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Preparation and second-order nonlinearity of organic/inorganic hybrid materials doped with organic chromophore

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Abstract. A kind of hybrid material was made through sol-gel process with the PMMA, TEOS, and 4-[N]-ethyl-N-(2-hydroxyethyl) amino-4'-nitro-azobenzene (DR1). And the films of sol were prepared by using the spin-coated method. Through all optical poling, it could be found that there exists an optimum thickness for film. In addition, the higher of sample temperature was, the smaller intensity of SHG was. The experiment showed that the SiO_2 network was existent, and hybrid materials significantly improved orientation stability.

PACS: 42.65.Ky
Key words: thin film, all-optical poling, SHG, temperature

1 Introduction

Second-order nonlinear optical (NLO) materials have been extensively studied for applications in optical communication and electro-optic modulators due to their large optical nonlinearity, fast response and easy processing. In order to produce second-order effects and ordered arrangement of molecular in films, they need to be polarized by using such as electric-field poling and all-optical poling (AOP) [1]. In recent years, second harmonic generation (SHG) intensity has been optically induced in NLO polymer materials by all optical poling process [2–5],especially, study on thin films of azo compound has been acquired marked achievement [6, 7]. All-optical poling was described for the first time by Charra *et al.* as a novel method in 1993 [8]. This method is simple and possible to work at ambient temperature and an automatic molecular organization with a period satisfying the phase-matching conditions.

On the other hand, PMMA is one of the most commonly non-linear organic substrate materials, easy to be prepared and compatible with the chromophore. Under normal circumstances, it has no interaction with the chromophore molecules. But such material is restricted

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to the application of optical devices for its lower glass transition temperature and fast relaxation. In order to overcome these shortcomings, the organic-inorganic composite materials have been extensively studied [9–11]. Sol-gel technology provides a synthesis of organic-inorganic composite materials approach. The composite material does not require harsh conditions, and it has the advantages of organic and inorganic materials, such as maintaining the film-forming organic polymer, transparency, thermal stability, abrasion resistance.

In this paper, we prepared a new kind of second-order nonlinear optical hybrid material doped disperse red 1 (DR1) from sol-gel method. The second-order nonlinearity was achieved by all-optical poling.

2 Experiments

2.1 Materials and preparation

The molecular structures of 4-[N-(2-hydroxyethyl)-N-ethyl] amino-4'-nitroazobenzene (disperse red 1) and Polymethyl methacrylate (PMMA) were shown in Fig. 1. The organic-inorganic hybrid film was prepared as follows: 0.5 gram of PMMA was dissolved in THF on the mass ratio of 1:10, and then 0.5 ml of TEOS was put into the solution, stirring 1h. The hydrochloric acid (0.15 mol/l) was added to the solution while stirring. The molar ratio of TEOS and H_2O was 1:4. With the addition of hydrochloric acid, hydrolysis reaction took place, with the process of hydrolysis reaction, the solution became turbid, and accompanied by heat release. After a period of timečňwe continue to stir the solution to clarify once again. 0.02 grams DR1 was added to the above solution, this solution was sealed at room temperature for 3 days. The sol was spin coated on glass substrates, and the resultant gel films were dried at 40^oC for 24h. The samples were subject to all-optical poling and second harmonic generation measurements.

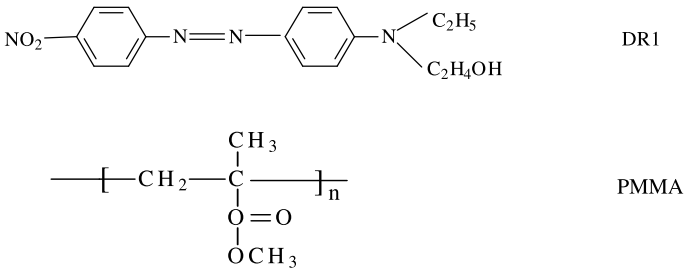

Figure 1: The molecular structure of DR1 and PMMA.

2.2 All-optical poling

The schematic diagram of the experimental setup is shown in Fig. 2. The laser beam was an Nd: YAG laser operating at wavelength of 1064 nm. The pulse-width and the repetition rate

of the output pulses from the laser were 35 ps and 10 Hz, respectively. The second-order NLO coefficients of the polymer films were obtained using a Z-cut quartz crystal plate as a reference. The fundamental beam (ω) which entered the dark box was split into two beams by mirror M2, one was reference light that passed through the z-cutted quartz crystal, the other passed through the sample platform which was used to place the thin-films. A KDP crystal was employed to double the fundamental beam (ω), and it can be removed in and out by a device in order to poling the thin-films and measure the signal of SHG. The photomultiplier tube (PMT) was used for exploring the signal of SHG after poling. F_2 and F_3 before PMT were used to filter the residual 1064 nm light. The experimental data was collected by boxcar and inputted to the computer. As the writing beams, the light of 1064 nm and 532 nm were co-linear and focused onto the film, and when measuring, KDP was removedčňonly the light of 1064 nm focused on the film. Temperature-controlled box was used for heating the thin films if needed. The laser power was 1.7 mJ and 58 μJ for 1064 nm and 532 nm.

