

SYNTHESIS AND OPTICAL PROPERTIES OF A NOVEL ORGANIC/INORGANIC HYBRID NONLINEAR OPTICAL POLYMER VIA SOL-GEL PROCESS*

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Abstract A new organic/inorganic hybrid nonlinear optical (NLO) material was developed by the sol-gel process of an alkoxysilane dye with tetraethoxysilane. A NLO moiety based on 4-nitro-4'-hydroxy azobenzene was covalently bonded to the triethoxysilane derivative, i.e. γ -isocyanatopropyl triethoxysilane. The preparation process and properties of the sol-gel derived NLO polymer were studied and characterized by SEM, FTIR, ¹H-NMR, UV-Vis, DSC and second harmonic generation (SHG) measurement. The results indicated that the chemical bonding of the chromophores to the inorganic SiO₂ networks induces low dipole alignment relaxation and preferable orientational stability. The SHG measurements also showed that the bonded polymer film containing 75 wt% of the akoxysilane dye has a high electro-optic coefficient (r_{33}) of 7.1 pm/V at 1.1 μ m wavelength, and exhibit good SHG stability, the r_{33} values can maintain about 92.7% of its initial value at room temperature for 90 days, and can maintain about 59.3% at 100°C for 300 min.

Keywords Sol-gel process, Nonlinear optical material, Alkoxysilane dye, Dipole alignment relaxation, Chromophore

INTRODUCTION

Nonlinear optics is presently an important topic of research because it forms the basis of photonics, which is expected to replace electronics in the next two decades for many applications such as fast waveguide electrooptic modulation, frequency doubling devices, signal processing, computers, etc. High NLO susceptibility, low optical losses, and high temporal stability of dipole orientation are the most desirable features of materials for such types of applications. In order to optimize optical nonlinearity and enhance the high temporal stability of NLO materials, various approaches have been developed^[1, 2]. But the optical properties of the existing NLO materials are still far from the necessary for the practical use of photonic device. It was found that the three-dimensional networks can effectively restrict the dipole alignment relaxation of the NLO chromophores, and thus lead to the required optical properties^[3]. Moreover sol-gel technology, because of the use of homogeneous liquid solutions and the ability to form gels at room temperature, provides an attractive route to the preparation of a three-dimensional inorganic network. Sol-gel processing has therefore become a new class of technology for preparing NLO materials of interest to many scientists. The three-dimensional network of organic/inorganic hybrid NLO materials can be prepared by doping optically active organics into sol-gel liquid solution or bonding the organic chromophores with the inorganics at a temperature below decomposition temperature (T_d) of the organic chromophores without risking the degradation of the organic components. The former, which has been studied extensively, affords ease of processing, but it is very difficult to further improve their NLO activity and stability due to the solubility limit of the organic chromophores in the inorganic sol^[4]. The latter, in which the chemical bonding of the chromophores to the inorganic networks, can effectively reduce dipole alignment relaxation of the

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Synthesis and Characterization of the Polymer Film

TEOS and NHAASD of desired molar ratio were hydrolyzed by mixing with water and C_2H_5OH . Concurrently, an appropriate amount of 1 mol/L HCl was slowly introduced into the mixture as the hydrolytic catalyst. Si—O—Si bond was formed via a condensation reaction of two kinds of hydrolyzed silicon alkoxides, and the SiO_2 network was formed via a subsequent polycondensation in which more extensive bonding of Si—OH species occurs. The hydrolysis and condensation reactions were allowed to proceed for 12 h at room temperature. Finally, the mixture solution was sealed and aged for four days to form a homogeneous and stable SiO_2 -sol (Si-sol) containing NHA, which has a pH of 3.3 and a viscosity of 6.1 mPa s.

The Si-sol containing NHA was diluted with 1,4-dioxane and then dispersed uniformly with ultrasound for 20 min to prepare the coating solution. Polymer films were deposited by spin-coating the Si-sol/1,4-dioxane solution onto 1-mm-thick glass substrates that had been previously cleaned with chromic acid mixture and then rinsed thoroughly with deionized water. The angular velocity of the spinner was 3500 ($^\circ$)/min. The wet films were left to dry further for two days at room temperature and then baked at 50 $^\circ$ C under vacuum for 2 h to remove residual solvent trapped in the samples. The resulting films are smooth, transparent and uniform with bright yellow color.

