OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 3, No. 11, November 2009, p. 1217 - 1220

Effect of cross-linked degree on thermal dynamic behavior of SHG in a polymer system based on melamine

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The temperature dependence of SHG (second harmonic generation) based on hexamethoxymethyl melamine (HMMM) and Disperse red 1 was experimentally investigated. The simultaneous poling and curing process was carried out under 120、140 and 160°C, respectively. The structure and thermal behavior of the sample was analyzed via FT-IR, DSC and TGA; UV-vis spectra and SHG measurement were utilized to characterize the linear and nonlinear optical properties. At elevated temperature, effect of cross-linked degree on thermal dynamic behavior of SHG was 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.

(Received September 27, 2009; accepted October 29, 2009)

Keywords: SHG, Thermal stability, Cross-linked degree, Melamine

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.

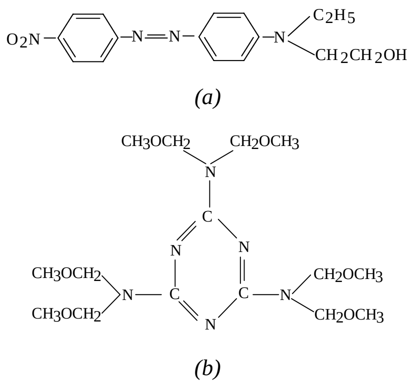
Over the past few years, several methods have been investigated to stabilizing the poling-induced optical nonlinearities in poling polymer, such as, cross-linkable polymer system [1], high glass transition temperature system (e.g. polyimides) [2] and nonlinear optically active sol-gel systems [3-4].

Melamine-based materials have been widely used in the lighting, coating, and decorating industries because of their good transparency. Jeng et al. reported the first complete study on melamine-based polymers by sol-gel process [5], their results showed that these materials with low optical loss, high Tg, and cross-linked features are good candidates for the second-order NLO system.

In this work, azobenzene chromophores DR-1 with reactive group of hydroxyl were incorporated into the matrix based on prepolymer of HMMM by sol-gel process. Under different temperature of simultaneous poling and curing, the structure and thermal behavior of the system was analyzed via FT-IR, DSC and TGA; UV-vis spectra and SHG measurement were utilized to characterize the linear and nonlinear optical properties. At elevated temperature, effect of cross-linked degree on thermal dynamic behavior of SHG was studied in details.

2. Experiment

2.1 Materials



(a)

(b)

Fig.1.Chemical structures of: (a) DR-1; (b) HMMM.

Disperse red 1 (ACROS ORGANICS) were recrystallized from ethanol. HMMM (Resimene747) was from Solutia and was used as received. Fig.1 shows their chemical structure. The prepolymer of HMMM was prepared by heating the monomer at 60℃ for 12 h, then 80℃ for 12 h in the presence of an acid catalyst. The prepolymer of HMMM (0.9g) and DR-1 (0.1g) was dissolved in cyclopentanone with water (0.1g) and acetic acid (0.1g) to aid the hydrolysis of the prepolymer. This solution was stirred for 1 h at room temperature, and then was filtered through a 0.2μ Teflon membrane. Finally, thin film was made by spin coating on glass substrates.

2.2 Measurements

The Fourier transfer infrared (FTIR) spectra were recorded using a Nicolet MAGNA-IR 750 spectrometer. The Differential scanning Calorimetry analysis (DSC) was performed on a Shimadzu DT-50 thermal analyzer under nitrogen flow in a range from room temperature to 300°C at a scan rate of 10°C/min. The thermogravimetric analysis (TGA) was preformed on a Shimadzu TGA-50H thermo-analyzer under an air flow rate of 6×10^{-5} m^3/min at a scan rate of 10°C/min. UV-vis absorption spectra were measured by transmission on a Shimadzu UV-3100.

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 polymer 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 *FT-IR*

The major cross-linking reaction was shown in equation (1), which results in the loss of –OH and $–OCH_3$ groups to form ether cross-link and liberate methanol [6]. Side reactions involve reactions of the melamine ether groups with either methylol or imino groups on other melamine molecules.

$$-NCH_2OCH_3 + ROH \overset{H^+}{\rightleftharpoons} -NCH_2OR + CH_3OH \qquad (1)$$

Methylol groups may be present in the original resin HMMM, or may be generated during the cure reactions through hydrolysis of the ether bond. Methylols, being alcohols,may react with ether groups of other melamine molecules to form ether cross-links, or methylene cross-links in the possible reactions[6].

