

Thermal stability of NLO sol–gel networks with reactive chromophores

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A series of transparent silica films with organic chromophores as side chain, main chain or cross-linking agent were prepared by the sol–gel process. The resulting films heated at 100–120°C under high corona field exhibited $d_{33} = 16\text{--}29 \text{ pm V}^{-1}$ in Maker-fringe measurement. The cross-linking type chromophore exhibited optimum poling orientation stability. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The sol–gel process for non-linear optical (NLO) silica films has received increasing attention^{1–4}. These compounds demonstrate excellent thermal stability and large optical non-linearity. The formation of silica glass using a sol–gel route has been studied for several years⁵. The reaction involves the hydrolysis of an alkoxy silane and the water and alcohol condensation of the silanol, leading to the formation of three-dimensional silicon oxide polymer networks.

The choice of sol–gel technology to prepare non-linear optical films has the following merits: (1) the solution properties of the sols allow relatively easy formation of the thin film on various substrates; (2) the gel formation during the chemical reaction allows processing at a rather low temperature. However, like other organic guest–host systems, doped sol–gel composites with high chromophore content suffer from phase separation. These chromophores tend to align themselves with an anti-parallel crystal lattice (in the case of the chromophore with centrosymmetric structure), thereby revealing no macroscopic second harmonic generation. To alleviate these problems, organic chromophores attached to the oxide backbone of gels by chemical linkage have been developed^{1–4,6–8}. All such experiments show highly promising results. In addition, they also show better orientational stability after electric field poling is applied to the specimen. Although various chemical methods have been proposed, temporal stability of the second-order non-linear optical properties of the sol–gel materials is achieved far below the decomposition temperature of the dry gels determined by t.g.a.

In this study, attempts were made to synthesize a series of chromophores with different linking sites with the silicon oxide matrix. Their temporal behaviour was evaluated. The main chain structures of the dry gel were comparable, so the difference in the long-term stability of second harmonic response should depend on the thermal stability of the chromophore and types of linkage.

EXPERIMENTAL

Preparation of chromophores

2,2'-(4-[(4-nitrophenyl)azo]phenyl)imino-bisethanol (DR-19). The NLO chromophore DR-19 was synthesized by the diazonium coupling reaction according to previous literature⁹. *p*-Nitroaniline (6.9 g, 50.0 mmol) was dissolved in 18% hydrochloride solution (30 mL) and diazotized with sodium nitrite (3.45 g in 5 mL of H₂O, 50 mmol) at 0–5°C. The mixture was then added dropwise to bis(hydroxyethyl) aniline (8.9 g, 50.0 mmol) in concentrated hydrochloride solution (25 mL) at 0–5°C. The mixture was stirred for another 1 h; saturated sodium acetate solution was then added to neutralize the mixture. The deep red precipitate was collected and washed several times with water. Recrystallization from ethanol yielded DR-19: 14.02 g, yield 85%, m.p. 198°C.

¹H n.m.r. (DMSO-d₆): $\delta = 8.32$ (2H, d, $J = 8.9$ Hz); 7.95 (2H, d, $J = 8.9$ Hz); 7.81 (2H, d, $J = 9.2$ Hz); 6.93 (2H, d, $J = 9.2$ Hz); 4.90 (2H, s); 3.61 (8H, s). U.v.–vis (acetone): $\lambda_{\text{max}} = 460$ nm.

2-[(2-hydroxyethyl)oxy]-4-nitroaniline (1). 2-Chloroethanol (2.60 g, 32.4 mmol) was added to a refluxed solution containing 2-amino-5-nitrophenol (5.0 g, 32.4 mmol) and KOH (1.82 g, 32.4 mmol) in 30.0 mL of ethanol. The mixture was refluxed for 8 h and then cooled to room temperature. The solvent was removed on a Rotovap. The product was then purified by silica gel column chromatography using EA–*n*-hexane (1:1 v/v) as eluent, followed by recrystallization from EA–*n*-hexane: 3.72 g, yield 58%.

¹H n.m.r. (CDCl₃): $\delta = 7.93$ (1H, d, $J = 8.8$ Hz); 7.71 (1H, s); 6.67 (1H, d, $J = 8.8$ Hz); 4.62 (2H, s); 4.24 (2H, t, $J = 4.5$ Hz); 4.11 (2H, t, $J = 4.5$ Hz). Molecular mass: calcd, 198.0641; found, 198.0639.

