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Synthesis and optical properties of novel side chain NLO organic/inorganic polymers via sol-gel process

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SUMMARY: Novel side chain NLO organic/inorganic polymers were developed by sol-gel process of dye-contained triethoxysilane with tetraethoxysilane. A NLO moiety based on 4-[N, N-bis(2-hydroxyethyl)amino]-4'-nitrostilbene (diol-DANS) was covalently bounded to the triethoxysilane derivative. The sol-gel derived NLO polymers were analyzed by analytic techniques, including FT-IR, TGA, solid state ^{29}Si-NMR, SEM, etc. The incorporation of the DANS dye into silicon oxide networks induces high dimensional stability of dipole alignment and the easy film fabrication. They exhibited a significant improvement in the thermal stability at high temperatures exceeding 270 °C. The electro-optic coefficient at 1.3 μm is 4.3 pm/V for the copolymer containing 50 wt % of the dye-contained triethoxysilane system poled with corona discharge and is shown excellent long-term stability with 80 % of initial value even after 3 hrs at 150 °C.

Introduction.

Second - order nonlinear optical(NLO) properties have been widely studied because of their potential applications in photonic technologies such as optical switching, optical waveguide, signal processing, etc. (1). The possibility of the practical applications of 2nd order nonlinear optical materials in photonic devices depends on the high temporal stability of dipole orientation, large optical nonlinearity, and good transmission in the near infrared region. As the transmission is intrinsic nature due to C-H overtone vibration, major research efforts have been focused on optimizing optical nonlinearity and enhancing the stability of poling-induced noncentrosymmetric order. To attain highly stable 2nd order noncentrosymmetric order and large optical nonlinear materials, various approaches have been developed such as crosslinkable polymer systems (2-4) and high Tg polymer systems (5-8). However, their optical properties are still needed to improve for the use of photonic device.

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Recently, sol-gel process has been studied to obtain highly nonlinear optical materials and this process has shown some advantages such as the easy film fabrication and high dimensional stability of dipole alignment by locking the chromophore in the silicon-oxide networks (9-13).

All the sol-gel derived materials reported can be classified into two kinds : one is simple physical blending or doping, and another is incorporating of NLO chromophores into silica networks by chemical bonding. The later kind has advantage over the former one of the higher chromophore concentration and the better orientational stability. Several researchers have recently reported NLO materials containing azo derivative chromophore using the sol-gel process (9, 14, 15). However, the more thermally stable stilbene derivative NLO chromophore-containing sol-gel system was not reported.

We report here some results of sol-gel process using a difunctional stilbene derivative 2nd-order NLO chromophore attached to silicon atoms by chemical bonding.

