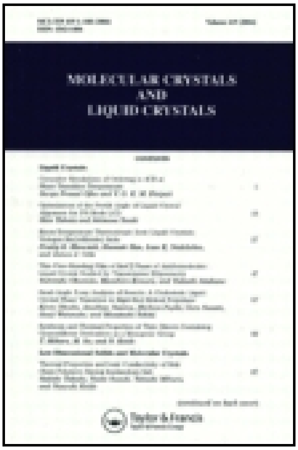

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Synthesis and Characterization of Functionalized Sol-Gel Materials for Electro-Optical Application

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SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED SOL-GEL MATERIALS FOR ELECTRO-OPTICAL APPLICATION

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Abstract We simply synthesized the triethoxysilane bearing the second-order nonlinear optical(NLO) active chromophore in the side chain. In order to improve the poor temporal stability of second-order NLO effect, we introduced the thermal crosslink between the side chain themselves. We prepared two different silane solutions; one is composed of triethoxysilane with NLO chromophore (SGDR1) only. The other consists of SGDR1 and 3-glycidoxypropyl trimethoxysilane. Thermal crosslink formation was traced with *in-situ* infrared spectroscopy. We achieved much improvement of the temporal stability of second-order NLO effect utilizing this crosslinked composite system.

INTRODUCTION

Sol-gel materials for photonic applications have drawn much interests in recent years.[1-3] Sol-gel reactions for silicon or metal alkoxides can form various microstructures in polymeric media. After the covalent bonding of chromophore to the silicon trialkoxide, it was subjected to be hydrolyzed and polycondensed. Curing the film at high temperature (>200°C) leads to proceed cross-linking of the inorganic matrix, but results in partial deterioration of the organic NLO chromophore in the silicon matrix. In an attempt to improve its temporal stability, we designed the composite system using NLO active triethoxy silane and 3-glycidoxypropyl trimethoxy silane (GPTS).

EXPERIMENTAL

Synthesis : Disperse red 1 (2.00 g, 8.1 mmole) were dissolved in the freshly dried tetrahydrofuran(30 ml) with a catalytic amount of dibutyltin dilaurate (DBTDL). Isocyanatopropyl triethoxysilane(1.27 g, 4.04 mmole) was added dropwise over 10 minutes. The reaction mixture was refluxed for 6 hours. The mother solution was

poured into cold hexane(200 ml) to collect the red precipitate. Yield 70-72%
^{1}H-NMR(DMSO-d_6): δ 8.25(d, 2H), 7.67 (d, 2H), 7.44 (d, 2H), 6.83(d, 2H), 4.25 (t, 2H), 3.84(q, 6H), 3.76 (t, 2H), 3.82(t, 2H), 3.14 (m, 2H), 3.00 (t, 3H), 1.63 (m, 2H), 1.27 (t, 9H), 0.61 (t, 2H)

FT-IR : NH stretching 3329cm^{-1} (hydrogen bonded), 3422cm^{-1}(isolated)
Carbonyl(C=O) 1698 cm^{-1}(hydrogen bonded), 1725 cm^{-1}(Isolated)
NO_2 1516 cm^{-1}

Material Processing: For thin film fabrication, sol-gel precursor solution was made in tetrahydrofuran. Preparing the solution for composite film, we mixed SGDR1 with GPTS (50 mole %). Taking infrared spectra of the samples, the films were cast on the polished KBr windows. The films were dried under argon for 6 hours thoroughly.

RESULTS AND DISCUSSION

The functionalized sol-gel precursor was prepared by simple urethane forming reaction between the alcohol and isocyanate in trialkoxysilane.[4] Synthetic scheme was illustrated in Figure 1. After reacting the NLO chromophore to the trialkoxysilane under argon, we found out that the given compound was observed quite stable in atmosphere. According to the FT-IR spectra, we could observed two superposed bands at 1698 cm^{-1} and 1725 cm^{-1}. Those two bands were assigned to hydrogen bonded and isolated carbonyl stretching. Simultaneously, two overlapped bands could be observed at 3329 cm^{-1} and 3422 cm^{-1}, which are assigned to hydrogen bonded and isolated NH stretching. Therefore, we could find out that the inter- or intra-molecular hydrogen bond existed between the carbamate groups.