*3-[(2-hydroxyethyl)oxy]-*N,N*-diethylaniline (2)*. 2-chloroethanol (3.06 g, 38.0 mmol) was added to a refluxed solution containing *N,N*-diethyl-*m*-aminophenol (6.28 g, 38.0 mmol) and KOH (2.24 g, 40.0 mmol) in 30.0 mL of ethanol. The mixture was refluxed for 24 h and then cooled to room temperature. The solvent was removed on a Rotovap and the

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residue was dissolved in dichloromethane and washed with water. The organic layer was dried over MgSO_4 . Finally, the solvent was removed on the Rotovap, producing an extremely viscous oily liquid: 4.68 g; yield 60%.

^1H n.m.r. (CDCl_3): $\delta = 7.16$ (1H, t, $J = 8.2$ Hz); 6.37 (3H, m); 4.09 (2H, t, $J = 4.5$ Hz); 3.38 (2H, t, $J = 4.5$ Hz); 3.38 (4H, q, $J = 7.0$ Hz); 1.20 (6H, t, $J = 7.0$ Hz). Molecular mass: calcd, 209.1417; found, 209.1418.

2, 2'-Bis[(2-hydroxyethyl)oxy]-4-diethylamino-4'-nitroazobenzene (Ch2). Compound 1 (1.98 g, 10.0 mmol) was dissolved in 5 mL of conc. sulfuric acid and diazotized with sodium nitrite (0.69 g in 5 mL of H_2O , 10 mmol) at 0–5°C. The mixture was then added dropwise to compound 2 (2.09 g in 15 mL of 2N aqueous NaOH, 10.0 mmol) at 0–5°C. The reaction mixture was stirred overnight at room temperature. Saturated sodium acetate solution was then added to neutralize the mixture. The deep red precipitate was collected and washed several times with water. Recrystallization from chloroform yielded Ch2: 1.50 g, yield = 36%, m.p. 68°C.

^1H n.m.r. (CDCl_3): $\delta = 7.89$ (1H, d, $J = 9.0$ Hz); 7.83 (1H, s); 7.79 (1H, d, $J = 9.1$ Hz); 7.64 (1H, d, $J = 8.8$ Hz); 6.45 (1H, d, $J = 8.9$ Hz); 6.15 (1H, s); 4.30 (2H, t, $J = 4.2$ Hz); 4.25 (2H, t, $J = 4.3$ Hz); 4.96 (4H, m); 3.50 (4H, q, $J = 7.0$ Hz); 1.28 (6H, t, $J = 7.0$ Hz). U.v.-vis (acetone): $\lambda_{\text{max}} = 515$ nm. Molecular mass: calcd, 418.1854; found, 418.1852.

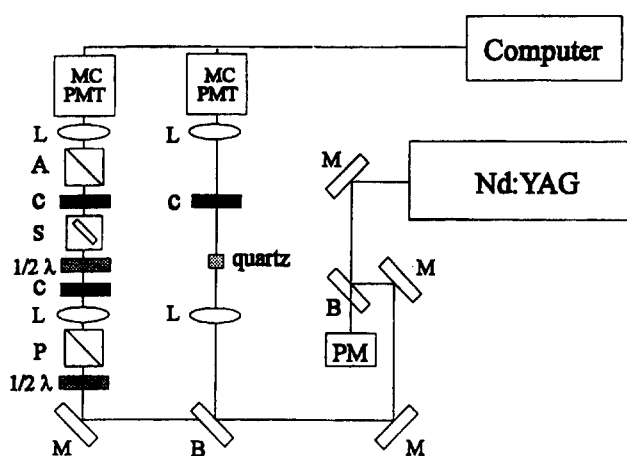
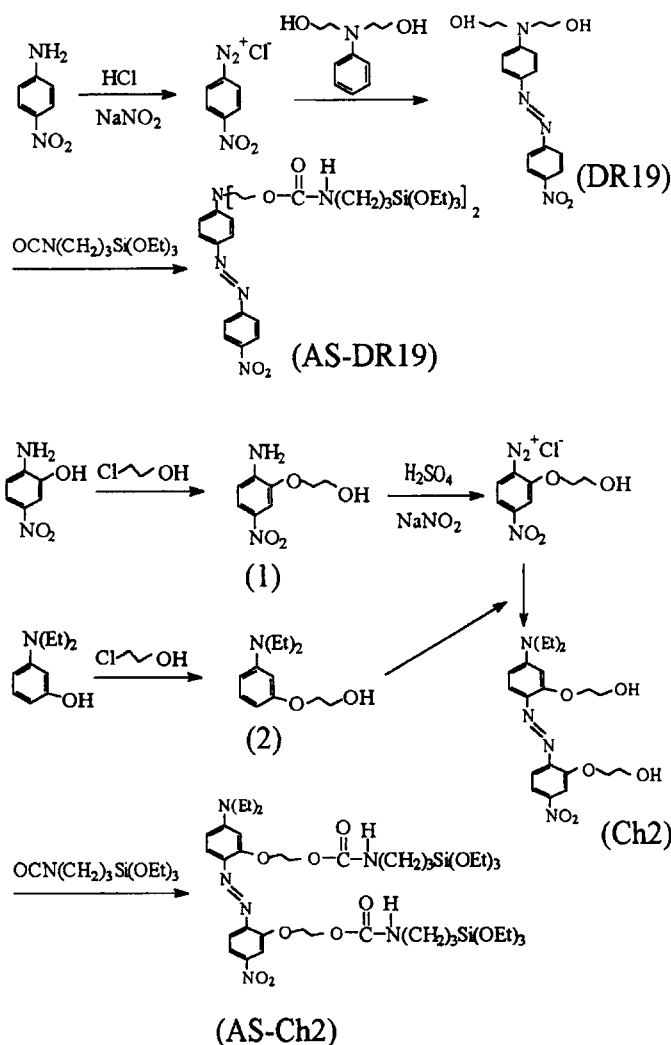