Poling/Cross-Linking and SHG Measurements of the Polymer Film

The polymer film was poled by the corona discharge method. After the film was poled at 70 $^\circ$ C and 8 kV for 10 min, its temperature was increased to 170 $^\circ$ C to vitrify the sample. The film was maintained at 170 $^\circ$ C and 8 kV for 1 h, and then cooled below 30 $^\circ$ C with the poling field still on. The curing temperature was chosen to be 170 $^\circ$ C according to the upper limit temperature of the poling setup and the T_g of the NHA and the NHAASD. The second-order NLO properties of the poled NHAASD films were determined by a SHG measuring setup at 1.1 μ m wavelength. The detailed experimental setup and calculations of the r_{33} have been previously discussed^[8].

RESULTS & DISCUSSION

Synthesis and Characterization of Alkoxysilane Dye

ICPTEOS is a kind of common organic silane intermediate. Under basic conditions, it can easily react with NHA having —OH group via active $O=C=N-$ group to form urethane (here refers to NHAASD) and yields a great deal of heat energy. Here no additional hydroxyl groups are generated, therefore no further nucleophilic addition reactions between —OH group and $O=C=N-$ group will take place. So this kind of urethane reaction provides an attractive route for preparing alkoxysilane dyes. However, the resulting —OCONH— group can further react with the $O=C=N-$ group of the ICPTEOS to form branched polyurethane. Therefore, the effective restraint of the latter polyurethane reaction is the key to prepare NHAASD successfully. Due to the lower activity of the —OCONH— group than the —OH group and the larger steric effect exerted on —OCONH— group, the nucleophilic addition reaction of the —OCONH— group with the $O=C=N-$ group usually proceeds under higher temperature than that needed for the —OH group. Effective restraint of the polyurethane reaction can be realized by controlling the reaction temperature. It was found that the nucleophilic addition reaction between the —OH group and the $O=C=N-$ group can proceed adequately at room temperature, and no subsidiary reactions take place^[4]. The FT-IR spectra of the reaction system at various stages are shown in Fig. 1. As time goes on, a gradual increase of asymmetrical stretching vibration of $O=C=N-$ group at 2277 cm^{-1} was observed, while the intensity of absorption peaks relative to NHAASD, such as acylamide peak (I) at 1700 cm^{-1} , acylamide peak (II) at 1518 cm^{-1} and stretching vibration peak of N—H at 3360 cm^{-1} , decreased gradually.

The reactive $O=C=N-$ group can also react easily with H_2O to form substituted urethane and liberates CO_2 , so the whole system must always be kept strictly dry during the process. In addition, an appropriate amount of triethylamine was added to the reaction system as the basic catalyst.

Synthesis and Characterization of the Polymer Film

NHAASD is in fact a silicon alkoxide just like TEOS^[9], so the sol-gel process of NHAASD can proceed under conditions similar to those used in the sol-gel process of TEOS. The initial molar ratios of TEOS:

NHAASD:water:ethanol were 1:3:12.5:5, and the initial concentration of the catalyst HCl was 0.07 mol/L. More detailed information about the chemistry of sol-gel process can be found in several review articles dealing with sol-gel science. However, it is worth mentioning that the steric effect makes the hydrolysis and polycondensation reactions of NHAASD more difficult than those of TEOS, so the sol-gel process of NHAASD should be made to proceed at an elevated temperature or for a prolonged time. By evaluating the properties of the Si-sols obtained under various reaction conditions, the hydrolysis and polycondensation of NHAASD at room temperature for four days was considered to be the optimum preparation conditions. The resulting sols were homogeneous, transparent and stable for a long time.

The chromophore content in the bonded polymer film, which is closely related to the activity of NLO material, is controlled by the amount of NHAASD introduced into the coating Si-sol. Bonding the chromophores to an inorganic matrix can improve the solubility of organics in inorganic sol, and the alkoxy silane dye and the inorganic components can be mixed in virtually any proportions necessary to obtain the desired properties in theory. The larger the added amount of NHAASD, the higher the NLO activity of the film. In fact, because NHAASD is also a silicon alkoxide, the coating Si-sol can be directly derived from the hydrolysis and polycondensation of NHAASD without TEOS, as Jeng has done previously^[10]. But the amount of hydrolysis groups in NHAASD is much less than that in TEOS, so an appropriate amount of TEOS must be added the initial reactants to increase the viscosity of the coating Si-sol. Here, TEOS actually acted as a binding agent or a plasticizing agent^[9]. In this paper, the molar ratio of TEOS:NHAASD was set at 1:3.