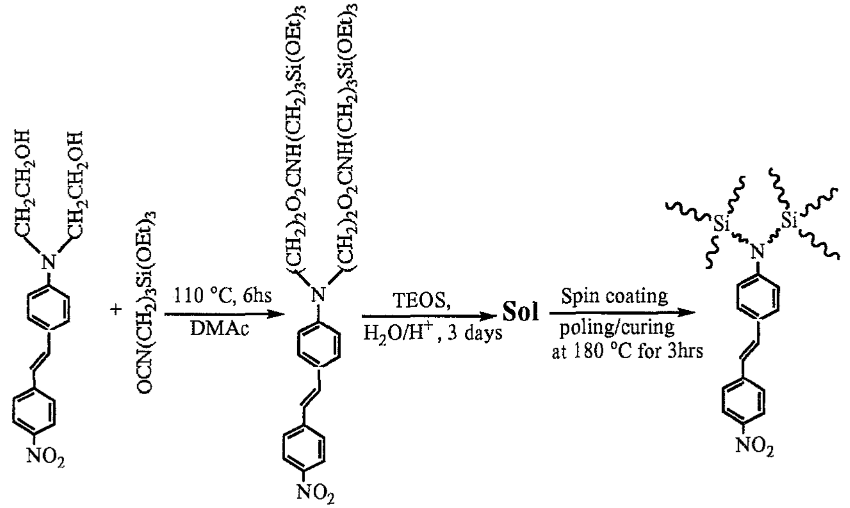
Experimental

1. Materials and film preparation

Materials : Tetraethoxysilane (TEOS : Aldrich) and 3- isocyanatopropyl triethoxysilane (Lancaster) were used without further purification. N,N-dimethylacetamide was dried over $MgSO_4$ and distilled under reduced pressure. The 4-[N,N-bis(2-hydroxyethyl)amino]-4'-nitrostilbene (diol-DANS) was synthesized according to literature procedure (16). Scheme I shows the synthetic route of the sol-gel materials. The alkoxysilane containing NLO dye was synthesized by the coupling reaction of diol-DANS (0.8g, 2.5×10^{-3} mol) and 3-isocyanatopropyltriethoxysilane (1.2g, 5.0×10^{-3} mol) in DMAc (10ml) solvent at 110 °C for 6hrs. For the spectral characterization of the product, a small portion of the solution (1 ml) was extracted via syringe and precipitated in the 20 ml dry hexane. After removal of the solvent, the product was dried in the vacuum oven for 2 days. The quantitative yield was obtained by NMR analysis. The dye-contained triethoxysilane has good solubility in common organic solvents such as $CHCl_3$, THF, pyridine, DMF and DMAc and moisture sensitivity in air environment. The structure of dye-contained triethoxysilane were characterized by NMR spectroscopy. ^1H NMR ($CDCl_3$): δ 0.58 (t, 4 H), 1.21 (t, 18H), 1.52 (m. 4H), 3.12 (t, 4H), 3.62 (t, 4H) 3.76 (q, 12H), 4.26 (t. 4H), 4.97 (t, 2H), 6.95 -8.16 (m, 10H). ^{13}C-NMR ($CDCl_3$) δ 7.5 (CH_2Si), 18.27 ($\underline{C}H_3CH_2OSi$), 23.1 ($\underline{C}H_2CH_2Si$), 43.4 ($NH\underline{C}H_2CH_2$) 50.9 ($N\underline{C}H_2CH_2O$), 58.4 ($CH_3\underline{C}H_2OSi$), 60.2 ($NCH_2\underline{C}H_2O$), 112.0. 112.4, 121.6, 121.9, 124.1, 126.1, 128.5, 133.4, 133.6, 145.0, (stilbene), 158 (OCON). UV:λ_{max} 435 nm (THF) .

Film preparation : To the dye-contained triethoxysilane solution were added tetraethylorthosilicate followed by stoichiometric amount of acidic water (pH 3). The solution was stirred for 3 days at room temperature. The sol was passed through 0.2 μm membrane filter and spin-coated on the ITO glass, KBr pellet and silicon wafer for several measurements on electro-optic coefficient, UV-visible spectra, FT-IR and refractive indices. The chromophore-contained films were dried to remove the residual solvent under vacuum oven for 6 hrs at room temperature. The remainder of sol was allowed to gel for use in thermal and solid state ^{29}Si-NMR analysis.

Scheme 1. Synthesis of 2nd order NLO chromophore-contained sol-gel material



diol-DANS

Dye-contained Triethoxy Silane (DTS)

Dye-incorporated in 3D SiO_2 network

Table 1. Preparation of sol-gel materials

Sample Number	DTS [a]	TEOS[b]	H_2O	DMAc
1	1.0 g	-	0.14g	10 ml
2	1.0 g	1.0 g	0.49g	10ml

[a] Dye-contained Triethoxy Silane (see Scheme 1)

[b] Tetaethylorthosilicate

2. Poling and further polymerization

To align the dipole moment of the NLO chromophore, the films were poled and thermally cured simultaneously using a corona discharge technique. The poling was started at ambient temperature and then the sample temperature was increased at the rate of 2 °C/min. The films were heated upto 180 °C and maintained for 3 hrs. The films were placed 2 cm under the corona tip and a potential of 14 kV was applied. After the poling of 3hrs, the film temperature was reduced to ambient temperature and then the electric field was removed.