Figure 1 Schematic representation of the experimental setup for SHG measurements. M, mirror; B, beam splitter; P, polarizer; A, analyser; PM, power meter; S, sample; L, lens; C, coloured glass filter; MC, monochromator; PMT, photomultiplier

2, 2'-[4-[2-(2-hydroxyethyl)oxy-(4-nitrophenyl)azo]-phenyl] imino-bisethanol (Ch3). Following the same procedure as described to prepare Ch2, Ch3 was obtained as red powder from compound 1 and bis(hydroxyethyl)aniline. Recrystallization from CHCl_3 -EA yielded Ch3: yield = 41%, m.p. 78°C.

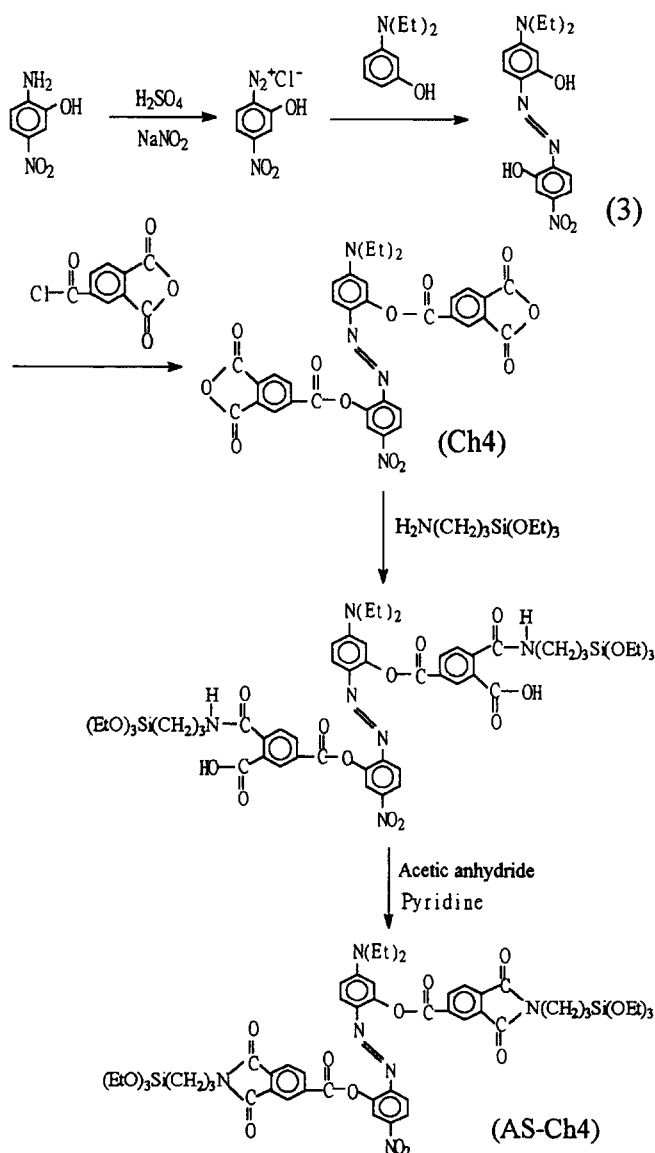
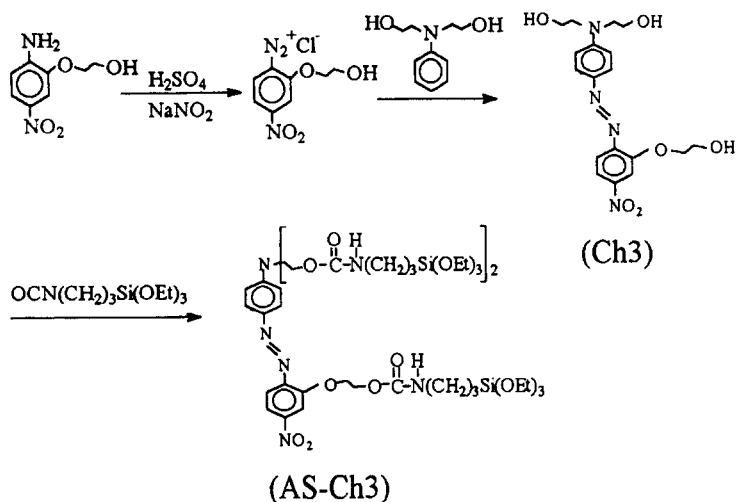


