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NLO Polymers Containing Anionic Chromophore

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Preparation of second order nonlinear optic (NLO) materials based on cellulose diacetate and melamine derivatives was tried. The NLO chromophore sodium [4′-(N, N-dihydroxyethyl) amino] phenyl-4-azo-benzene sulfonate incorporated into the crosslinking network resulted from cellulose diacetate and trimethylolmelamine or hexamethylolmelamine. The poled and cured NLO materials exhibited the electro-optic coefficient r_{13} of 1.72 pm/V or 1.15 pm/V at the laser wavelength of 1550 nm, modulation frequency of 12.7 kHz, and the r_{13} value decreased to 71.5% or 81.5% of the initial values after 4 days. The laser transmission loss was 0.94 dB or 1.76 dB. The crosslinking materials showed better temporal stability than the material of the host/guest type. The results of FTIR, dielectric relaxation, and TGA proved the formation of the crosslinking structure and that the dielectric relaxation was suppressed by higher crosslinking density.

Keywords cellulose diacetate, trimethylolmelamine, hexamethylolmelamine, NLO material, sodium [4′-(N, N-dihydroxyethyl) amino] phenyl-4-azo-benzene sulfonate

Introduction

Development of optical communications led to great interest in the research on nonlinear optical (NLO) materials, especially those based on organic polymers, which could possess the advantages of large susceptibility, high laser damage threshold, faster response time, low light loss, versatility of molecular structure and good mechanical performance (1). However, because of the rotational freedom of the chromophores and relaxation of the macromolecular chains, the second order nonlinear optical property was generally not very stable, when the temperature approached the glass transition temperature (Tg) of the NLO material (2). For a material useful in optical devices, the NLO polymer should be chemically and physically stable (3). Therefore, most research was focused on polymers of high glass transition temperature (Tg) (4, 5) or crosslinking polymers (6, 7).

Cellulose derivatives (8) are noted for its toughness, surface gloss, smoothness, and clarity owing to the glucose units. Moreover, hydroxyl groups are attached to the molecule of cellulose derivative and can react with some crosslinking agents to form a crosslinking network. Therefore, cellulose derivatives might be useable for preparing NLO material.

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Melamine derivatives are widely used for lighting, coating, and decorating because of their good transparency (9). The preparation of the materials based on melamine derivatives involved condensation reaction, which could provide an attractive way for formation of crosslinking polymer network (10) to stabilize the oriented NLO chromophores by decreasing their mobility. In addition, melamine-based polymer could show low optical loss and high Tg. Some literature (11, 12) reported that methylated hexamethylolmelamine was taken for preparing NLO polymer materials.

Attention to chromophores containing anionic groups was widely drawn to prepare second order NLO materials because of their large susceptibility (13). The chromophores containing anionic groups could be used in the way of intercalation (14), inclusion (15) or self-assembly (16, 17).

In the present work, preparation of second order NLO materials based on cellulose diacetate and chromophore sodium [4′-(N,N-dihydroxyethyl) amino] phenyl-4-azo-benzene sulfonate (SDPS) with trimethylolmelamine or hexamethylolmelamine as a crosslinking agent was tried.

Experimental

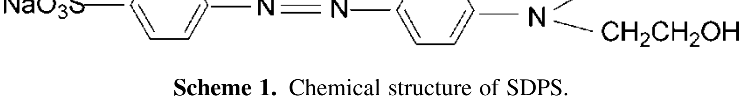
Materials

Cellulose diacetate $[C_6H_7O_2(OCOCH_3)_{2.4}(OH)_{0.6}]_n$ [8], N,N-dihydroxyethylaniline was an industrial product and available from Shanghai Chemicals Reagent Co. and Haining Chemicals Co., respectively. Other starting materials and solvents were of reagent grade and used as received.

