the T_0^0 unit which represents the TDP monomer. As alkoxy groups are replaced by hydroxyl groups, the peaks shift to higher frequency. Those peaks at -44.2, -42.5, and -41 ppm were easily assigned to T_0^1 , T_0^2 , and T_0^3 , respectively. On the basis of a previous

study³² the peaks around -49.9, -51.5, and -58 ppm were assigned to T_1 , T_{2c} , and T_{2L} , respectively. The peak designated for the crosslinking unit T_3 (around 64 ppm) was not observed even after 24 h of reaction at 30 °C. The amount of monomer and the extent of the hydrolysis and condensation as a function of time were determined by comparing the integrals of the T_0 , T_1 , and T_2 species NMR peaks.

Figure 10 shows the distribution of the monomeric and condensed siloxane species as a function of time. Figure 10a indicates that the TDP monomer disappeared very quickly (in less than 1 h) and that the T_0^1 , T_0^2 , and T_0^3 species were produced through the following hydrolysis reactions:

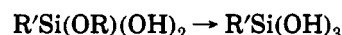
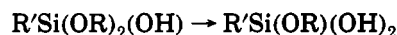
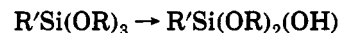


Figure 10b shows that the dimeric species, T_1 , along with some cyclic structural units, T_{2c} , were produced during the early stages of the reaction and that the linear chain species, T_{2L} , was produced at the expense of the dimeric or cyclic species. The average number of bridging oxygens per silicon was calculated based on the silicate species distribution and is shown in Figure 12b. If the condensation reaction goes to completion, the average number of bridging oxygens per silicon should reach 3. After 3 h of reaction, the number of bridging oxygens reached 1.2, which means that the condensation reaction of TDP is only 40% of the way toward completion. After 24 h, the extent of the condensation reaction reached only 48%. This shows that the sol used for the TDP film was composed of mostly dimeric and linear chain species with no crosslinking units and that these chains were of low molecular weight. The pace of the condensation reactions was probably slowed in two ways. The bulky chromophore would have provided some steric hindrance and the amine group attached to the chromophore would have made the acid catalyst less effective. These effects are clearly seen when we compare the pace of TDP condensation with that of TEOS condensation in Figure 11. This figure shows the ^{29}Si NMR spectra of an acid-catalyzed sol-gel solution of TEOS during the first 4 h of reaction at 30 °C. On the basis of previous NMR studies,^{33,34} the peak at -81.8 ppm was assigned to pure TEOS, and those peaks at -79, -76.2, -74, and -71.9 ppm were assigned to Q_0^1 , Q_0^2 , Q_0^3 , and Q_0^4 species, respectively. The peaks about -83, -93, and -101 ppm were assigned to Q_1 , Q_2 , and Q_3 species, respectively.

Figure 12a shows the distribution of the monomeric and condensed siloxane species from TEOS polymerization. Compared to TDP, the TEOS monomer, Q_0 , disappears much faster, and the Q_1 and Q_2 species appear at very early stages of the reaction. The Q_3 species, which represents the cross-linking units, increases slowly yet is appreciable after only 1 h. The average number of bridging

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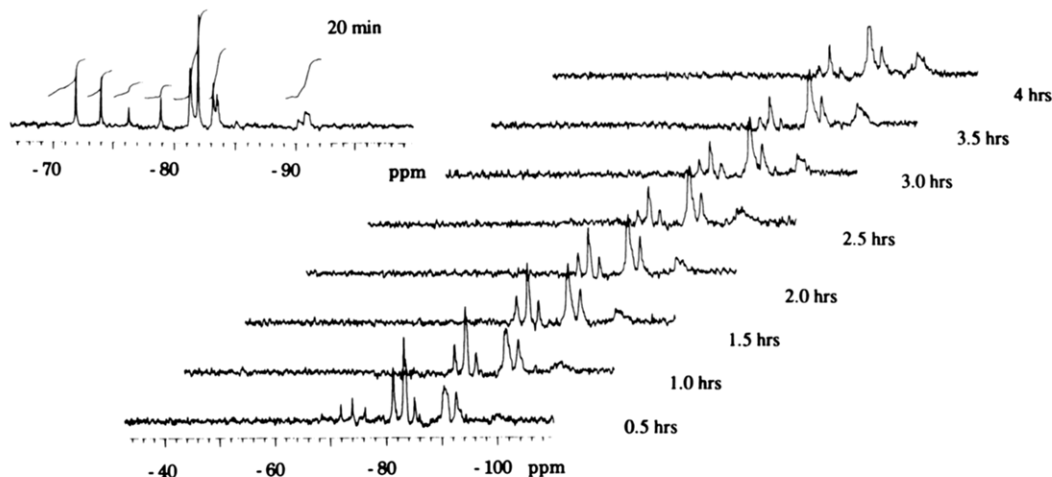


Figure 11. ^{29}Si NMR analysis of the early stages of TEOS polymerization.

