Anchoring Both Ends of Chromophores into Sol–Gel Networks for Large and Stable Second-Order Optical Nonlinearities

Zhixin Yang, Chengzeng Xu, Bo Wu, and Larry R. Dalton*

Loker Hydrocarbon Research Institute, University of Southern California,
Los Angeles, California 90089-1661

Srinath Kalluri and William H. Steier

Center for Photonic Technology, Department of Electrical Engineering, University of Southern California, Los Angeles, California 90089-0483

Yongqiang Shi and James H. Bechtel

TACAN Corporation, 2330 Faraday Ave., Carlsbad, California 92008

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We have synthesized a new nonlinear optical (NLO) sol–gel material. In this material, the NLO chromophores, at their ends, are covalently anchored into heavily cross-linked sol–gel networks. The poled and cured sol–gel films exhibit second-order optical nonlinearities (d_{33} = 27 pm/V). Long-term stability of the nonlinearity at 100 °C, in air, has been realized.

Second-order nonlinear optical (NLO) properties of poled polymeric materials have been extensively studied in the past decade.[1] One of the major problems encountered is the poor thermal and temporal NLO stability of the materials. To realize good NLO stability for device applications, one needs not only chemically stable materials but also thermally stable poling-induced noncentrosymmetric lattices. Good lattice stability has been found to be very difficult to achieve, given the thermodynamically unfavorable nature of the ordered structure. Several methods have been studied for stabilizing the poling-induced optical nonlinearities in the second-order nonlinear optical polymers. Of these methods, cross-linkable polymer systems and high glass transition temperature polymer systems (e.g., polyimides) have been shown to be particularly promising.[2,3] Nonlinear optically active sol–gel systems represent a third type. Sol–gel materials for optical applications are of interest for a number of reasons.[4] These include their excellent optical quality, low-temperature processing capability, high thermal stability, and ease of fabrication of devices. Other interesting properties include the flexibility to incorporate secondary components to the sol, which are then trapped in the gel, and the control of the refractive indexes of the sol–gel films.

Sol–gel technology provides an attractive route to preparation of NLO chromophore-containing three-dimensional networks by chemical reactions at low temperatures. This is analogous to step polymerization reactions in organic systems.[5] However, similar to other organic guest–host composites, doped sol–gel systems suffer from phase separation and thermal relaxation problems.[6] To overcome these problems, organic NLO chromophores were covalently incorporated into the silica networks. Several investigators have incorporated *N*-[(3-triethoxysilyl)propyl]-2,4-dinitroaniline (TPDNA) into tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) gels, which, after poling with an electric field, yield materials exhibiting second-order NLO effects.[7–11] The preparation of a second-order NLO polyimide/inorganic composite has also been reported.[12,13] All these previous studies have attached only one alkoxysilane group to the NLO chromophores. The presence of only one alkoxysilane unit makes it very difficult for the formation of a highly cross-linked sol–gel network. The NLO dye has a high mobility in the free volume of the host network, causing relaxation of the poling-induced order. In this communication, we report the preparation of a new organic–inorganic composite material, in which the NLO chromophores are covalently bonded to a heavily cross-linked sol–gel network. We also present the NLO properties as well as the thermal and long-term stability of the second-order optical nonlinearity of the cured sol–gel polymer films.

Figure 1 illustrates the scheme for synthesis of NLO chromophore-containing sol–gel materials. The basic

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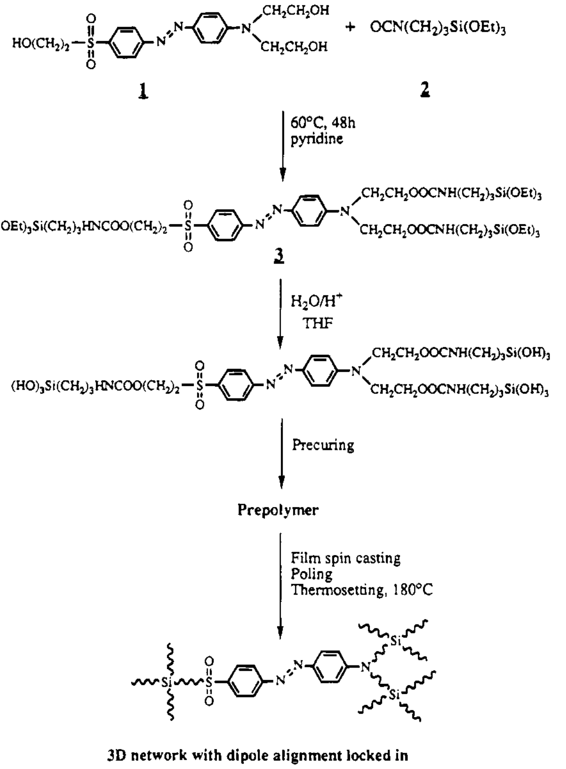