Scheme 1 Chemical structures of starting materials and reaction sequence

^1H n.m.r. (DMSO- d_6): δ = 7.98 (1H, s); 7.89 (1H, d, J = 8.8 Hz); 7.79 (2H, d, J = 9.1 Hz); 7.62 (1H, d, J = 8.8 Hz); 6.89 (2H, d, J = 9.2 Hz); 4.97 (1H, s); 4.87 (2H, s); 4.30 (2H, t, J = 4.85 Hz); 3.81 (2H, s); 3.58 (8H, s). U.v.-vis (acetone): λ_{max} = 488 nm. Molecular mass: calcd, 390.1541; found, 390.1539.

4-Diethylamino-2,2'-dihydroxy-4'-nitroazobenzene (3)

Compound 3 was synthesized by the diazonium coupling reaction according to previous literature¹⁰. In a typical reaction, 3.72 g of 2-amino-5-nitrophenol (24.17 mmol) was dissolved in 15 mL of conc. sulfuric acid and 15 mL of water; 1.67 g of sodium nitrite dissolved in 20 mL of



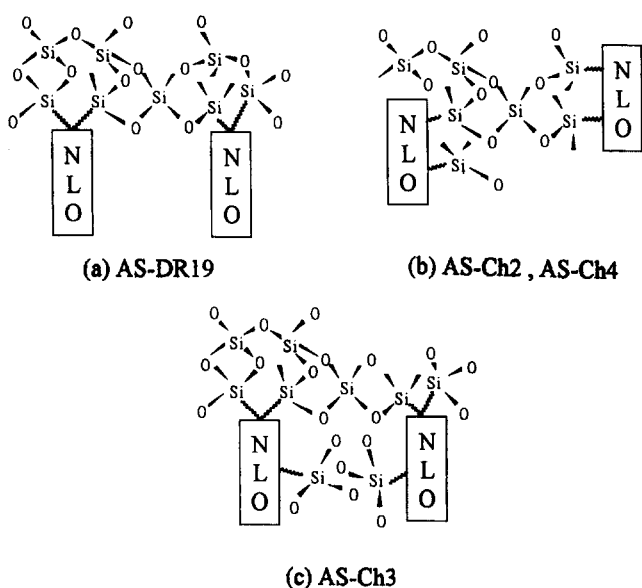


Figure 2 Structures of the organosilicate gels

water was slowly added at $< 5^{\circ}\text{C}$. To the cooled solution, 23 mL of 2N aqueous NaOH with 4.00 g of *N,N*-diethyl-*m*-aminophenol was added and the reaction mixture was stirred overnight at room temperature. The product, 3, was filtered, washed with water and dried under vacuum at 60°C . This dye was purified by recrystallization from chloroform: 5.18 g, yield = 65%, m.p. 175°C .

^1H n.m.r. (CDCl_3): $\delta = 13.48$ (1H, s); 12.61 (1H, s); 7.81 (2H, s); 7.57 (1H, d, $J = 9.3$ Hz); 7.38 (1H, d, $J = 9.0$ Hz); 6.44 (1H, d, $J = 9.4$ Hz); 6.12 (1H, s); 3.51 (4H, q, $J = 7.1$ Hz); 1.29 (1H, t, $J = 7.1$ Hz). U.v.-vis (acetone): $\lambda_{\text{max.}} = 530$ nm.