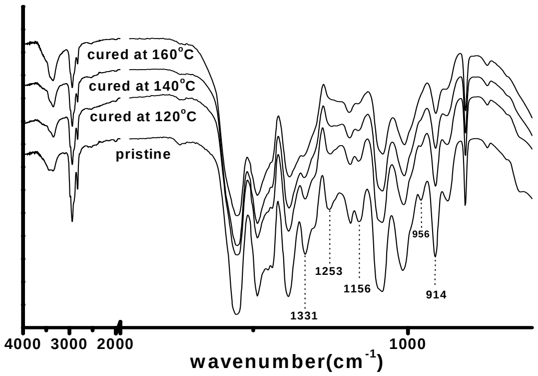


Fig. 2. FT-IR of cured HMMM/DR-1 at different temperature for 1 h.

As was shown in Fig. 2, there are several marked changes in FT-IR, before and after the curing process under increased temperature for HMMM resin. The loss gradually at 1331 and 1253 cm^{-1}, was assigned to the β (O-H) in methylol groups; the loss at 956 cm^{-1}, was assigned to the γ (O-H) in methylol groups; the loss at 1156, and weakness at 914 cm^{-1}, were due to the ν (C-O-C) in methoxymethyl groups. These changes are due to the primary cross-linking reaction. In the same time, they are according with different degree of cross-linking under different temperature, that is to say, cross-linked degree of the substrate of HMMM was increased prominently with the elevated temperature from 120 to 160°C.

3.2 *DSC and TGA*

Figs. 3 and 4 shows the DSC and TGA of the cured HMMM-DR-1 system under different temperature, respectively. In Fig. 2, an endothermic peak at 208°C was observed apparently, after the HMMM-DR-1 system was treated under 120 °C. With the increased cured temperature, the endothermic peak disappeared gradually. For the sample treated at 160 °C, the glass transition temperature (Tg) appeared obviously at about 180 °C.

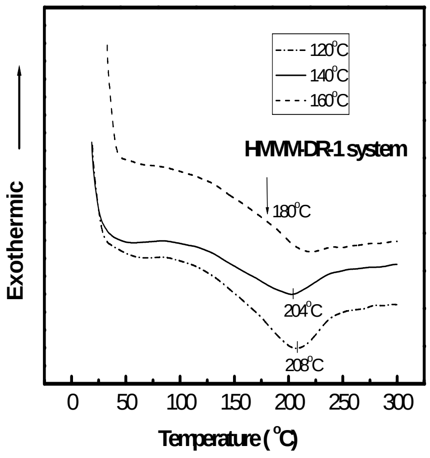


Fig. 3. DSC of cured HMMM/DR-1 at different temperature for 1 h.

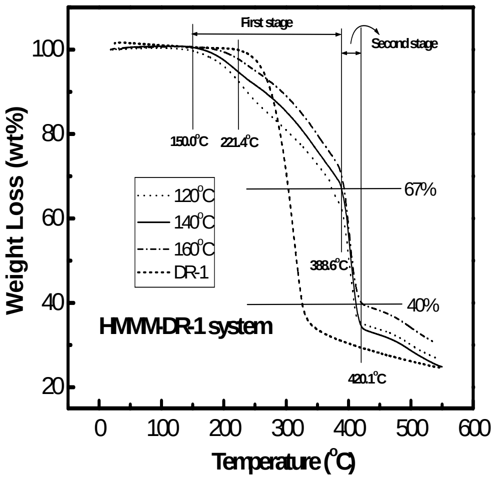


Fig. 4. TGA of cured HMMM/DR-1 at different temperature for 1 h.

For the HMMM-DR-1 system, the appearance of endothermic peak was mainly due to advanced sol-gel cross-linking reaction of the substrate of HMMM [7], and not including the sublimation of the chromophore DR-1, because the initial decomposition temperature of DR-1 was 221.4 °C in Fig. 4. In the same time, the disappearance of endothermic peak was in accordance with different degree of cross-linking, and it also shows that optimized curing conditions was under 160 °C ,that is, the advanced sol-gel cross-linking reaction was basically completed, and a better cross-linked degree of the HMMM-DR-1 system can be obtained.

