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Sol–gel process of non-linear optical silica films with organic chromophore as side chain

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A transparent silica film with organic chromophore, Disperse Red 1(DR1), as side chain was prepared in this study by the sol–gel process. Next, the film was baked at 120 °C with corona discharge poling. The resulting films exhibited a second harmonic response, $d_{33} = 46$ pm V^{-1}. High poling stability was observed when the film was maintained at 60 °C. The effects of HCl concentration on the molecular orientation and the thermal stability of the specimens were also investigated.

1. Introduction

Organic chromophores with large, second order, non-linear optical properties have recently received a significant amount of attention [1, 2]. Many known organic chromophores have been synthesized. However, some of the compounds with centrosymmetric structure tend to align themselves with an anti-parallel crystal lattice which shows no macroscopic second harmonic generation.

The incorporation of organic chromophore with a glassy polymer matrix and alignment with a high d.c. electric field is a newly developed technique to overcome the above mentioned problem [3–5]. However, due to the rotational freedom of the chromophore and relaxation of the main chain, the second order, non-linear optical properties are generally not very stable while the temperature approaches the glass transition temperature of the matrix. An effort to increase the thermal stability entails selecting high glass transition temperature matrices, e.g. crosslinking [6, 7], main chain chromophores [8] or high glass transition polymers [9].

A handful of sol–gel matrices with chromophore as side chain or doping material have been reported in recent years [10–13]. 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 many years [14]. The reaction involves the hydrolysis of alkoxy-silane, and the water and alcohol condensation of the silanol,

(hydrolysis)

$$\equiv\text{Si–OR} + \text{H}_2\text{O} \rightarrow \equiv\text{Si–OH} + \text{ROH}$$

(polycondensation)

$$\equiv\text{Si–OH} + \text{HO–Si}\equiv \rightarrow \equiv\text{Si–O–Si}\equiv + \text{H}_2\text{O}$$

$$\equiv\text{Si–OH} + \text{RO–Si}\equiv \rightarrow \equiv\text{Si–O–Si}\equiv + \text{ROH}$$

where R is an alkyl (CH_3, C_2H_5 etc.). Theoretically, 2 moles of water are required for complete conversion to SiO_2 glass. A linear chain and incomplete reaction would be obtained if less than 2 moles of water per mole of alkoxy-silane are present.

The sol–gel silica glass modified with organic non-linear optical (NLO) chromophore, Disperse Red 1 is investigated in this study. The sol–gel was processed with and without an addition of HCl as catalyst. Also, tetrahydrofuran (THF) is used as the solvent for the reaction.

2. Experimental procedure

2.1. Materials

4-nitroaniline, 2-(N-ethylanilino)ethanol, sodium nitrite, toluylene-2,4-diisocyanate (2,4-TDI), tetraethoxysilicate (TEOS), and γ-aminopropyltriethoxysilane (γ-APS) were used without further purification. (THF) was dried before use.

2.2. Synthesis

2.2.1. Disperse Red 1(DR1)

In a typical reaction, 1.725 g of 4-nitroaniline was dissolved in 7.5 ml of 6 N HCl by warming. Sodium nitrite (0.863 g) dissolved in 3 ml of water was quickly added at a temperature below 5 °C. To the cooled solution, 0.8 g of glacial acetic acid with 2.06 g of 2-(N-ethylanilino)ethanol was added. After stirring for 1 h at room temperature, the solution was titrated by adding 10% NaOH. The product, DRI, was filtered, washed with water and dried under vacuum at 60 °C. This dye was purified by recrystallization from methanol. The yield was 72% and the m.p. was 159–160 °C.