Figure 1. Synthesis of NLO chromophore-containing sol–gel materials.

idea of this research is to introduce multi-alkoxysilane groups at both ends of a chromophore, which upon hydrolysis and subsequent precuring in organic solvents lead to a viscous prepolymer solution. The prepolymer solution can then be spin cast into good-quality films, whose thickness can be controlled by tuning the viscosity of the solution or the film spinning speed. After vacuum drying, the films are poled at relatively low temperatures by an electric field to attain noncentrosymmetric dipole alignment. The poled films are further annealed at elevated temperatures under the poling field to form heavily cross-linked three-dimensional silicate networks with both ends of the chromophores anchored. This ensures that the mobility of the NLO dye molecules in the glass matrix is drastically reduced, leading to excellent thermal stability of the optical nonlinearity. Indeed, as reported in this communication, we have realized long-term stability of second-order nonlinearity of the sol–gel material at 100 °C.

The NLO chromophore **1** was synthesized by the diazonium coupling reaction according to the literature procedures.[14] Compound **3** was prepared by refluxing a pyridine solution containing (3-isocyanatopropyl)triethoxysilane (**2**) and **1**, at a molar ratio of 3.3:1, for 72 h. The product **3** was isolated by vacuum evaporation of the pyridine solvent. The solid product was then dissolved in THF, precipitated from hexane, and dried under vacuum. The reaction between **1** and **2** was monitored by FTIR. The FTIR spectra obtained at different reaction time intervals demonstrated that the isocyanate peak (2271 cm^{-1}) from **2** decreases and the urethane bands (1709 and 3378 cm^{-1}) from **3** increase with the progress of the reaction. The FT-IR spectrum of the organosilane monomer is given in Figure 2, which shows formation of the alkoxysilane terminated chromophore monomer (**3**). The structure of **3** is also verified by NMR spectra. ^{1}H NMR chemical shifts (δ): compound **1** (DMSO-d_6 solvent) 3.41–3.72 (m, br, $HOCH_2CH_2N$, $HOCH_2CH_2SO_2$); **2** ($CDCl_3$ solvent), 3.80 (q, $SiOCH_2$); **3** ($CDCl_3$ solvent), 4.02–4.55 (m, br, $NHCOOCH_2CH_2N$, $NHCOOCH_2CH_2SO_2$). ^{13}C NMR chemical shifts (δ): compound **1** (DMSO solvent), 53.4, 55.1, 57.7, 58.2 ($HOCH_2CH_2SO_2$, $HOCH_2CH_2N$); **2** (DMSO solvent), 57.7 ($SiOCH_2$); **3** (DMSO solvent), 54.7, 56.1, 59.4, 60.7 ($NHCOOCH_2CH_2N$, $NHCOOCH_2CH_2SO_2$).

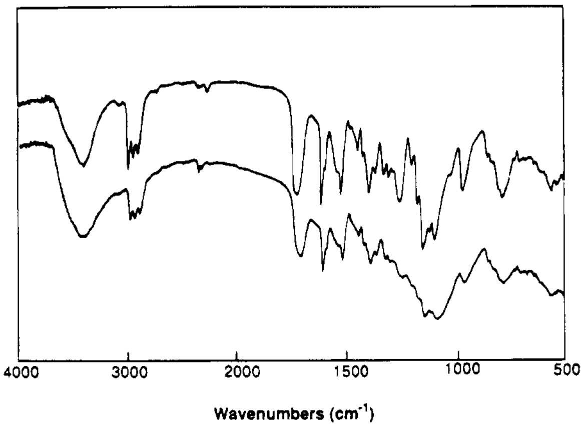

Figure 2. Infrared spectra of monomer **3**, from top to bottom: pristine, cured.

The basic sol–gel process involves sequential hydrolysis and polycondensation of silicon alkoxide.[7,15] To prepare the coating solutions, the alkoxysilane terminated chromophore (**3**) was mixed with tetraethoxysilane (TEOS) and water at a 1:3:21 molar ratio in THF. A small amount of hydrochloric acid was also added as a catalyst. The THF solution (10%) was stored at room temperature for several hours to hydrolyze the alkoxysilane groups and precured to increase the viscosity. The viscous THF solution was filtered through a 0.2 μm nylon filter and subsequently spin cast onto indium–tin oxide (ITO) coated glass slides. The films were vacuum dried at room temperature and poled by an electric field using a Corona setup.[16] To achieve optimum poling efficiency and cross-linking density, the films were poled using multistep poling schedules. The films were cured at 180 °C for 36 h under the poling field at the last stage of multistep poling to fix the poling-induced noncentrosymmetric lattices. The details of the poling will be presented elsewhere.[17] The cured films (thickness of 1–2 μm) are very tough and resistant to organic solvents. In their FTIR spectra, the absorption peak of Si–OEt bonds (1131 cm^{-1}) decreases and the absorption peak of Si–O–Si (1071 cm^{-1}) increases after curing. This indicates formation of the Si–O–Si linkage due to thermal condensation of silicon hydroxyl or ethoxyl groups. No glass transition temperature (T_g) was observed from DSC scans of the cured samples.