2,2'-Bis[anhydric trimellitoxy]-4-diethylamino-4'-nitroazobenzene (Ch4). To a solution of compound 3 (1.65 g, 5.0 mmol) and trimellitic anhydride chloride (2.316 g, 5.0 mmol) in THF (dry) 20.0 mL, triethylamine (1.11 g, 11.0 mmol) was added. The mixture was stirred for 2 h at

room temperature and then refluxed for 8 h. After the mixture was cooled, the resulting precipitate was filtered and the solvent was removed by evaporation. The red solid obtained was recrystallized from chloroform (dry) which yielded Ch4: 2.64 g, yield = 78%, m.p. 108°C .

^1H n.m.r. (DMSO-d_6): $\delta = 7.98$ (1H, s); 7.89 (1H, d, $J = 8.8$ Hz); 7.79 (2H, d, $J = 9.1$ Hz); 7.62 (1H, d, $J = 8.8$ Hz); 6.89 (2H, d, $J = 9.2$ Hz); 4.97 (1H, s); 4.87 (2H, s); 4.30 (2H, t, $J = 4.85$ Hz); 3.81 (2H, s); 3.58 (8H, s). U.v.-vis (acetone): $\lambda_{\text{max.}} = 507$ nm. Molecular mass: calcd, 678.1235; found, 678.1234.

Preparation of alkoxy silane containing chromophores

In a typical reaction, As-DR 19, As-Ch2 and As-Ch3 were prepared by refluxing for 48 h in THF solution containing 3-isocyanatopropyltriethoxysilane and DR-19, Ch2 or Ch3, with a small amount of triethylamine as catalyst. The product was isolated by vacuum evaporation of the solvent. The product was then dissolved in THF, precipitated from *n*-hexane and dried under vacuum. As-Ch4 was prepared by refluxing in THF solution containing 3-aminopropyltriethoxysilane and Ch4, at a molar ratio of 2:1. The mixture was stirred at room temperature for 6 h. Pyridine and acetic anhydride were then added to the mixture, which was refluxed for 48 h. The solvent was removed under reduced pressure and used for the next sol-gel step without further purification.

Measurements

Infrared spectra were recorded on a Perkin-Elmer 1600 spectrophotometer. U.v.-vis absorption spectra were measured by transmission on a Hitachi U-2000 spectrophotometer. ^1H n.m.r. was conducted with a Bruker AC-F300 spectrometer with TMS as internal reference. Thermogravimetric analysis was performed with a Du Pont TGA-951 thermal analyser at $10^{\circ}\text{C min}^{-1}$ under N_2 .

Second harmonic generation (SHG) measurements were taken using a standard Maker-fringe technique. A diagram of the experimental setup is shown in Figure 1. The light source was an injection-seeded Q-switched Nd:YAG laser

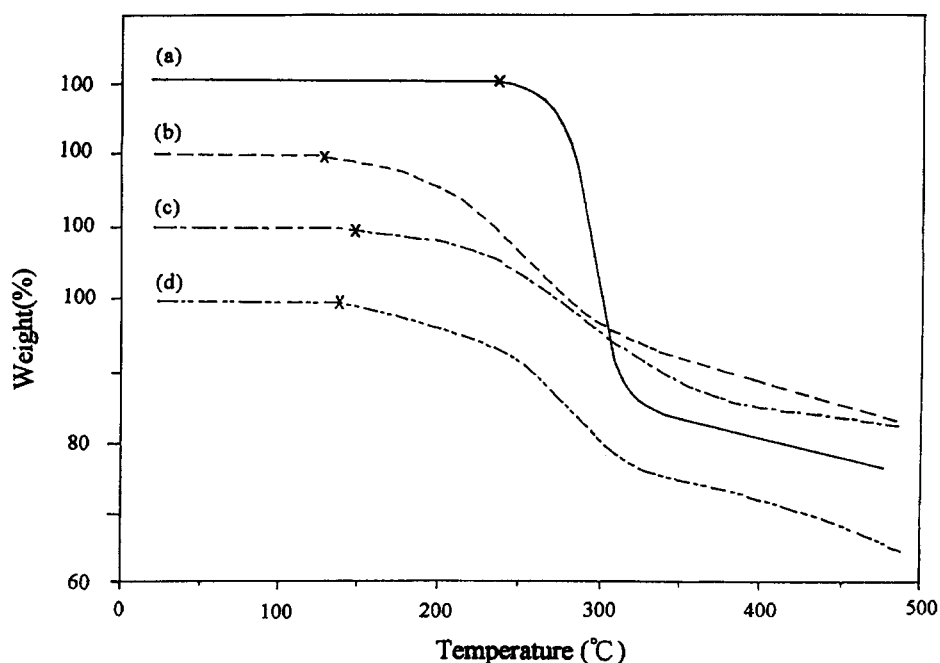


Figure 3 T.g.a. trace of chromophores: (a) DR-19; (b) Ch2; (c) Ch3; (d) Ch4

at a wavelength of 1.064 μm . The typical energy per pulse was < 10 mJ. The transmitted beam was passed through coloured glass filters and a monochromator to eliminate all traces of the fundamental light. The SHG signal intensity was measured by a photomultiplier tube. The second harmonic coefficients of the poled polymers were then calculated for comparison with the second harmonic intensity generated by a quartz sample.