2.2.2. Compound A

DR1 (0.506 g) and TDI (0.316 g) were added to 30 ml of THF in a three-necked flask, and 0.1 ml of triethylamine was added as a catalyst. The mixture

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TABLE I Formulations of the starting solutions for non-linear optical silica films

Designation	H_2O/TEOS (mole ratio)	DR1/ TEOS (wt %)	A/(A + TEOS)[c] (wt %)	HCl/TEOS (wt %)
S-1[a]	2	20	0	0
S-2[b]	2	0	16.7	0
S-3[b]	2	0	16.7	1.66×10^{-3}
S-4[b]	2	0	16.7	2.76×10^{-3}

[a] S-1: silica film doped with DR1.

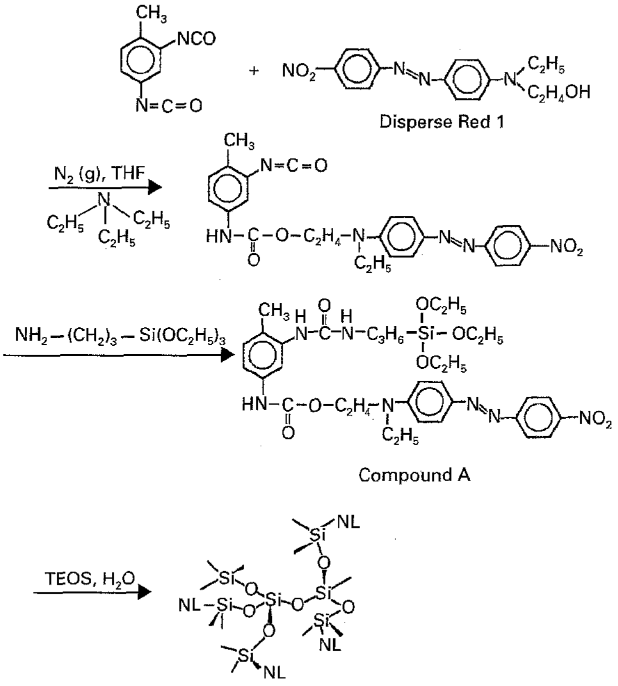
[b] S-2, S-3, S-4: silica films with DR1 as the side chain.

[c] A: compound A.

was stirred at 60 °C for 2 h under nitrogen atmosphere. To the solution, 0.352 g of γ-APS was added. After reaction for 1 h at room temperature, the solvent was pumped out and stored under nitrogen ambient atmosphere. The degree of reaction was monitored by the Fourier transform infra-red (FT-IR) method.

2.3. Preparation of the thin film

Compound A and TEOS were dissolved in THF (THF/compound A = 80/20, w/w). The basic formulations of the specimens are listed in Table I. The solution was then filtered through a 0.22 μm Teflon filter and stood for 8 to 168 h at room temperature (depending on the acid concentration) before spin-casting onto transparent ITO (indium tin oxide) glass. After ageing for over night at room temperature, the sample temperature was raised to 120 °C under vacuum for 48 h to remove the residual solvent. Next, the film obtained was heated to about 120 °C and poled by using a corona discharge apparatus. The applied voltage on the corona wire was maintained at 6 kV with the current of 1.5 μA. Cooling of the substrate was conducted under applied field.



Scheme **I** Synthesis and sol–gel processing of the cross-linked polymer.

3. Results and discussion

Schematics of the chemical structures of the starting material and fully crosslinked polymer are shown in Scheme **I**, where DR1 was selected as the chromophore because it possesses an extremely high microscopic hyperpolarizability, 125×10^{-30} e.s.u [15]. Another reason to select DR1 as the side chain is that the hydroxyl group can react with the isocyanate group to form urethane linkage. To accelerate the reaction, triethylamine was used as a catalyst. The rest of the unreacted isocyanate group was then reacted with γ-APS to form urea linkage. The isocyanate group is well known to have a characteristic i.r. absorption peak at 2270 cm^{-1} [16]. Therefore, it can be used as an indication of the degree of the reaction. As shown in Fig. 1, the intensity decreased at the first stage of urethane reaction and then diminished during the second stage of the urea reaction, thereby revealing the completeness of the reaction.