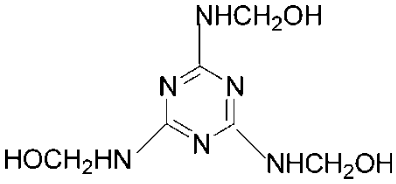
Synthesis

Chromophore of Sodium [4′-(N,N-Dihydroxyethyl) amino] Phenyl-4-azo-benzene Sulfonate (SDPS). A water solution of sodium *p*-amino benzene sulfonate containing 17.3 g of *p*-amino benzene sulfonic acid and 5.3 g of sodium carbonate was mixed with 19.8 g of sulfuric acid (concentration of 98%). 7.0 g of sodium nitrite was added dropwise at 0°C. After 40 min, 1.0 g of carbamide was added. After 20 min, a 18.1 g solution of N,N-dihydroxyethylaniline was added, and the resultant was neutralized by the solution of sodium carbonate until the pH value reached 7.8. After 3 h, 100 g of sodium chloride was added. At last, 25.5 g of orange solid was obtained by filtration and recrystallization from water. Its Tm = 279.5, Td = 286.8. The result of elemental analysis for $C_{16}H_{18}N_3NaO_5S$: C, 49.43%; H, 4.87%; N, 11.2%: (calculated: C, 49.61%; H, 4.65%; N, 10.85%).

Trimethylolmelamine (TMM). A revised procedure reported by Reference (18) was used. According to the reference, formaldehyde (160.0 g, concentration of 37 wt%) was neutralized with triethanol amine (2.0 g), until the pH value reached 8. Then, water (100 g) and



Scheme 1. Chemical structure of SDPS.



Scheme 2. Chemical structure of TMM.

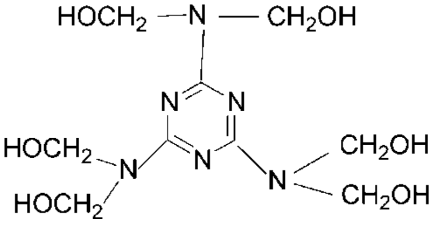
melamine (75.0 g) were added gradually. The solution was heated to 78°C for 30 min. Then, water was added.

In the present work, the water was not added after keeping the solution at 78°C for 30 min, but the solution was directly cooled to room temperature, stored for 24 h and filtrated. Solid TMM (40.0 g) was obtained after the filter cake had been washed with water several times and dried below 50°C under vacuum.

Hexamethylolmelamine (HMM). A revised procedure reported by Reference (19) was used. According to the reference, formaldehyde (91.3 g, concentration of 37 wt%) was mixed with water (24.2 g), and then neutralized with a solution of sodium hydroxide (concentration of 10%), until the pH value reached 9.0. Melamine (23.6 g) was added gradually. Then, the solution was heated to 60°C and maintained at this temperature for 3–4 h. It was then cooled to room temperature and filtrated. Hexamethylolmelamine (42.7 g) was collected after the filter cake was washed with water several times and dried below 50°C under vacuum.

In the present work, 152.2 g formaldehyde was used instead of 91.3 g.

The Solution of NLO Materials. CDA, TMM or HMM was dissolved in N,N-dimethylformamide (DMF) to form the solution of CDA in DMF with the concentration of 8.0%, the solution of TMM in DMF with the concentration of 20.0% and the solution of HMM in DMF with the concentration of 20.0% (by weight), respectively. Every solution was filtered to remove impurities. The NLO polymer solution containing 25% SDPS and without any crosslinking agent (sample I) was prepared by mixing 0.125 g of SDPS and 4.7 g solution of CDA in DMF, The NLO polymer solution containing TMM and 25% SDPS (sample II) was prepared by mixing 0.125 g of SDPS, 0.875 g solution of TMM in DMF and 2.5 g solution of CDA in DMF. The NLO polymer solution containing HMM and 25% SDPS (sample III) was prepared by mixing 0.125 g of SDPS, 0.875 g solution of HMM in DMF and 2.5 g solution of CDA in DMF.



Scheme 3. Chemical structure of HMM.