RESULTS AND DISCUSSION

The design involves more than two reactive sites in the azo compounds at either one end or both ends. Chemical structures of the starting materials and the reaction sequence are shown in *Scheme 1*. As observed, DR-19 has two hydroxyl groups in the electron-donating part of the chromophore. Ch2 and Ch3 have two and three hydroxyl groups on both sides of the chromophore. To enhance the thermal stability, Ch4 contains two anhydride groups on both sides of the chromophore which can be further converted into an imide linkage. Except DR-19, all the compounds contain extra electron-donating groups attached to the chromophores. These donating groups will affect the dipole moment in both the ground state and excited state. The U.v.-vis absorption peaks (acetone as solvent) for DR-19, Ch2, Ch3, and Ch4 are at 460, 515, 488 and 507 nm.

Scheme 1 also outlines the approach for synthesizing alkoxy silane containing chromophores. As-DR19, As-Ch2 and As-Ch3 were synthesized by coupling DR-19, Ch2, Ch3 with 3-isocyanatopropyltriethoxysilane. The isocyanate group is well known to have a characteristic i.r. absorption peak at 2270 cm^{-1} . Therefore the reaction was curtailed when the absorption peak had diminished. As-Ch4 was prepared by treating Ch4 with 3-aminopropyltriethoxysilane. Amic acids have two strong i.r. absorption peaks around 1730 cm^{-1} for amide carbonyl groups and 1650 cm^{-1} for carboxylic carbonyl groups. After adding acetic anhydride and pyridine, these peaks markedly decreased and the two characteristic peaks of the imides at 1785 and 1728 cm^{-1} simultaneously appeared¹².

To prepare the coating solution, the alkoxy silane terminated chromophores were mixed with tetraethoxy silane (TEOS) and water at 0.1:1:2.2 molar ratio in ethanol. A small amount of 1N aqueous HCl was also added as a catalyst. The ethanol solution (10%) was stirred at room temperature for several days to increase the viscosity. The viscous solution was then filtered through a $0.22\text{ }\mu\text{m}$ Teflon filter before spin-casting on to transparent ITO (indium tin oxide) glass. The coated films were then vacuum-dried at room temperature for 6 h to remove the solvent. *Figure 2* shows the structures of the organosilicate gels.

The thermal properties of the chromophores and films were determined by thermogravimetric analysis (t.g.a.). The initial decomposition temperatures of DR-19, Ch2, Ch3, and Ch4 are 235, 125, 140 and 132°C respectively, as *Figure 3* shows. However, the organosilicate film As-DR19, As-Ch2, As-Ch3 and As-Ch4 exhibited higher decomposition temperatures (257, 164, 190 and 196°C), as *Figure 4* shows. The temperatures increased by ~ 20 – 60°C . To achieve optimum poling efficiency, conventional specimens are usually poled at a temperature close to the glass transition temperature (T_g) for a long period. However, no T_g could be observed in the organosilicate films, owing to the high T_g of the silica matrix ($> 1000^\circ\text{C}$). In the sol-gel silica film system, the polycondensation reaction is extremely slow at room temperature. The coated solutions are composed of partly condensed organosilicates. This is why the chromophores of the cross-linking type organosilicate films are still able to align under the electric field. To increase the reaction rate, an elevated temperature is always chosen. Therefore the chromophore must not be decomposed under such an atmosphere. For this reason, the u.v. absorption of the organosilicate film at different temperatures was chosen to assess the long-term ageing properties. *Figure 5* shows the temporal behaviour of the organosilicate films held at different temperatures for 8 h. According to this figure, the maximum temperature that can be tolerated is far below the decomposition temperature obtained by t.g.a.

