Thermal dynamic behavior of SHG in a novel interpenetrating hybrid polymer material

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A novel interpenetrating hybrid polymer material for second-order NLO was synthesized by sol-gel process. The structure of the hybrid polymer films were analyzed via FT-IR and SEM; UV-vis spectra and SHG measurement were utilized to characterize the linear and nonlinear optical properties. When the simultaneous poling and curing process was carried out under different temperature, the thermal dynamic behavior of SHG of different hybrid polymer films were studied in details. Results showed that the better thermal dynamic stability of NLO can be achieved when the poling and curing temperature was at 160°C.

1. Introduction

Second-order nonlinear optical properties of poled polymer materials have been researched extensively for a number of years because of their highly promising potential applications in photonic technologies such as doubled-frequency laser source, electro-optical modulation, optical signal processing, optical inter-connects, etc.

It is well-known that the noncentrosymmetric alignment of NLO chromophores results from the poling process is the origin of second-order nonlinearity, which is not in a state of thermodynamic equilibrium. So, the alignment would decay to an equilibrium isotropic state when poling electric field is removed. Therefore, the relaxation of chromophore orientation is minimized, raising the poling-induced orientation efficiency as well as prolonging temporal stability at temperature employed, are most important issues in practical devices.

Over the past few years, several methods have been investigated to stabilizing the poling-induced optical nonlinearities in poling polymer, such as, cross-linkable polymer system,[1] high glass transition temperature system (e.g. polyimides)[2] and nonlinear optically active sol-gel systems.[3-4]

Sol-gel technology provides an attractive route to the preparation of the three-dimensional inorganic network. Sol-gel based nonlinear optical materials can be divided into two classes, the guest-host matrixes and chromophore-linked hybrid. Hou et al. studied the second-order optical nonlinearity of hybrid materials by mixing DR-1, PMMA and TEOS, but it is a simple physical doping or blending.[5] In the latter, many investigators prepared sol-gel precursors by linking chromophores and silane coupling agent, for example, 3-isocynatopropyltriethorysilane, then were processed under sol-gel hydrolysis/condensation to yield a hybrid materials.[6]

In this communication, we developed a new route to achieve second-order NLO hybrid material, that is, the organic macromolecule chains and inorganic silica networks interpenetrated in one system. Firstly, we synthesized a copolymer covalently incorporating NLO azobenzene and silane-coupling agent, then the interpenetrating hybrid polymer films was obtained under sol-gel hydrolysis/condensation process by adding TEOS. Under different temperature of simultaneous poling and curing, the structure of the hybrid film was analyzed via FT-IR and SEM, UV-vis spectra and SHG measurement were utilized to characterize the linear and nonlinear optical properties. At last, effect of different temperature on thermal dynamic behavior of SHG was studied in details.

2. Experiment
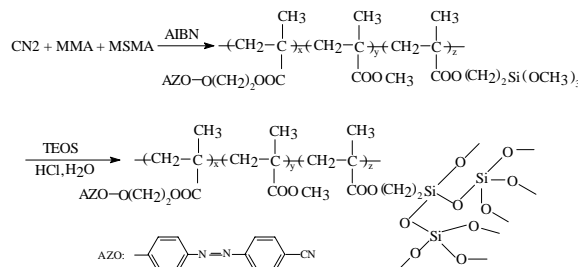
2.1 Materials and film preparation

Fig.1. Synthesis of the hybrid polymer sol.

for the SHG under laser pulses at 1064 nm.

Methyl methacrylate (MMA, ACROS ORGANICS) was purified by distillation before use. 3-(trimethoxysilyl) propyl methacrylate (MSMA) was a commercial product (Nanjing Yudeheng Fine Chemical Co., Ltd), and distilled under reduced pressure. The monomer CN2 with azo group was synthesized in our lab.

The synthesis of the hybrid polymer sol in Fig.1, was as follows: MMA (0.2074g) and MSMA (0.1327g), azo monomer CN2(0.5074g), the initiator AIBN(0.089g), and the solvent THF, were added into a 250ml reaction flask and were polymerized at 60 °C under nitrogen flow for 0.5 h. Then, a homogeneous THF solution of TEOS (0.1119g), appropriate deionized water and hydrochloric acid (1M) were added dropwise over 1h into the reaction mixture simultaneously and respectively with rigorous stirring to avoid local inhomogeneities. The reaction was allowed to proceed at 60 °C for another 3 ~4 h, and then the hybrid polymer sol were obtained. The amount of THF solvent was adjusted to avoid gelation. The obtained hybrid sol was filtered through a 0.2µ Teflon membrane. Finally, thin film was made by spin coating on glass substrates.