Poling/Curing of Films. Every above described solution was spin-coated on an ITO glass plate to form film with the thickness of about 3 μm. The film was dried at 75°C under vacuum for 24 h., and then the film was poled and cured under voltage of 6 kV and at a temperature of 90°C. After 20 min, the voltage was increased to 6.5 kV while temperature was kept at 90°C. Then the voltage was increased stepwise until it reached 8 kV and the temperature was increased stepwise to 180°C. The process was shown in Figure 1. The whole poling/curing process was carried out for about 150 min. The film was then cooled to room temperature in the electric field.

Measurement

The weight loss of the samples was determined by using the WRT-2P TGA instrument at the heating rate of 10°C/min. The Nicolet AVATAR 360 FTIR spectrometer was used to characterize the chemical composition of the NLO materials. Elemental analysis was carried out with the Heraeus CHN-RQPID instrument. The dielectric relaxation of the NLO materials was tested with the CONCEPT 40 dielectric spectrometer (provided by Novercontrol GmbH). The laser transmission loss was measured with the Anritsu MS9710B optical spectrum analyzer.

Second Order Nonlinearity r_{13}. For measuring the value of susceptibility $\chi^{(2)}$, the Pockels effect was determined with a Mach-Zehnder interferometer prepared by Shanghai Jiaotong University, The electro optic coefficient r_{13} values of the materials were found under the conditions of laser wavelength 1550 nm and modulation frequency 12.7 KHz. The schematic diagram of the experiment setup is shown in Figure 2. The main part is an optical fiber Mach-Zehnder interferometer consisting of two fiber couplers (2 and 5). A piezoelectric tensor (PZT) phase modulator is put in one of the two light paths between the two couplers to adjust the phase difference. The polarization controller (3) is used to control the state of polarization of the interference laser beam. The polymer film is inserted into the other light path (1) perpendicularly. The optical signal output is detected with a PIN diode and a lock-in amplifier (11).

The electro optic coefficient r_{13} could be calculated by the following equation:

$$r_{13} = \frac{2I_{m0}\lambda}{\pi n^3 V_{m0}(I_{\max} - I_{\min})}$$

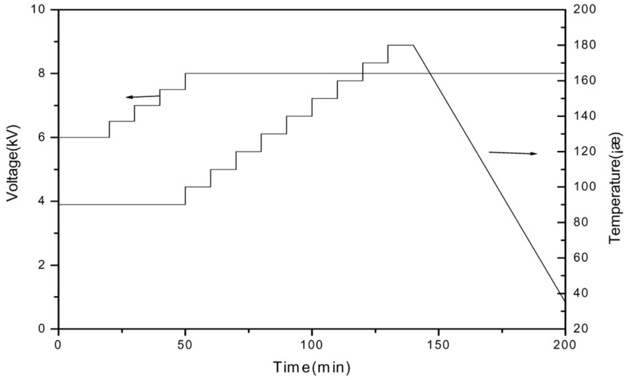


Figure 1. The process of stagewise poling/curing of the films.

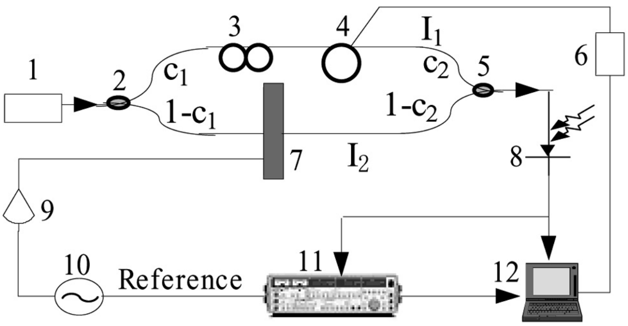


Figure 2. Setup of the measurement system.
(1, Laser; 2, Coupler 1; 3, Polarization controller; 4, PZT; 5, Coupler 2; 6, DC voltage source; 7, Polymer sample; 8, Detector; 9, Amplifier; 10, Waveform generator; 11, Lock-in amplifier; 12, Computer.)

where I_{m0} is the modulation intensity, λ is the wavelength, n is the refractive index of the polymer film, V_{mo} is the modulation voltage, I_{max} and I_{min} are the maximum and minimum of output light intensity.