To compare the structural effects on the thermal

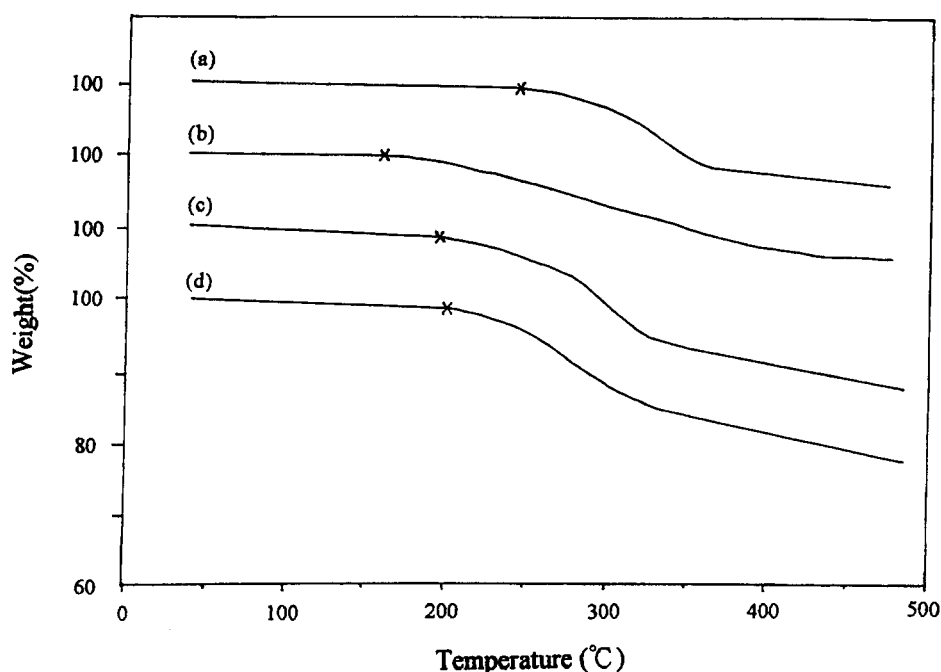


Figure 4 T.g.a. trace of organosilicate films: (a) As-DR19; (b) As-Ch2; (c) As-Ch3; (d) As-Ch4

behaviour of the organosilicate film, the As-Ch2, As-Ch3 and As-Ch4 films were heated to $\sim 100^\circ\text{C}$ (before the chromophore started to degrade) and poled using a corona discharge apparatus for 9 h. The voltage applied to the corona wire was maintained at 6 kV, with a current of $1.5 \mu\text{A}$. The substrate was cooled under an applied field. In addition, As-DR19 was poled under the same conditions at 120°C .

The U.v.-vis absorption spectra of the films before and after poling are shown in Figure 6. The absorption intensity decreased due to the alignment of the chromophores along the poling field. The order parameter is defined by $\Phi = 1 - A_\perp/A_0$, where A_\perp and A_0 are the absorbances of the poled and unpoled films respectively¹³. Theoretically it can be used to estimate the degree of chromophore orientation. The values for As-DR19, As-Ch2, As-Ch3 and As-Ch4 are 0.29, 0.28, 0.16 and 0.20 respectively. Since As-Ch3 has the highest degree of cross-linking density (functionality equal to 3), it is more difficult to pole than the other samples.

Myers *et al.*¹⁴ found that the glass also showed significant SHG response when the plate was poled at a temperature $>250^\circ\text{C}$. To assess the effectiveness of the poling

procedure, glass plate and TEOS coated film were prepared and poled at 120 and 200°C under the same electric field. Our results showed no SHG response. The main chain structures of the matrix and chromophore contents of these four types of organosilicate film are nearly identical. Hence the relaxation rate of orientational order in these systems depends on the thermal stability of the chromophores and rotational movement of the chromophores. Our systems can be divided into three categories: (1) side chain type, As-DR19; (2) main chain type, As-Ch2 and As-Ch4; (3) cross-linking type, As-Ch3. Regardless of the thermal stability of the chromophore, the retention of SHG response is estimated to be in the order $\text{As-Ch3} > \text{As-Ch4} > \text{As-Ch2} > \text{As-DR19}$. Figure 7 shows the temporal behaviour of the organosilicate films. Indeed, exactly the same trend was observed before the chromophores started to decompose ($T < 100^\circ\text{C}$). At a higher temperature, the chromophores started to degrade. Their retention rate is therefore significantly influenced by the thermal stability of the chromophores. The second harmonic response, d_{33} , of As-DR19, As-Ch2, As-Ch3 and As-Ch4 is 29, 18, 20 and 16 pm V^{-1} respectively. Those moderate values may