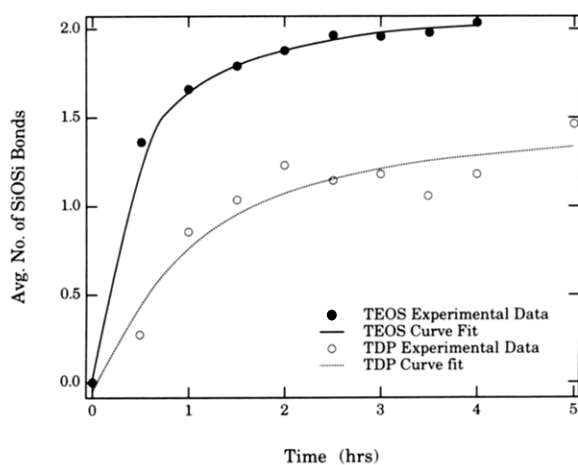
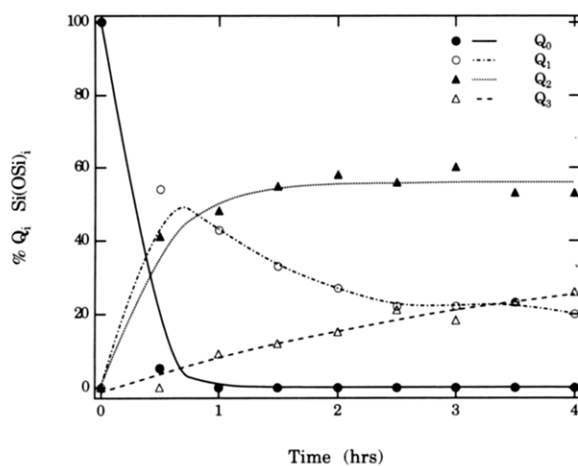
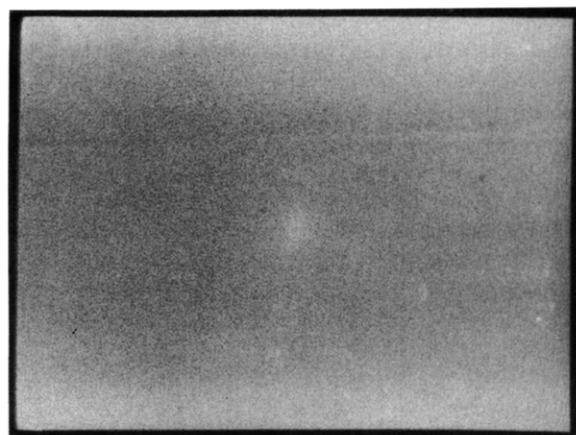


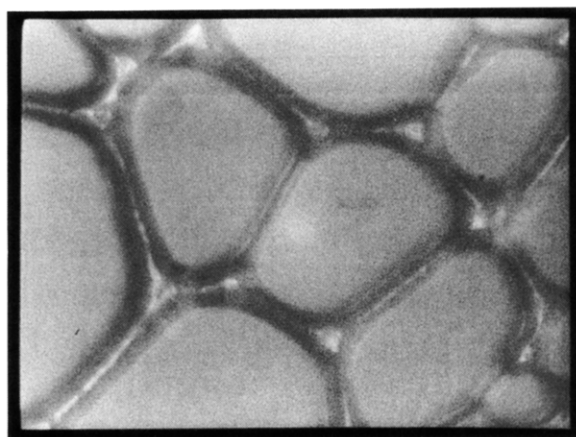
Figure 12. (a) Evolution of condensed TEOS silicate species during the initial stages of polymerization at 30 °C [$[\text{Si}(\text{OR})_4:\text{H}_2\text{O}:\text{HCl}:\text{solvent}] = 1:2:0.01:20$]. (b) Average number of SiOSi bonds formed per Si monomer during TDP and TEOS polymerization.

oxygens per silicon was calculated based on the silicate distribution and is shown in Figure 12b. If the condensation reaction goes to completion, this number should approach 4. After 4 h the average number of bridging oxygens per silicon reached 2, indicating predominantly linear chains and a reaction extent already reaching 50%, 6 times faster than the TDP reaction.