Results and Discussion

Characterization of the Samples Before and After Curing

Because of the hydroxyl groups attached to CDA and SDPS which were able to react with the N-hydroxymethyl groups of TMM or HMM (20), and of the self-condensation of N-hydroxymethyl groups between themselves (10), the samples II and III could form crosslinking network in the process of curing/poling. The sample I, however, was a simple host/guest type and could not form crosslinking network. Figures 3, 4, and 5 are the IR spectra of samples I, II and III before and after curing respectively. No difference can be found between the two IR spectra in Figure 3. The peaks at 3374 cm^{-1}, 1557 cm^{-1} and 1007 cm^{-1} in Figure 4 represent hydroxyl groups, N-hydroxymethyl groups and primary hydroxyl groups (21) of the sample II. In Figure 5, the peaks at 3373 cm^{-1}, 1554 cm^{-1} and 1009 cm^{-1} represent hydroxyl groups, N-hydroxymethyl groups and

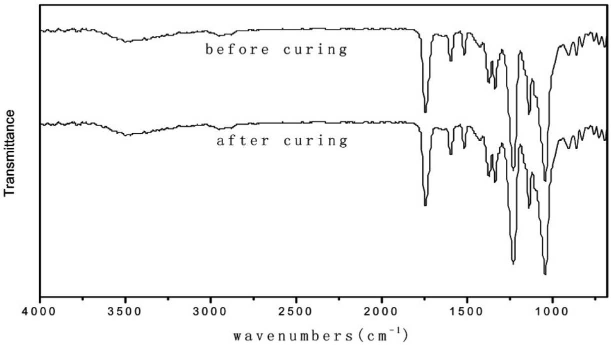


Figure 3. Infrared spectra of sample I.

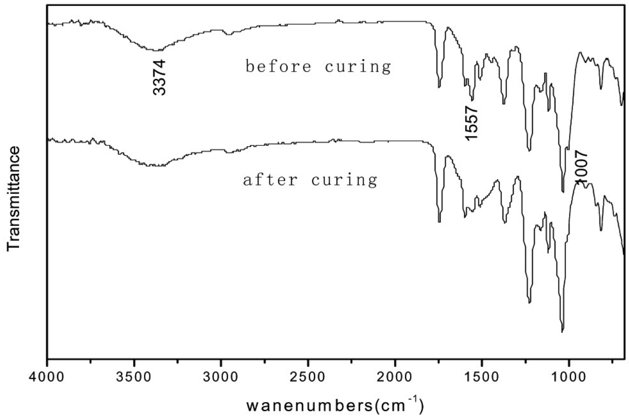


Figure 4. Infrared spectra of sample II.

primary hydroxyl groups of the sample III. The area of these peaks decreased after curing, suggesting reactions of them for forming crosslinking network.

The molecular chain relaxation of the samples would be hindered by crosslinking network. Broadband dielectric spectroscopy is effective for studying the relaxation behavior of NLO polymer (22). The temperature dependence of the dielectric loss "log (tanδ)" of the cured samples I, II, and III is given in Figures 6, 8 and 10, and that of the uncured samples II and III in Figure 7 and 9. The dielectric relaxation experiments were carried out under the conditions from 1 Hz to 1000 kHz and from −60°C to 220°C. The relaxation of chain segments would be too late to be matchable for higher frequency if the temperature was not high enough. Therefore, the temperature should increase to capture the relaxation of chain segments under the condition of high frequency, or the frequency should be low. This means that the relaxation could be shown apparently at low frequency at same temperature (23). For this reason, the data at 1 Hz were used for discussion. The β relaxation, observed near 60°C in the figures of cured samples I, II and III and near 20°C in the figures of uncured samples II and III, is attributed to the motion of methylene or methylene ether bridge and of some unreacted