The above Si-sol containing the organic chromophore cannot be used directly for the coating of the polymer films before adding an appropriate amount of diluting agent, otherwise the resulting films are liable to crack or become translucent. The Si-sol containing the organic chromophore can mix homogeneously with the diluting agent in any necessary ratio, so the volatility, rather than the solubility of solvent, becomes the decisive factor for controlling the quality of polymer film. If the volatility of chosen diluting agent is too high, the fast volatilization of the solvent from a wet film will result in heat-crack of the film in the subsequent drying processing. On the contrary, if the volatility is too low, the residual solvent will greatly reduce the purity of the resulting film. Therefore, an appropriate diluting agent must have a moderate volatility. In addition, the appropriate diluting agent also must have a good affinity for the glass support. It was found from our experiments that DOX or tetrahydrofuran (THF) was the most suitable diluting agents, and the optimum ratio of the Si-sol to the diluting agent was 5:1 by volume in order to obtain integrated, transparent and uniform polymer films. The morphology of the resulting film is shown in Fig. 2.

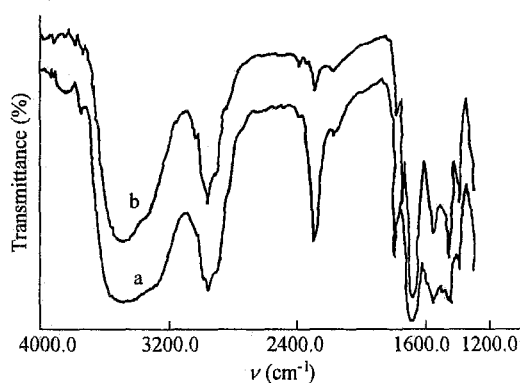


Fig. 1 FTIR spectra of NHA-ICPTEOS system at various stages
a) 5 min; b) 30min



Fig. 2 The morphology of NHAASD film

Optimization of Poling and Curing Conditions for the Polymer Film

A DSC scan using a scanning rate of 10 K/min showed that the dried NHAASD film had an extremely broad T_g zone from 49°C to 139°C due to its broad molecular weight distribution. After curing at 170°C for 1 h, the T_g shifted to a much higher temperature region from 107°C to 230°C. This implies that the curing reactions have already occurred in the Si-sol. These curing reactions also can be confirmed by IR spectra. As shown in Fig. 3, after heating for 1 h at 170°C, an appreciable change of absorbance in the IR spectra was observed due to the drastic decrease of the intensity of hydroxyl stretching vibration around 3400 cm^{-1} , bending vibration of H-O-H bonds at 1640 cm^{-1} and Si-ethoxyl bonds at 945 cm^{-1} . Moreover, the intensity of the absorption peak of stretching vibration of Si—O—Si bonds at 1100 cm^{-1} increases significantly after the curing process.

A further study showed that a higher curing temperature is necessary for high T_g systems because of low reaction rates after vitrification, so the higher the poling and curing temperature of the NHAASD film, the better the thermal stability of the NLO material. According to the upper limiting temperature of the poling setup and the T_d of NHA and NHAASD, the curing temperature was chosen to be 170°C. From the IR spectra, the absorption peaks of the NLO chromophore such as stretching vibration of nitro groups at 1518 and 1342 cm^{-1} , —C=C— groups at 1602 and 1433 cm^{-1} , and —N=N— groups at 1405 cm^{-1} remained almost unchanged in intensity and shape. So did acylamide peak (I) at 1700 cm^{-1} and acylamide peak (II) at 1518 cm^{-1} . It is, therefore, confirmed that thermal decomposition of the organic chromophores can be neglected at these poling and curing conditions.

As shown in Table 1, with increasing curing time, the T_g gradually increases, but the net increase of the T_g gradually decreases. When the curing time increases to 100 min, no net increase of the T_g could be seen. So 100 min was considered to be the optimum curing time.

Table 1. The relationship between crosslinking time and T_g of NHAASD-Sol

Crosslinking time (min)	0	60	80	100	120	140
T_g (°C)	49–139	107–230	114–235	121–241	122–241	122–243

Finally, the NHAASD film cured at 170°C for 100 min was soaked in DOX or THF (good solvent for both NHA and NHAASD) for 1 h. The two solvents did not show any color change. This implies that the NHA molecules were already firmly locked inside the inorganic matrix.