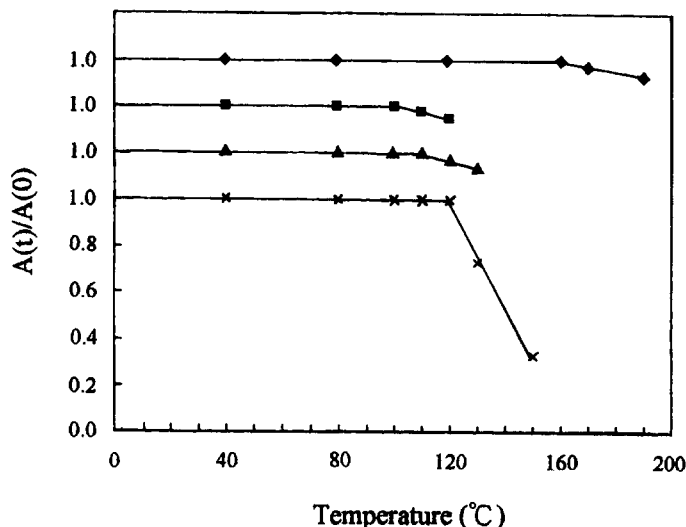


Figure 5 Relative u.v. absorbance of organosilicate films held at different temperatures for 8 h: ◆, As-DR19; ■, As-Ch2; ▲, As-Ch3; ×, As-Ch4

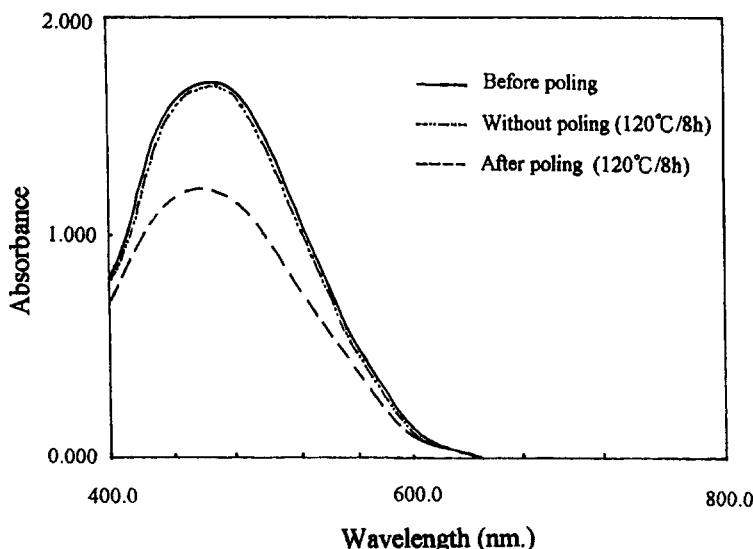


Figure 6 U.v. absorption spectra of As-DR 19 before and after poling

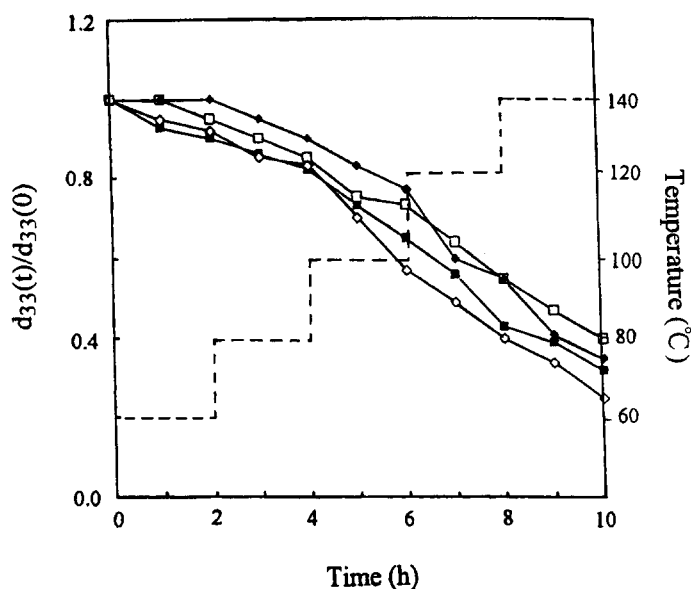


Figure 7 Thermal ageing test on organosilicate films: \diamond , As-DR19; \blacksquare , As-Ch2; \blacklozenge , As-Ch3; \square , As-Ch4

account for the relatively low loading of chromophores incorporated in the polymer.

CONCLUSIONS

The present results demonstrate that non-linear optical molecules can be covalently attached to the silicon oxide matrix as side chain, main chain or crosslinking types. The polymers display excellent processing ability at room temperature. Preliminary experiments indicate that the chromophores cross-linked to the glass matrix exhibit the highest poling orientation stability. A high sintering (poling) temperature converts wet gel into dry gel with a more condensed structure, further confining the chromophore's rotational movement. Obtaining a highly stable non-linear optical silica film is necessary for synthesizing a chromophore with high decomposition temperature and more than three reactive sites. This approach is currently being investigated.

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