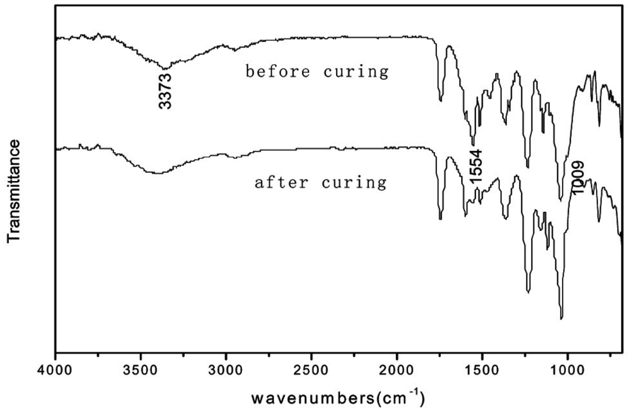


Figure 5. Infrared spectra of sample III.

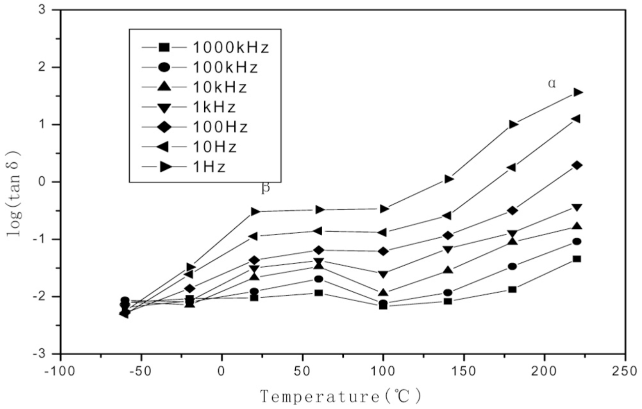


Figure 6. Temperature dependence of log (tan δ) of the cured sample I.

groups (24). Compared to the cured samples, the low β relaxation temperature of β relaxation of the uncured samples implied less restriction on the above mentioned motion in the samples without crosslinking network. The cured sample I revealed higher amplitude (-0.484) than the cured sample II (-0.866) and III (-0.644). This should be also in relation to the fact that the sample I did not contain any crosslinking structure. The cured sample III with HMM containing more functional groups showed, however, higher amplitude of β relaxation than that of the cured sample II with TMM containing less functional groups. This abnormal phenomenon might be resulted from the more opportunities for self-condensation of HMM, which led to unhomogeneity of the crosslinking density of the sample III.

The α relaxation in the figures is associated to the chain segment mobility in the glass transition of the samples (25). Compared to the amplitude of the cured sample II (-0.699) and III (-0.469), the larger amplitude ofαrelaxation of the uncured sample II (1.425) and III (-0.047) was due to the low crosslinking density of the uncured samples. The amplitude of α relaxation of the uncured sample II was higher than that of the uncured sample III because TMM could only form lower crosslinking density than HMM during the test period. The cured samples II and III show lower values of log (tan δ) than the cured sample I (1.563 at 1 Hz), indicating formation of crosslinking structure of the

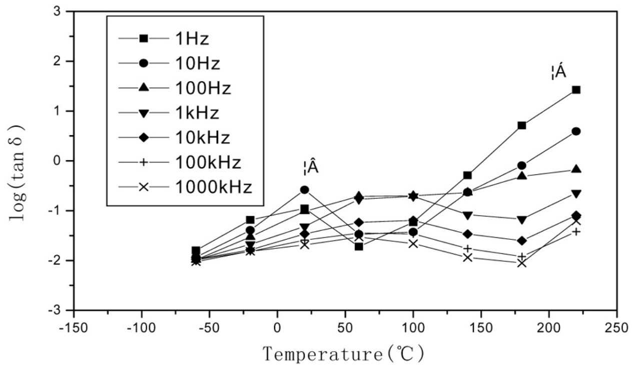


Figure 7. Temperature dependence of log (tan δ) of the uncured sample II.