3. Characterizations and measurements

^{29}Si-NMR spectra were recorded on Bruker Am-300 spectrometer. FT-IR spectra were measured on a Bomem Michelson using a KBr pellets. UV-visible spectra were obtained from a Shimadzu UV-3100S spectrometer with Aminco-XY recorder. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 10 °C/min with Dupont 9900. The film thickness was measured with α–step surface profiler and the refractive indices of the samples were measured by prism coupler method. The values of electro-optic coefficient , r_{33} , were measured at 1.3 μm wavelength by using simple reflection technique reported by Teng et al (16).

Results and discussion

The synthetic route of sol-gel materials is outlined in scheme I. The dye-containing silane was synthesized by coupling of diol-DANS and 3-isopropyl triethoxy silane in DMAc solvent. To this resulting solution were added the TEOS and a stoichiometric amount of acidic water. The reaction solution was stirred at room temperature for 3 days to hydrolyze the alkoxy group and then was polymerized in a condensation manner. The sol was spin coated on the ITO glass. The chromophore-containing films were cured and poled at 180 °C for 3 hrs. The film thickness is in the range of 1.89 -2.35 μm measured by α-step surface or depth profiler. All of the cured films are transparent and no phase separation was detected by SEM. When the cured samples were soaked in DMAc, which is a good solvent for DTS, the solvent did not extract any measurable concentration of dye from the samples. These observation imply that the NLO dye is firmly incorporated in the silicon-oxygen network.

The structure of sol-gel material was investigated by FT-IR and ^{29}Si-NMR spectroscopy. Figure 1 shows the FT- IR spectra of the sol-gel material. After curing process, the peaks of hydroxyl group (3400 cm^{-1}), Si-ethoxy bond (1136 cm^{-1}) and hydroxyl and ethoxy groups (951 cm^{-1}) were decreased and the absorption peak of Si-O-Si (1070 cm^{-1}) become strong. This indicates that the formation of Si-O-Si bond is increased due to further thermal condensation by removal of hydroxy and ethoxyl moieties.

The ^{29}Si-NMR spectroscopy was also carried out to monitor the condensation reaction of dye-containing triethoxysilane and TEOS. Figure 2 shows the ^{29} Si MAS NMR spectra of the sol-gel materials. Before curing the samples, the ^{29} Si MAS spectrum shows three components of T species due to T^1(49.5), T^2 (56.6), and T^3(65.1 ppm) units and also three components of Q species corresponding to Q^1 (81), Q^2 (90.0), and Q^3 (99.4ppm) units. After curing at 180 °C for 3 hrs, the peaks of T^1 , Q^1, and Q^2 species disappeared and those of T^3 and Q^4(109.2 ppm) species (fully condensed) increased. This indicates that the condensation degree of siloxane network was increased and that crosslinked silicon-oxygen network was developed.

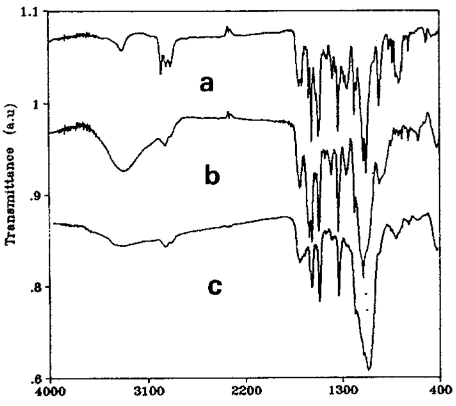


Figure 1. FT - IR spectra of sol-gel material of 50:50 wt % of DTS and TEOS; (a) DTS, (b) precursor polymer, and (c) cured at 180 °C for 3h.

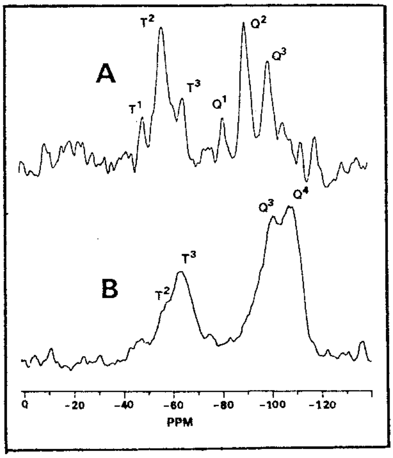


Figure 2. Solid state ^{29}Si MAS NMR spectra of sol-gel material of 50:50 wt % of DTS and TEOS; (a) before curing, (b) cured at 180 °C for 3h.