The thermal properties of the films were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In the S-1 (doped) sample, there is a sharp endothermic peak at 160 °C, i.e. the melting point of the chromophore, DR1 (Fig. 2). However, DSC analysis also showed a slight temperature transition around 160 °C (Fig. 3) for the side chain film, S-2. This result indicates the side chain modified silica film contains a minute fraction or minute domain size of crystallinity. There are no obvious glass transitions in the DSC traces, but a broad exothermic peak was observed in sample S-1. This broad peak actually involves the decomposition of the

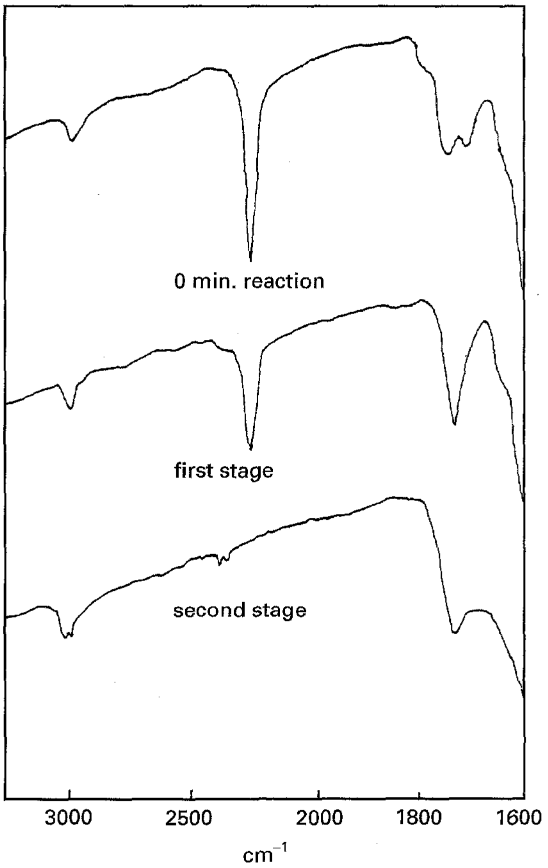


Figure 1 FT-IR spectra of pristine material and compound A.

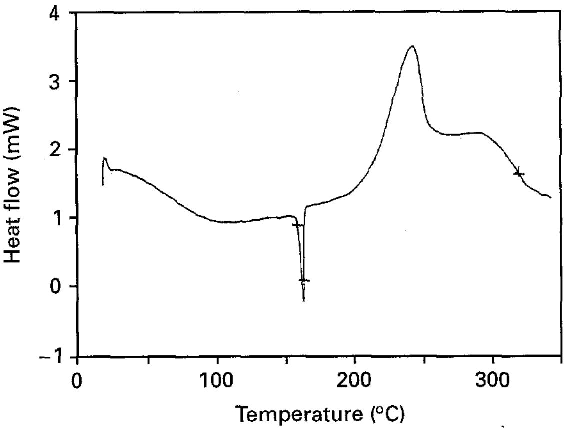


Figure 2 DSC trace of the doped silica material.

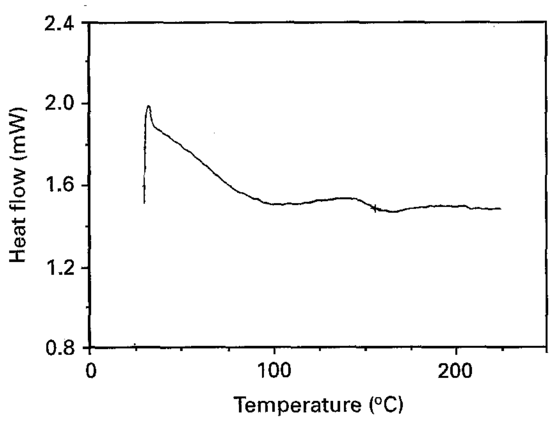


Figure 3 DSC trace of the side chain silica material.