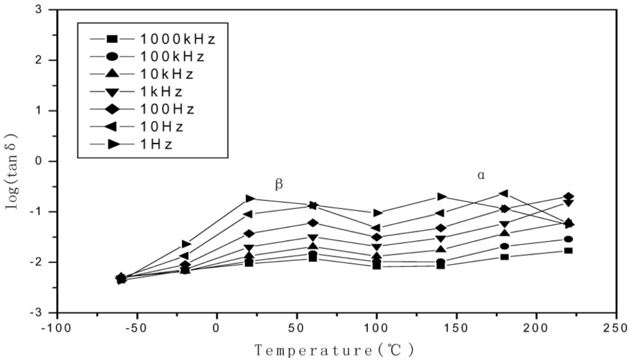


Figure 8. Temperature dependence of log (tanδ) of the cured sample II.

cured samples II and III after poling/curing process. The crosslinking structure could decrease the amplitude of α relaxation (26). The higher value of the α relaxation of the cured sample III than that of the cured sample II should also result from the more opportunities for self-condensation of HMM.

The α relaxation temperature of the cured samples I, II, III and uncured samples II and III was near 220°C, 140°C, 180°C, 220°C, and 220°C at 1 Hz, respectively, in Figures 6–10. The temperature of α relaxation of the cured samples II and III was lower than that of the cured sample I, which might be due to some unreacted molecules of TMM and HMM or some condensates of themselves which could weaken the intermolecular force of the samples and behave similar to "plasticizer" (27). The cured sample III reveals higher temperature of α relaxation than that of the cured sample II, meaning that the crosslinking density of the former was higher than that of the latter. As for the uncured sample, the α relaxation is intensified with increasing temperature, because it form network of lower crosslinking density during the test period.

Figure 11 shows the TGA curves of samples II and III after curing. No evident weight loss below 285°C was found, indicating the high heat resistance of the cured samples.

The Electro Optic Coefficient r_{13}

Figure 12 depicts the temporal behavior of electro optic coefficient r_{13} of the three cured samples. It can be seen that the initial r_{13} values of samples I, II and III are 1.59 pm/V,

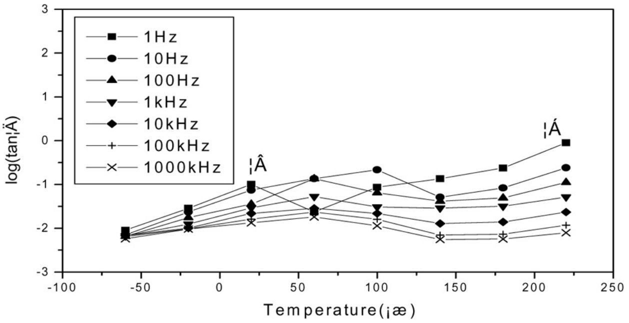


Figure 9. Temperature dependence of log (tan δ) of the uncured sample III.

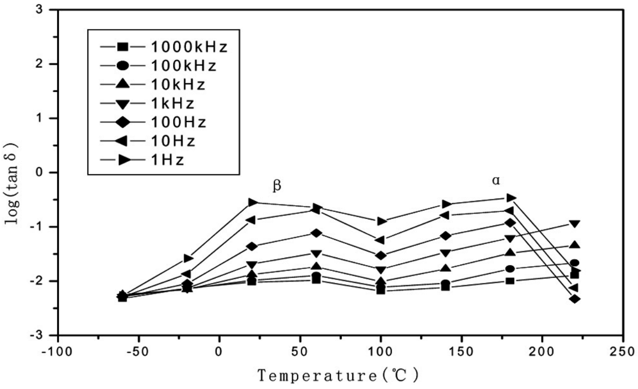


Figure 10. Temperature dependence of log (tan δ) of the cured sample III.