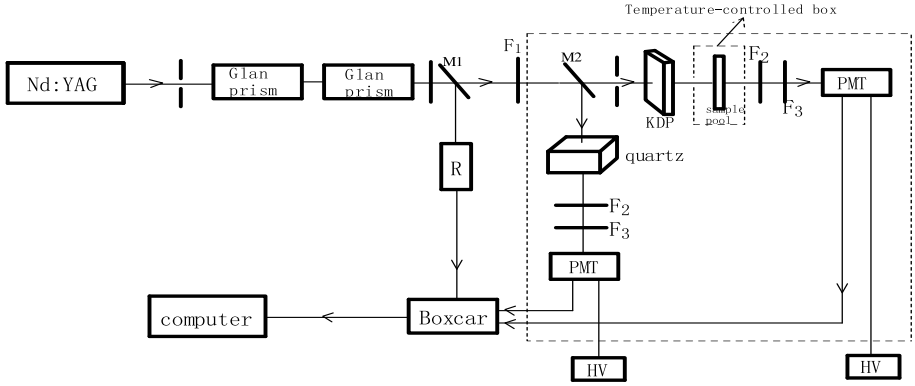

Figure 2: Schematic diagram of all optical poling.

3 Results and discussion

3.1 UV-Vis absorption spectra and thickness of the films

Fig. 3 shows the absorption spectra of the PMMA/DR1 film and PMMA/SiO_2/DR1 film in uv-vis wavelength region. The sold line is the absorbance spectrum of PMMA/DR1 film, and the dot line is the absorbance spectrum of PMMA/SiO_2/DR1 film. From Fig. 3, it can be found that there was a difference of 12 nm between the absorption peak of PMMA/DR1 film and PMMA/SiO_2/DR1 film. It was caused that the (Si-OH) in gel has great interaction with the (-OH) of DR1 molecules. And the existence of acid can make the organic materials protonated. For the above reasons, the dipole moment changes, the position of absorption peak makes red shift. Fig. 4 shows the spectrum of PMMA/SiO_2/DR1 films under different thickness. The thicknesses of five samples were shown in Table 1.

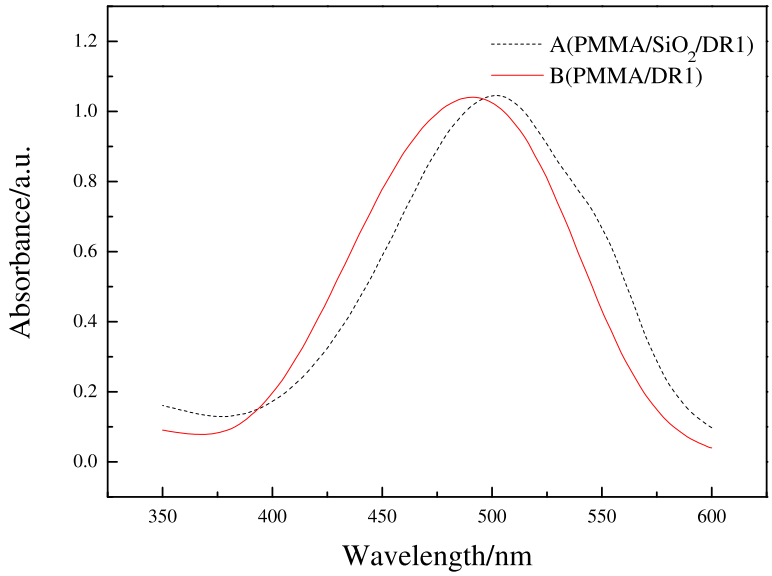

Figure 3: Absorption spectrum of PMMA/DR1 and PMMA/SiO_2/DR1 film.