The formation of crosslinked silicon-oxygen networks induces the increase of the Tg and the dimensional stability of the NLO material. The increase of T^3 and Q^4 peaks indicates the production of the fully condensed silicon species, which agrees with FT- IR results.

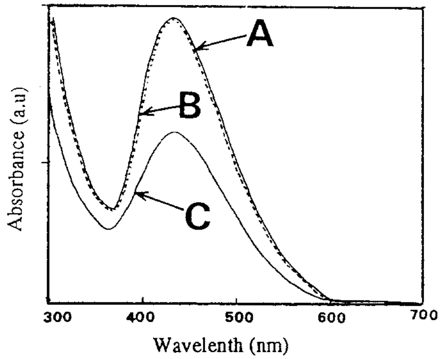


Figure 3. UV-visible absorption spectra of the sol-gel material of 50:50 wt % of DTS and TEOS;(a) pristine, (b) cured, (c) cured/poled at 180 °C for 3h,

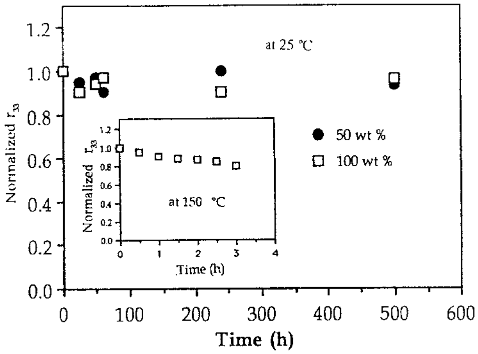


Figure 4. Temporal stability of elctro-optic coefficients; (a) 100 % of DTS and (b) 50 wt % with TEOS at 25 °C and 150 °C.

The UV-visible spectra show a typical absorption pattern with a absorption maximum at 446 nm due to stilbene NLO chromophore (see figure 3). After curing/poling process, hypochromic and blue shift was observed due to induced dipole alignment (2, 10, 15, 18).

The sample showed no absorption change after only curing process at 180 °C for 3 hrs. It is important to note that the NLO chormophore was not degraded or sublimed during curing process at 180 °C for 3hrs.

Table 2. Physical properties of sol-gel materials

Sample	λ_{max}(nm)	Thickness (μm)	T_d[a] (°C)	n^b (1.3 μm)	r_{33}, pm/V[c] (1.3μm)
100 % DTS[d]	446	1.89	273	1.600	3.7
50 :50 wt % DTS/TEOS	443	2.35	278	1.564	4.3

[a] Decomposition temperature of NLO-dye incorporated in silicon-oxygen network

[b] Indices of refraction were determined from wave guide experiment

[c] Electro-optic coefficient

[d] Dye-contained Triethoxy Silane

We measured the values of electro-optic coefficients, r_{33}, for poled films by using simple reflection technique reported by Teng et al.. Table 2 shows the electro-optic coefficient of chromophore incorporated film measured at 1.3 μm wavelength according to weight composition. The poled/cured films have r_{33} values of 3.7, 4.3 pm/V for the NLO materials of 100 and 50 weight percent, respectively. All of the r_{33} values remained unchanged at room temperature within 20 days. In figure 4, we present the temporal stability of the EO coefficient of the films. The film of 50 wt % shows excellent thermal stability. The 80 % of initial r_{33} value was remained after heating even at 150 °C for 20 hrs. It indicates that the cross-linked silicon-oxygen network was developed and the Tg of film was higher than 150 °C. In the 100 wt %, the r_{33} signal was vanished after annealing of 100 °C for 2 hrs because the effective cross-linked network was not developed. In present, the study of the optimum conditions to attain higher EO coefficient and thermal stability is in progress.

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