2.2 Characterizations and measurements

UV-vis absorption spectra were measured by transmission on a Shimadzu UV-3100. The Fourier transfer infrared (FTIR) spectra were recorded using a Nicolet MAGNA-IR 750 spectrometer. The cross-sections of the hybrid polymer film were observed via SEM (XT30 ESEM-TMP, Philips, Netherland).

The corona poling process for the polymer films was carried out using the in-situ poling technique. The corona discharge was generated from a tungsten wire, which was 1.0 cm gap above the film. The corona field was applied on the film accompanied by being slowly heated to different temperature, further curing was maintained for 1 h, and then cooled down to room temperature. In this process, the corona current was maintained at 2µA with a potential of 4.0 kV.

The source was a mode-locked YAG laser delivering 36 ps pulses at 1064 nm at a repetition rate of 10 Hz. The beam waist diameter at the sample location was 2 mm. The energy in each laser shot is 1 mJ, which gives a fluence of 0.9 GWcm^{-2}. A home-made oven was added to control the sample temperature; thermal dynamic behavior of SHG was monitored with the elevated temperatures. In the same time, the SHG signal from the PMT was integrated by a boxcar integrator and averaged over ten shots by computer software.

The Second-order NLO coefficient d_{33}, was evaluated by use of a Y-cut quartz crystal as the reference material, for which a value of $d_{11} = 0.5$ pm/V was assumed.

3. Results and discussion

3.1 UV-Vis

Fig. 2 shows the absorption spectrum of the hybrid polymer film. The maximum absorption wavelength is about 360 nm. Apparently, the absorbance at 532nm is weak; this can be avoided absorbance from material itself,
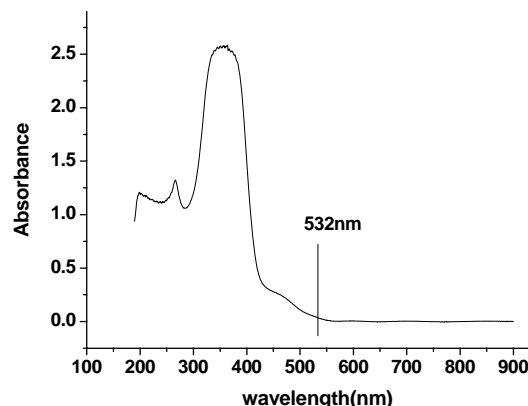

Fig. 2. UV-vis absorption spectra of the hybrid polymer film.

3.2 FT-IR

The infrared spectra of the hybrid polymer films are shown in Fig 3, including the original and the poling and curing samples at different temperature. The peak at 3347 cm^{-1} is assigned to O–H vibrations, 2870 cm^{-1} is due to the C-H symmetric stretching, 1140 cm^{-1}is Si-O-Si asymmetric stretching, 926cm^{-1} is associated with SiOH bands, 790cm^{-1}for Si-O-Si symmetric stretching. [7]
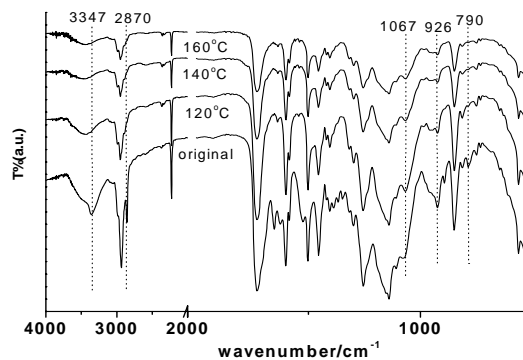

Fig. 3. FT-IR of hybrid polymer films treated at different temperature.

Compared with the original sample, further condensation reaction between –OH and Si-OH in the hybrid film occurred after heat treatment at different temperature. The peaks at 3347 and 926 cm^{-1} disappear gradually, confirming the above condensation reaction. Simultaneously, further cross-linked Si-O-Si structure formed in the hybrid polymer films after heat treatment at different temperature. We can see the peak at 1067 cm^{-1}for Si-O-Si asymmetric stretching was further apparent.[8] In addition, the symmetric stretching vibration peak at 2870

and 790 cm^{-1} also disappeared after heat treatment, which maybe due to the limitation of cross-linked Si-O-Si structure in the films.