Copolymerization of TDP and TEOS. The results of our individual kinetic studies suggested that the most profitable route for producing stable, highly responsive films would be to add hydrolyzed TDP to partially



(a)



(b)

Figure 13. (a) TDP-TEOS copolymer formed by mixing both reactants at the start of the polymerization. (b) TDP-TEOS copolymer formed by adding TDP to prepolymerized TEOS.

polymerized TEOS. TDP would act as the cross-linking agent. Hydrolyzed TDP was added to partially polymerized TEOS (average number of bridging oxygens = 2) to form a 50:50 mixture of TEOS and TDP. After aging for 1–2 h (4 h total reaction time at 30 °C), the mixed sol was spun to make film. Extensive phase separation was observed with TDP being the continuous phase and TEOS being the dispersed phase. This indicated poor incorporation of TDP into the TEOS backbone. The phase separation did not occur when both TDP and TEOS were mixed at the start of the reaction.

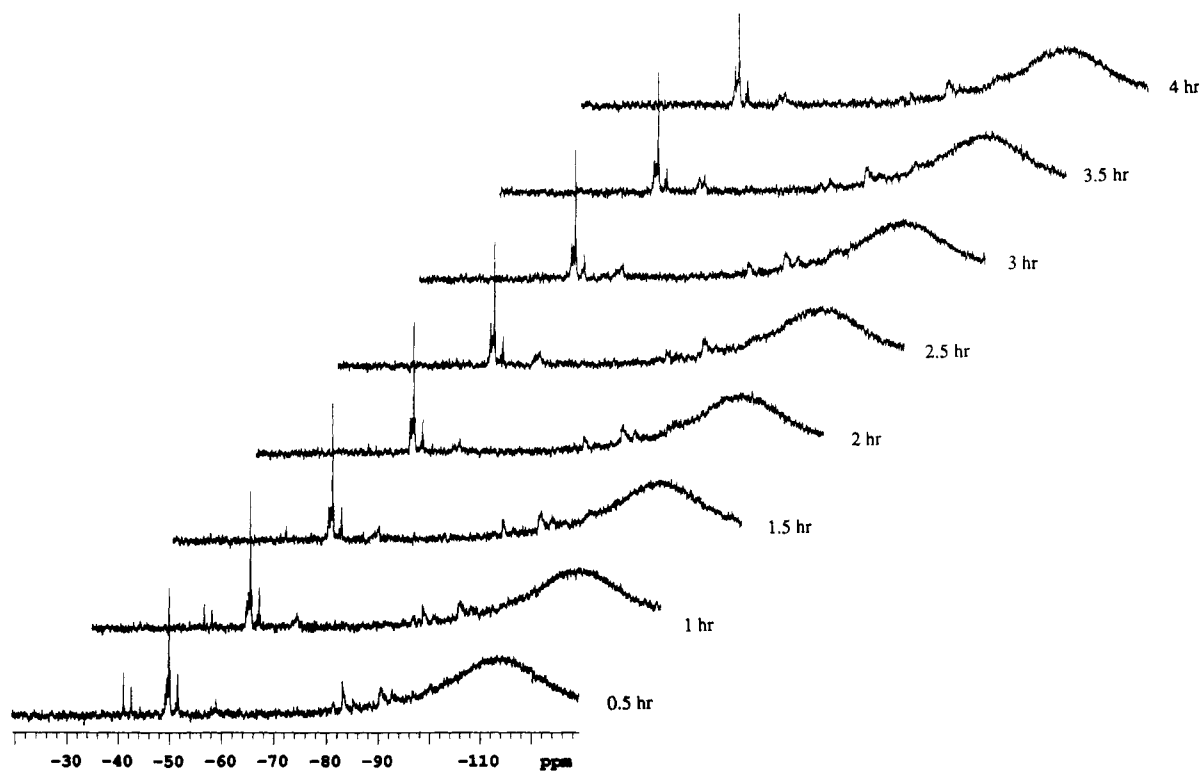


Figure 14. ^{29}Si NMR analysis of the early stages (0–4 h) of TDP–TEOS copolymerization.