1.72 pm/V, and 1.15 pm/V, respectively. The lowest initial r_{13} value of the sample III could be a result of the lower orientation degree of SDPS chromophores, which was due to too fast and early crosslinking of the sample III containing HMM. The r_{13} values of the samples I, II and III after 4 days were 1.01 pm/V, 1.23 pm/V, and 0.96 pm/V, respectively. The r_{13} value of the sample I decreased to 63.5% of its initial value, while those of the samples II and III to 71.5% and 83.5% of their initial values, respectively. As an explanation, the samples II or III formed a crosslinking network, which could hinder the relaxation of oriented chromophore. Because the crosslinking density formed by TMM was lower than that formed by HMM, the stability of the electro optic coefficient r_{13} of the sample II should also be lower than that for the sample III. It could be further found in Figure 12, that the r_{13} values of the cured samples II and III increased at first and then decreased. This phenomenon might be attributed to the fact that the electret (28) formed easily during the corona poling process when the NLO material contained the anionic chromophore. The local electric field induced by electrons which had entered into the NLO material during the corona poling process could make the chromophores orient further so that transient increase of r_{13} value could be found after the polarization electric field was removed, but the oriented chromophores

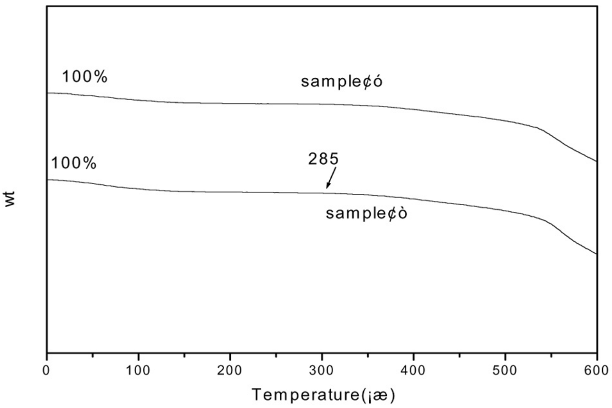


Figure 11. TGA curves of sample II and III after poling/curing.

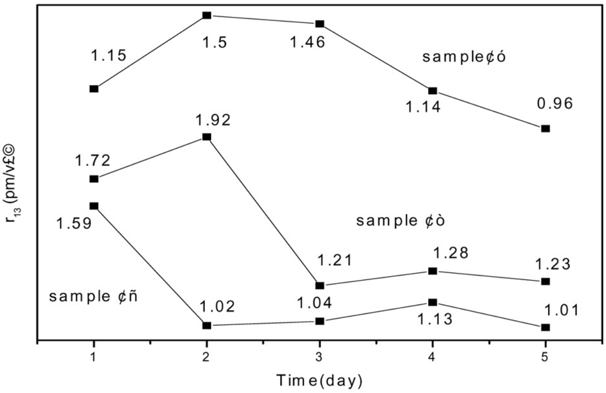


Figure 12. The temporal dependence of electro optic coefficient r_{13} of the cured samples 3, the transmission loss of laser.

could relax again due to the attenuation of electrons, which resulted in a decrease of the r_{13}. By comparison to the sample II, the r_{13} value of sample III decreased slower, also indicating that the sample III had higher crosslinking density than the sample II.

The transmission loss for the cured samples I, II, and III was less than 0.68 dB, 0.94 dB, and 1.76 dB at the laser wavelength of 1100–1600 nm, respectively. By comparison to the sample I, the slightly higher values of transmission loss of the cured samples II and III might be due to some structure defects such as the unhomogeneity of the crosslinking density in the samples, which could cause light scattering.

Conclusions

The electrooptic coefficient r_{13} of the crosslinked second order NLO materials based on cellulose diacetate and melamine derivatives was 1.72 pm/V at the laser wavelength 1550 nm and modulation frequency 12.7 KHz, and decreased to 71.5% of its initial value after 4 days, if TMM was used as a crosslinking agent. Its transmission loss of laser was 0.94 dB at the laser wavelength of 1100–1600 nm. The corresponding values of the NLO material with HMM as a crosslinking agent were 1.15 pm/V, 83.5% and 1.76 dB. No evident weight loss below 285°C was found in the samples II and III. The relaxation was suppressed by crosslinking, but the unreacted crosslinking agent and its self-condensate could weaken the intermolecular force of the material and exert an influence on relaxation.

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