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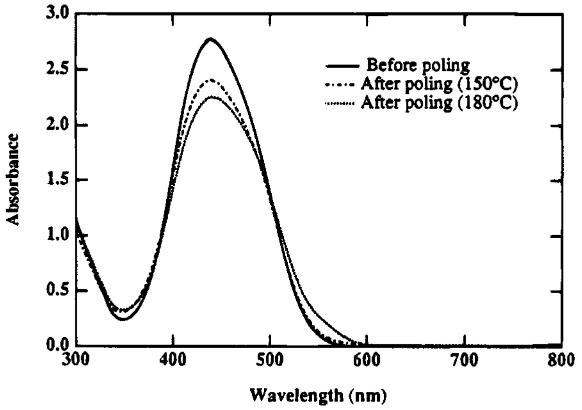

Figure 3. Ultraviolet–visible spectra of a sol–gel film on an ITO glass slide before and after poling.

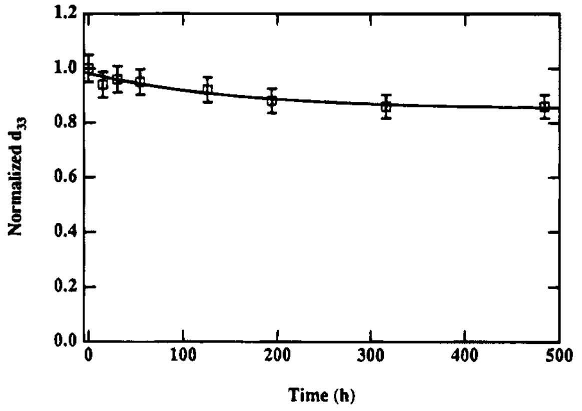

Figure 4. Plot of normalized d_{33} coefficients of a sol–gel film as a function of annealing time at 100 °C under air atmosphere.

UV–vis absorption spectra of the same film, before and after electric poling and thermal curing at different temperatures, are shown in Figure 3. The pristine sample shows an absorption peak at 440 nm, which is identical to the charge-transfer band of the chromophore monomer. After poling for 2 h at 150 °C, the peak absorbance decreased. This decrease is caused by alignment of chromophore dipoles along the poling field direction (also the incident light direction). The peak absorbance is further reduced after poling and curing at 180 °C. The SHG measurements demonstrated that the optical nonlinearities were increased after poling at 180 °C, which was consistent with optimized poling efficiencies as indicated by the peak absorbance decrease. The optical quality of the films after poling and curing remains excellent.

The second-order NLO properties of the films were characterized by second harmonic generation (SHG) at 1064 nm fundamental wavelength. A quartz crystal (d_{11} = 0.5 pm/V) was used as the reference in the measurement. A SHG d_{33} coefficient of 27 pm/V was calculated by comparing the second harmonic intensities between the sample film and the reference.[16] This d_{33} value is somewhat resonance enhanced due to the tail absorption of the material at the second harmonic wavelength 532 nm. Nevertheless, this thermosetting approach yields interesting optical nonlinearities, considering the moderate molecular hyperpolarizability (β) of the chromophore used. The high chromophore loading density, facilitated by covalent bonding, and good poling efficiency, realized through multistep poling and curing, are responsible for the improvement in the nonlinearities relative to those observed for composite materials.

The long-term stability of nonlinearity was studied by monitoring the SHG signal as a function of time at 100 °C (see Figure 4). The moderately good temporal NLO stability can be attributed to two factors. First, the system is heavily cross-linked due to the large number of available cross-linking sites and relatively small steric hindrance for the condensation reaction. Second, both ends of the chromophore are anchored into the silicate network by covalent bonds. These dramatically reduce the mobility of the chromophore and therefore enhance the thermal NLO stability. Conceivably, the thermal NLO stability can be further improved by curing the films for a longer time or at a higher temperature, and the optical nonlinearities can be increased by incorporation of large-β NLO chromophores.

In conclusion, we have prepared heavily cross-linked nonlinear optical sol–gel networks with both ends of the chromophores covalently anchored. Moderate second-order optical nonlinearity, stable at 100 °C, has been realized with the sol–gel system. The generalized synthesis scheme can be extended to prepare new materials with optimized NLO properties.

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