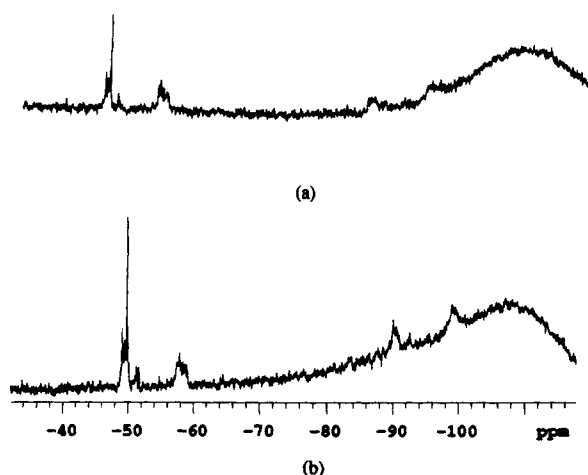


Figure 15. ^{29}Si NMR analysis of TDP–TEOS copolymerization: (a) 12-h reaction time; (b) 24-h reaction time.

Figure 13 shows the surface of the spin cast sol-gel film when hydrolyzed TDP was added to the TEOS after (a) 30 min of reaction (TEOS), and (b) after 4 h of reaction (TEOS). A uniform copolymer was formed in (a), but a phase separated system is seen in (b). To investigate what occurs during the copolymerization, ^{29}Si NMR spectra for the mixed monomer solution were obtained. Figure 14 shows the spectra for the first 4 h of reaction and Figure 15 shows spectra after 12 and 24 h of the reaction. In this system, the TDP and TEOS were mixed at the start of the reaction. At the earliest stages of the reaction, the TDP monomeric species, T_0' , are still appreciable while little or no TEOS monomers are present. The hydrolysis of TEOS occurs much faster than TDP and the rate appears unaffected by the presence of TDP. As the reaction proceeds, it appears that both monomers are unaffected by the presence of the other. After 4 h of reaction, TDP is composed of dimeric, cyclic, and linear units, while TEOS

has become predominantly linear chains with some minor amount of cross-linking.

Figure 15 indicates that many more cross-linking units were formed from the TEOS portion of the mixture after 24 h of reaction, but no cross-linking units were appreciable from the organosilane group. Even though the overall degree of cross-linking was increased by adding TEOS, there is no indication that any true copolymerization occurred or that TDP was incorporated into the TEOS backbone. This may indicate why the glass transition temperatures of the mixture were so low. The polymerization of each silane was unaffected by the other's presence, so if the amine on the chromophore was reducing the effectiveness of the acid catalyst, it was only acting to retard the rate of TDP polymerization, not the rate of TEOS polymerization.

Conclusions

Second-order nonlinear optical materials were fabricated by sol-gel processing using an organosilane, TDP, and TEOS. The intensities of the second harmonic signal of the films were dependent on various process parameters such as the type of substrate, the poling temperature, the extent of reaction, and the poling voltage. The film formation and thermal stability of the SHG signal was dependent on the silicate structure and ^{29}Si NMR was used to investigate this.

^{29}Si NMR data show that the sol derived from the organosilane, TDP, was mainly composed of dimeric species and linear chains with no cross-linking units, even after reaction for 24 h at 30 °C. By contrast evidence of cross-linking in TEOS occurred after only 1 h of reaction. It was postulated that the bulky chromophore attached to silicon retarded the condensation reaction and that after spinning to form a thin film, no further cross-linking could occur. The linear structure of the siloxane chains coupled

to their low molecular weight resulted in poor thermal stability of the optical response. Addition of TEOS provided better stability but still not within potential limits. The addition of TDP as a second cross-linking agent to partially polymerized TEOS resulted in phase separation, and homogeneous films were obtained only when TDP and TEOS were mixed at the early stage of the reaction.

While the overall degree of cross-linking was increased by adding TEOS to TDP, the copolymerization proceeded in such a way that cross-linking occurred only among the TEOS derived species and the TDP derived species remained as linear units. Though the films made from

TDP-TEOS-derived sols had better thermal stability, they were still not satisfactory because cross-linking between TDP and TEOS units was poor. Much more quantitative work on the polymerization behavior and kinetics of organo-silanes and the sol-gel processing parameters is necessary before commercially viable sol-gel-derived NLO materials can be made.

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