DR1. As for the side chain film, there is no significant exothermic region. As shown in Figs 4 and 5, the TGA trace revealed that S-1 has a decomposition temperature at ca. 218 °C and S-2 at ca. 228 °C. The side chain film was more stable than the doped film, as indicated in the DSC and TGA diagrams.

The order parameter is defined by $\phi = 1 - A_{\perp}/A_0$ (where $A_{\perp}$ and A_0 are the u.v.-visible absorbance of the poled and unpoled film, respectively) [17]. The order parameter can be used to estimate the degree of the chromophore orientation. Fig. 6 is the result of the side chain silica film with different HCl concentration poling at the same condition. This figure indicates that the order parameter decreased as the acid concentration increased. This is due to the interaction between motive ionic species and electric field. Tripathy and colleagues also found a similar phenomena [13]. Ultraviolet-visible absorption spectra of unpoled and poled silica films (S-2) are plotted in Fig. 7. The absorbance at $\lambda_{max} = 472$ nm decreased depending on the degree of chain orientation. This figure also indicated that the u.v.-visible absorption of poled silica film (without HCl) had no measurable change after 700 h ageing at room temperature. This result reveals that the relaxation of the non-linear optical properties of silica film at room temperature is negligible.

Second harmonic generation (SHG) measurements were performed by using a Nd:YAG laser at a wavelength of 1.06 μm. Next, the second harmonic

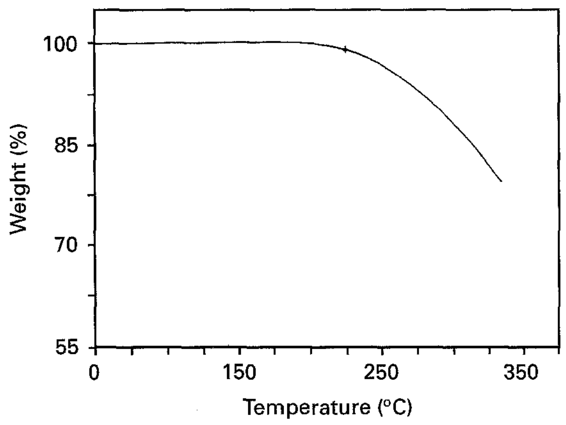


Figure 4 TGA trace of the doped silica material.

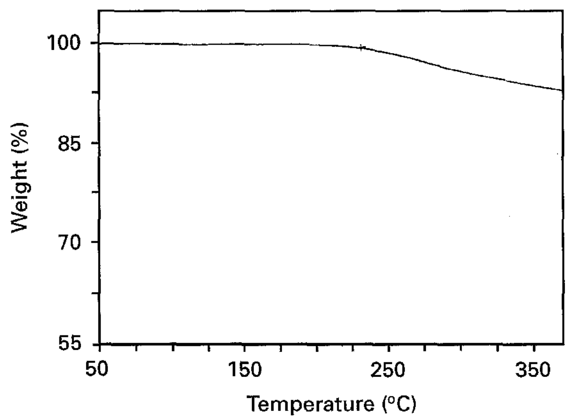


Figure 5 TGA trace of the side chain silica material.

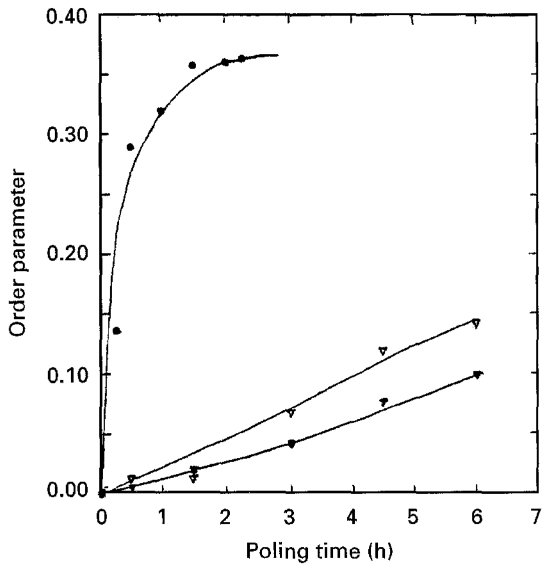


Figure 6 Acid concentration effect on the chromophore orientation of the side chain silica film. Poling conditions: 6 kV, 1.5 μA, 120 °C. ● S-2; ▽ S-3; ▼ S-4.