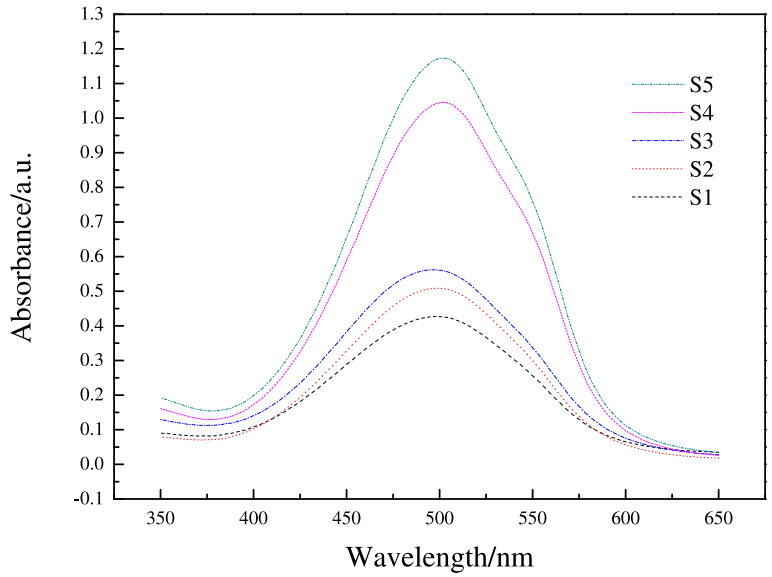

Figure 4: Absorption spectrum at different thickness of PMMA/SiO_2/DR1 film.

Table 1: The thickness of five samples.

Sample	S1	S2	S3	S4	S5
Thickness/nm	1027	1227	1402	2785	3103

3.2 Poling at different thickness

In order to investigate the influence of thickness for PMMA/SiO_2/DR1 film, the samples were poled using all optical poling at different thickness. The results were shown in Fig. 5. Curves S1-S5 shown the growth of the optically induced SHG signal from the different thickness films at room temperature. It can be seen that different thickness films have different saturation values. Through all optical poling, it could be also found that there exists an optimum thickness. The second-order nonlinear susceptibility is relevant to three factors: one is the dye contain azo group. At the time of all optical poling, fundamental (ω) and its second harmonic signal (2ω) acted on the films together, and leaded to orientational hole burning and isomerization orientation effect. The presence of azo group directly affects the possibility of isomerization elements. The second is the dipole size of molecule itself, from the molecular point of view, the domain of π donor and acceptor induced molecular dipole moment which determines the second-order nonlinear effects. Third is the absorption of the films at 532 nm, light absorption that is too much or too small has influence to the signal after poling (self-absorption). The more azo molecules for made the probability for generating SH bigger, but the more absorption at 532 nm made the SHG weaker during AOP. The absorption at 532 nm for thin-films was shown in Fig. 4. So there was an appropriate thickness for PMMA/SiO_2/DR1 film. In this paper we acquire that the optimal thickness is about 1500 nm.

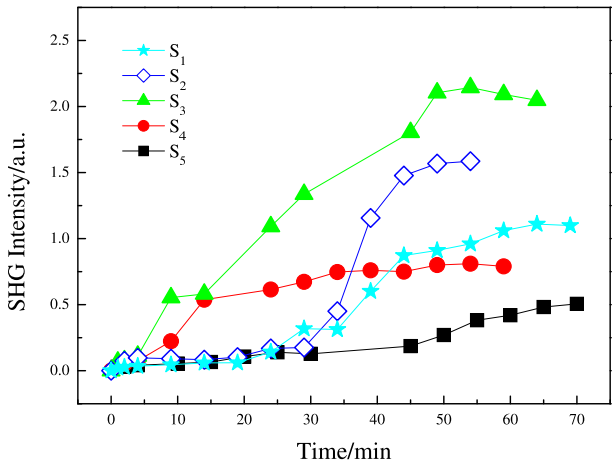

Figure 5: Dependence of SHG intensity on poling time at different thickness.

3.3 Poling at different temperatures

Fig. 6 shows the saturated SHG intensity of PMMA/SiO_2/DR1 film at 25°C, 30°C, 50°C, 70°C, 90°C. It can be seen from the figure that the higher of the poling temperature was, the weaker of the SHG intensity was. In other words, the better poling temperature of the films was at room temperature. All-optical poling lead to three processes: the molecular at excited-state, the trans-cis isomerization and the reorientation of azobenzene molecules [12]. At the same

time during all optical poling, with the temperature increasing the lifetime of azo molecule at excited state was decreasing, and on the other side the thermal relaxation of azo molecule could not be ignored in the time interval of adjacent laser pulses. The repetition rate of the laser output pulses was 10 Hz, therefore the interval of laser pulse was 100 ms, which was longer than the lifetime of the excited state of the azobenzene molecule (60 ms), so the cis-trans thermal back isomerization was still an important role to the macroscopic SHG signal. Therefor the SHG intensity was decreased with the increase of temperature.