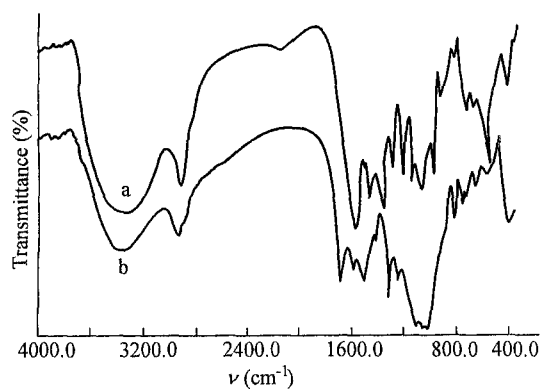


Fig. 3 FTIR spectra for NHAASD

- a) Original
- b) Right after poling and curing

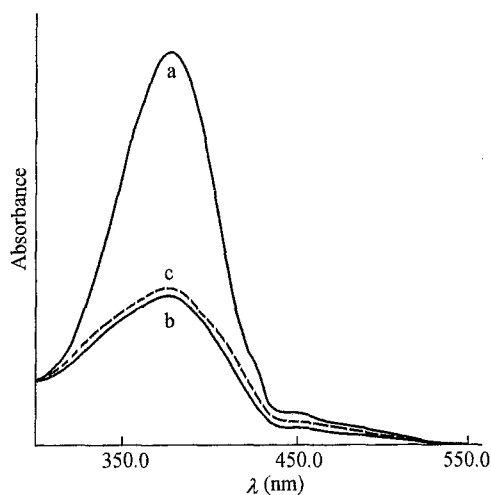


Fig. 4 UV-Vis spectra of NHAASD

- a) Original
- b) Right after poling and curing
- c) Cured at 100°C for 5 h

Figure 4 shows the UV-Vis absorption change of the NHAASD film in the process of thermal treatment. Immediately after poling and curing, a drastic decrease in absorbance was observed as expected (curve b). This is partly due to the orientation of the organic chromophores in the direction of poling field and the sublimation of the NHA molecules. The absorption spectrum of the cured NHAASD film is similar to that obtained before curing, which confirms that the NHA molecules incorporated in the inorganic network were not degraded after the curing process. However, the UV-Vis absorption spectrum shows a slight blue-shift due to the further crosslinking of Si-sol. Moreover, a small increase in absorbance (curve c) was observed when the cured NHAASD film was subjected to thermal treatment for additional 5 h at 100 °C. Apparently, the dipole alignment of NHA relaxed slightly due to the permanent heating at a temperature adjacent to the initiative T_g of the resulting NHAASD film. However, the temporal stability and the dipole alignment relaxation of the bonded polymer film were all greatly improved relative to those of the doped film.

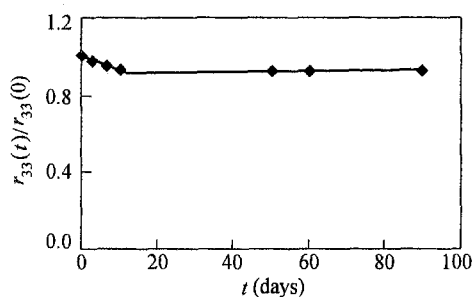


Fig. 5 SHG decay of the poled and cured NHAASD at RT

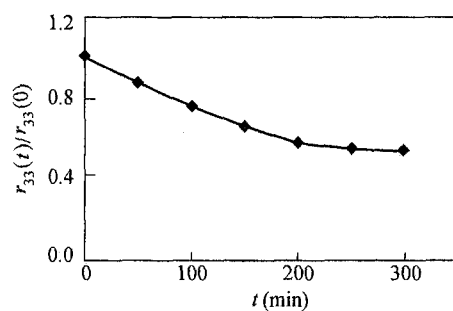


Fig. 6 SHG decay of the poled and cured NHAASD at 100 °C

SHG Values and NLO Properties of Polymer Film

The SHG measurement showed that the bonded polymer film mentioned above had a much higher r_{33} value of 7.1 pm/V at 1.1 μm wavelength, compared to the doped film containing the same amount of the organic chromophores (3.6 pm/V)^[11]. It was confirmed that chemically bonding organic chromophores to the inorganic network could greatly improve the NLO activity of the polymer films. As shown in Fig. 5, the r_{33} value of the bonded film is quite stable at room temperature, and only 7.3% decay was observed after 90 days, while the r_{33} value of the doped film had a 19.5% decay under the same conditions^[11]. Moreover, the decay of the r_{33} value almost ceased after this time. Figure 6 shows that the r_{33} of the bonded film subsequent to heating at 100 °C for 300 min has only a reduction of 40.7% of its initial value, while the r_{33} value of the doped film showed a 60.5% decay under the same conditions^[11]. The above results show that the resulting bonded film has higher NLO susceptibility, and better stability either at room temperature or at higher temperatures. All these observations imply that the chemical bonding of the chromophores to the SiO₂ networks could effectively reduce the dipole alignment relaxation of the chromophores, and thus lead to the better orientational stability.

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