In Fig. 4, two-stage thermal degradation behaviors were also observed, similar to the literature [7], however, the mechanism is different. The first-stage degradation from about 150.0 to 388.6°C included two components, one is the advanced sol-gel reaction of the HMMM-DR-1 system, and the other is the decomposition of DR-1, especially after 221.4 °C; for the second stage, it is mainly contributed from the decomposition of DR-1, the similar TGA profiles from 40 to 67% weight loss for DR-1 and three samples from 388.8 to 420.1°C were the apparent evidence.

From Table 1, with the increased cured temperature, the three decomposition temperature also increased, this proved the different cross-linked degree of the samples. Moreover, all the initial decomposition temperature is greater than the corresponding cured temperature; it showed that the selected cured temperature is an important factor to affect the cross-linked degree of the system. In the meanwhile, initial decomposition temperature of the system should be smaller than the chromophore DR-1, and then the corresponding cured temperature will be reasonable. Therefore, the best curing conditions should be under 160 °C for HMMM-DR-1 system.

Table 1. TGA parameter of DR-1 and cured HMMM/DR-1 at different temperatures.

sample TGA parameter (℃)	HMMM/DR-1			DR-1
	120℃	140℃	160℃	
Initial decomposition temperature	129.68	145.59	173.84	221.4
decomposition temperature Ⅰ (5% weight loss)	206.51	218.87	252.42	263.21
decomposition temperatureⅡ (10% weight loss)	239.11	269.13	299.14	273.81

3.3 UV-Vis

The typical UV-vis absorption spectrum of the cured HMMM/DR-1 at 140 °C was showed in Fig. 5.The maximum absorption wavelength($\lambda_{\max}$) of the system before poling/curing was at around 500.5nm, after poling/

curing, a decrease in absorption and a blue shift to 486.5nm were observed in the spectrum, and this was due to orientational dichroism[5] and electrochromism[8] resulting from the induced dipole alignment, however, not included the degradation (or sublimation) of DR-1, this is otherwise to previous report[5,9].

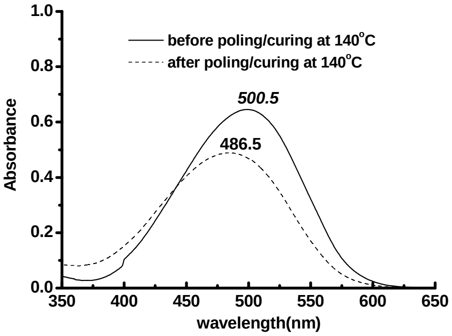


Fig. 5. UV-vis absorption spectra of the cured HMMM/DR-1 at 140 °C.

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 [10], 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. 6, 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.

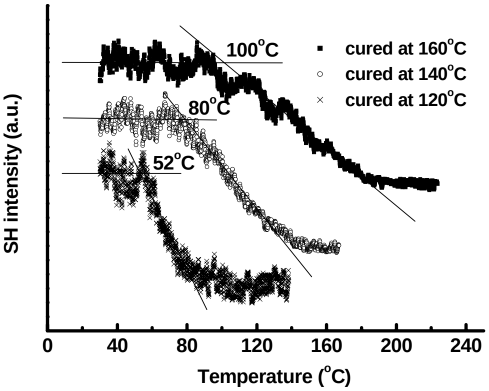


Fig. 6. Temperature dependence of the dipole reorientation dynamics of the cured HMMM/DR-1.

For the three samples in Fig. 6 , T_0 value is as 52,80,100℃, respectively. This difference is related to the different cross-linked degree of the 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 polymeric HMMM network frame restricted randomization of the oriented chromophore[7,10]. 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 13.25 pm/V for the sample of cured at 160℃,which was determined from the SHG intensity by the equation(5) in literature [11].

Acknowledgements

This work was supported by the China Postdoctoral Science Foundation funded project (20080441013), Jiangsu Ordinary University Science Research Project (08KJB430008), National Natural Science Foundation of China (10704042 and 60178030), "Qing-lan project" of Jiangsu province (2006), Open Project (M05003) of Laboratory of Solid State Microstructures, Nanjing University.

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