3.3 SEM

The fracture surface of the hybrid polymer film was observed using SEM, which can give important information about the morphology of this hybrid material.
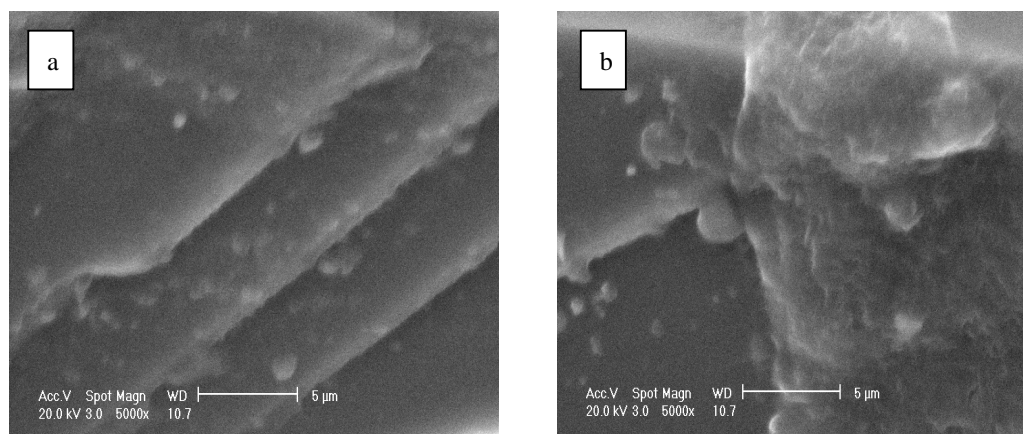
Fig 4(a) clearly show the SiO$_2$ particles in hybrid films were well-distributed in the continuous polymer matrix, the good compatibility between inorganic SiO$_2$ and organic polymer chains can be observed, which resulted from the interpenetrated covalently hybrid system. Fig 4(b) also illustrates the morphology of SiO$_2$ particles in the polymer matrix, the interface between SiO$_2$ and polymer matrix was not separate obviously, which confirms further the chemically connection between them.

Fig.4. SEM of hybrid polymer film treated at 140 ^{o}C (a, b).

3.4 Thermal dynamic behavior

Considering the application in device, the temporal and thermal stability of the materials are two important factors. To investigate the thermal dynamic stability, effective SH intensity as a function of temperature was measured. Similar to previous report,[9] a parameter of specific temperature T_0 was defined as effective relaxation temperature. The T_0 value provides information on maximum device operating temperature that the film can endure, and allows quick evaluation of the thermal stability of the materials.

As shown in Fig. 5, a heating rate was controlled at 2 ～ 3℃/min, temperature dependence of the dipole reorientation of three samples were observed. The SH intensity of samples were stable at lower temperature, but decayed significantly at the specific temperature T_0.
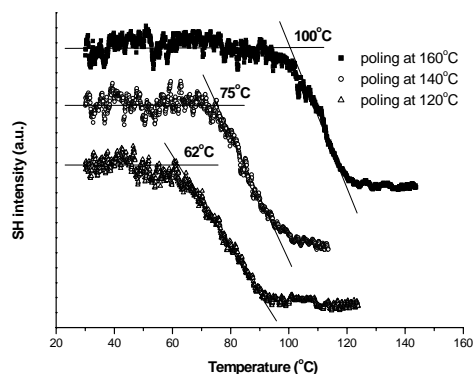
For the three samples in Fig. 5, T_0 value is as 62,75,100℃, respectively. This difference is related to the different cross-linked degree of the so-gel systems. Obviously, the higher cross-linked degree, the better thermal dynamic stability would be. For instance, for the sample of cured at 160℃, the higher cross-linked degree didn't provide enough local free volume to rotate the oriented chromophore when the operating temperature was under about 100℃, that is, the interpenetrating hybrid polymer network restricted randomization of the oriented chromophore, [9] therefore, a better thermal dynamic stability can be attained, compared to other samples. In addition, by comparing with d_{11} of the quartz (d_{11} = 0.5 pm/V), the initial second-order nonlinear optical coefficients d_{33} were estimated to be 9.52,11.16,12.50pm/V for the samples treated from 120 to 160℃, which was determined from the SHG intensity by the equation(5) in literature.[10]

4. Conclusions

A novel hybrid polymer material for second-order NLO was synthesized. The structure and morphology of the hybrid polymer films were analyzed via FT-IR and SEM. UV-vis spectra shows the weak absorption at 532nm, which is benefit for SHG device under the laser of 1064nm. The relationship between the simultaneous poling and curing process temperature and thermal dynamic behavior of SHG for different hybrid polymer films were studied, and the better thermal stability of NLO was obtained when the poling and curing temperature was at 160°C. Our results suggest that this hybrid polymer material has potential applications in photonic devices.

Fig. 5. Thermal dynamic stability of NLO for the hybrid polymer films.

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