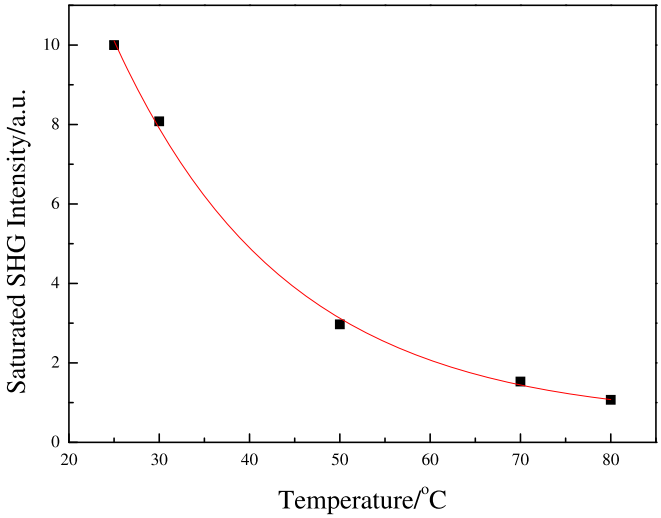

Figure 6: The saturated SHG intensity at different temperature.

3.4 Relaxation process of PMMA/DR1 film and PMMA/SiO_2/DR1 film

The PMMA/DR1 film and PMMA/SiO_2/DR1 film were poling under the same condition. When the SHG signal reached saturation values, the seed light (2ω) was blocked and the decay evolution was measured. The experimental result was shown in Fig. 7, it can be fitted with a exponential function:

$$y(t) = A_0 + A\exp(-t/\tau_A), \tag{1}$$

$$y(t) = \frac{I^{SHG(t)}}{I^{SHGmax}}, \tag{2}$$

where constant A_0 represented the clear valid orientation molecular number after stopping AOP, is the time constant for relaxation process. The values of the kinetic constants about Eq. (2) were listed in Table 2. According to Table 2, we can see that A_0 and of PMMA/DR1 film are bigger than A_0 and of PMMA/SiO_2/DR1 film. This can be explained that the stability were improved of organic-inorganic hybrid materials, because there have a strong network of interactions between organic chain and SiO_2, such as hydrogen bonding and van der Waals

force, the strong interaction force structure which improve the material hardness, thus limiting the activities of the organic chain movement. This shows that the existence of the network as a result of SiO_2 hybrid second-order nonlinear materials significantly improved stability.

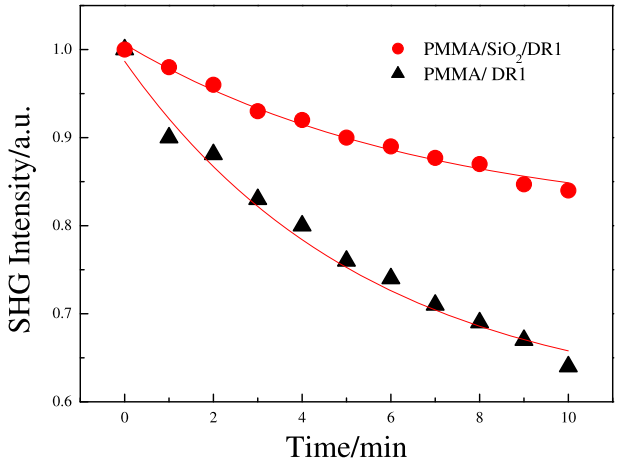

Figure 7: Relaxation of PMMA/DR1 film and PMMA/SiO_2/DR1 film.

Table 2: Fitting values about the relaxation kinetic constants of films.

Sample	A_0	A	τ_A
PMMA/DR1 film	0.73	0.27	10.9
PMMA/SiO_2/DR1 film	0.54	0.45	7.3

4 Conclusion

In conclusion, we had synthesized a new kind of hybrid material via sol-gel process with the PMMA, TEOS, and 4-[N]-ethyl-N-(2-hydroxyethyl) amino-4'-nitro-azobenzene (DR1). The films were studied by AOP method. From the absorption spectra, the absorption peak of PMMA/SiO_2/DR1 film was red shift about 12 nm compare with that of PMMA/DR1 film. Through the all optical poling, it could be found that there exists an optimum thickness. And the higher the temperature is, SHG smaller is. Through the relaxation figure, it shows that the existence of SiO_2 network, hybrid materials significantly improved orientation stability.

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