coefficients of the silica film were calculated by making a comparison of the second harmonic intensity with that generated by the quartz sample. Our experiments showed that the film (S-2) with a coating thickness of 0.9 μm had a second harmonic response, $d_{33} = 46$ pm V^{-1}. Izawa and co-workers [18] had investigated a sol–gel system base on doped DR1 by

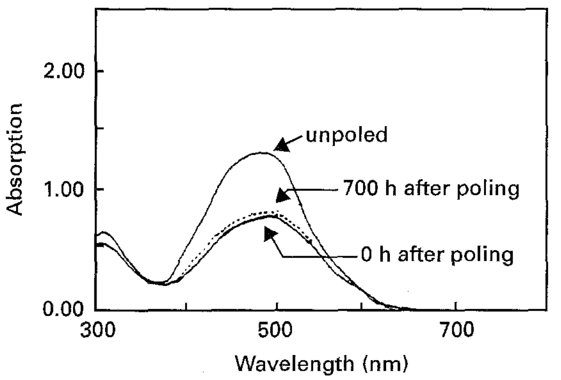


Figure 7 Ultraviolet absorption spectra of the side chain silica film before and after poling.

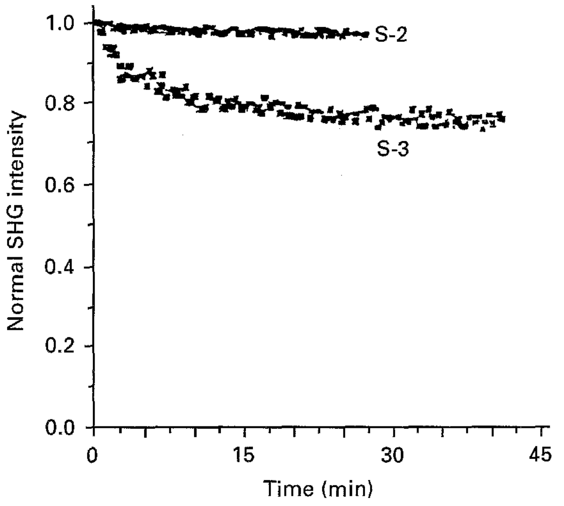


Figure 8 Temporal behaviour of the relative SHG intensity, at 60 °C

acid catalysis. They concluded that with higher poling conditions (12 kV, 150 °C), the pores in the oxide matrix would tend to shrink. Therefore, they are able to produce a thermally stable chromophore doped silica film with HCl as catalyst. In our experiment, the temporal behaviour of the relative SHG intensity is shown in Fig. 8 as a function of time. A high poling stability was observed for the silica film without HCl, which correlates with above mentioned u.v.-visible result. However, the sample with HCl (S-3) showed a substantial signal decay with time. The reasons may be accounted for as follows. In the sample preparation, HCl will increase the formation rate of wet gel, thereby the molecular types of by-products (H_2O, ethanol) are trapped in the pores more easily than those without HCl. This occurred because the entire process proceeded under a low temperature without sintering. Therefore, the chromophores located on those pores have a sufficient amount of free volume to rotate.

4. Conclusion

A second order, non-linear optical silica film containing DR1 as side chain was synthesized in this study. The electrically poled film exhibits a very stable thermal behaviour at room temperature and also at 60 °C. Experimental results indicated that the HCl could inhibit the molecular orientation under electrical poling conditions as well as decrease the thermal stability.

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