IR spectral analysis of SGDR1 film

We used the thin film of SGDR1 on KBr window for in-situ FT-IR spectral analysis. After hydrolyzing and aging the sample, the films shows the same behavior of the existence of hydrogen bond between the side chains. At 25°C, the fraction of hydrogen bonded carbonyl group was calculated around 0.86 analyzing the peak based on Gaussian function. As can be seen in Figure 2, the fraction of isolated carbonyl group increase gradually with heating. During cooling, the hydrogen bond was observed to be recovered slowly in some extent. In cooling cycle, the fraction of hydrogen bonded carbonyl group was determined 0.85 at 25°C. Therefore, in the SGDR1, the formation of hydrogen bond was found quasi-reversible. Shortly, with increasing the temperature around 100°C, the hydrogen bond in the side chains were destroyed so that the side

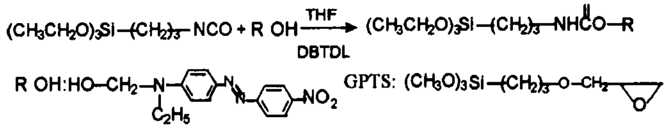

FIGURE 1. Synthetic procedure of NLO functionalized silane and GPTS.

chain mobility may increase. Increase of mobility in the side chain was attributed to the poor temporal stability of second-order NLO effect after poling at high temperature.

IR spectral analysis of composite film (SGDR1/GPTS)

In the case of homogeneous SGDR1, we had to increase the temperature to 200-210°C for densifying the silicon structure. During sintering, some portion of the chromophore was decomposed. Excluding the severe thermal condition, we made an effort to induce thermal crosslink in the organic side chains besides the network in silicon group. Particularly, the crosslink should be induced at lower temperature than that in conventional sintering process. Secondary amine can attack the less crowded carbon in epoxide to open a ring. In this conversion, tertiary amine was generated after diminishing a part of secondary amine. In the *in-situ* IR spectroscopy could give us the good information how the internal structure changed. With the annealing temperature, the hydrogen bond was broken gradually. Raising the temperature at 180-190°C, new carbonyl band started to appear around 1748cm^{-1}. At the same sequence, the intensity of secondary amine decreased. The strength of carbonyl double bond in the vicinity of tertiary amine group may be larger than that of carbonyl in the original carbamate. The force constant and definite double bond character can ascribe to form a new band at higher wavenumber. Then, we cooled the samples to room temperature again. Compared to the previous SGDR1, we could observe the irreversibility of hydrogen bond in the composite. We poled the composite film at 100°C under 5kV for 10 minutes and then cured at 150°C for 30 minutes. We measured the EO signal under 632nm wavelength. Aging at 100°C for 30 minutes, 30pm/V of initial r_{33} was maintained without decay. 85-90% of the initial EO effect was maintained at 150°C even after 30 minute annealing. Shortly, the proposed heterogeneous sol-gel system showed much improvement in temporal stability compared to 80% decay of initial r_{33} in SGDR1 annealed at 100°C for 30 minutes. We also did *in-situ* SHG experiment under 1064nm wavelength. The result was well consistent with the previous EO decaying behavior. We are pursuing our endeavor to optimize the relationship between the poling time and

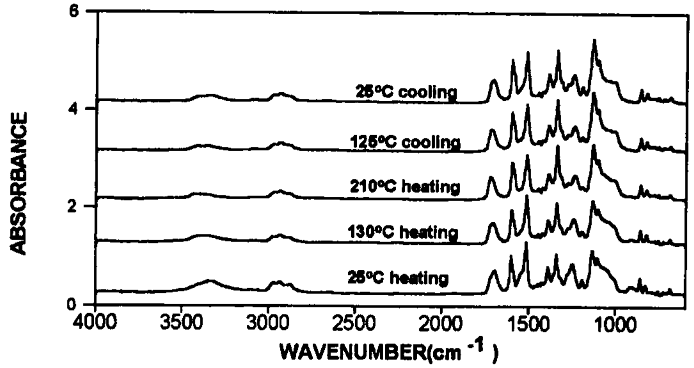

FIGURE 2. Infrared spectra of SGDR1 film

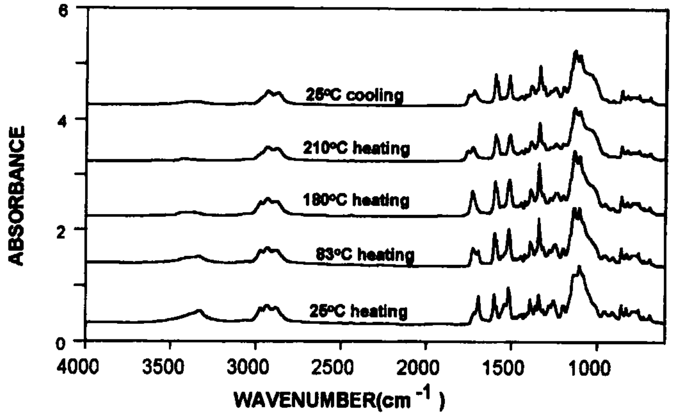

FIGURE 3. Infrared spectra of composite film. (SGDR1/GPTS).

temperature in order to maximize the second-order NLO effect of the sol-gel film.

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