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Thermally Stable Organic-Inorganic Sol-Gel Materials for Second-Order Nonlinear Optics

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Summary: A series of the organic-inorganic nonlinear optical (NLO) materials based on the melamine prepolymers containing azobenzene dye as NLO chromophore and an alkoxysilane prepolymer have been investigated. The NLO-active melamine prepolymers were blended with the alkoxysilane prepolymer at various weight ratios. Excellent compatibility between two components was obtained for this all sol-gel type material due to the simultaneous polymerizations, and hydrogen bonding interactions among the residual hydroxyl and silanol groups after curing. Dielectric results indicates that the thermal behavior of the melamine-based NLO material has been improved when blended with 25 wt % alkoxysilane. This series of all sol-gel materials exhibit large second-order optical nonlinearity (d_{33} = 9~30 pm/V at 1064 nm, and 3~10 pm/V at 1542 nm) after poling and curing at 220 ℃ for 1 h. Moreover, the temporal stability of the effective second harmonic coefficient at 100 ℃ is also reported.

Introduction

Second-order nonlinear optical (NLO) polymers are of much interest for applications in photonic devices, such as frequency doubling and electro-optical (EO) modulation, due to their large optical nonlinearity, excellent processibility, low dielectric constants, and high laser damage thresholds1). The optimization of the second-order NLO response of hybrid sol-gel matrices with grafted chromophores is currently under investigation by several research group2). Sol-gel materials with second-order nonlinear optical properties are promising for applications in photonic devices for a number of reasons. These include their low temperature processing capability, excellent optical quality, good thermal and temporal stabilities, refractive index control of films, and ease of device fabrication 2).

The approaches discussed so far mainly dealt with incorporation of organic dyes into a typical sol-gel polymerization scheme. In this work, the sol-gel concept was extended to the polymerization of a multifunctional organic compound. Melamine-based sol-gel materials have been widely used in the lighting, coating, and decorating industries because of their good transparency3). High crosslink density with uniformity can be obtained via a sol-gel process involving sequential hydrolysis and condensation reactions4). Based on the above, melamine

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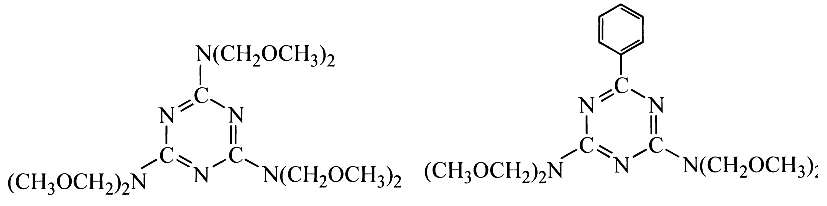
is a good choice as the polymeric matrix for the NLO material. By the sol-gel process, NLO-active chromophore was covalently bonded with the melamine-based organic network via the condensation of amino and methylol groups$^{5)}$. Subsequently, a series of the organic NLO sol-gel materials based on the melamines and azobenzene dye was obtained in our previous study$^{6)}$.

In this study, an alkoxysilane was incorporated into melamine-based NLO prepolymers with different weight ratios. Water produced from simultaneous sol-gel reactions aids subsequent hydrolysis of the melamine and alkoxysilane. Moreover, this simultaneous route is often used to avoid phase separation of a multicomponent system$^{7)}$. One more important feature of this all sol-gel type is that the residual hydroxyl groups and silanol groups after curing will be shown to exhibit hydrogen-bonding interactions between silicon oxide networks and organic networks. This would promote the compatibility between the inorganic network and organic network. In addition, the inorganic networks will be densely and uniformly packed throughout the organic chain segments by the sol-gel process. The interactions between an inorganic oxide and organic polymer will reduce the molecular motions during the glass transition and subsequently enhance long-term NLO stability$^{8)}$.

Experimental

Hexa(methoxymethyl)melamine (HMM1; Figure 1(a)), (hydroxymethyl) benzoquanamine (HMM2; Figure 1(b)), and 4-[(4'-nitrophenyl)azo]phenylaniline (DO3, Figure 1(c)) were obtained from Monsanto and Aldrich, respectively, and were used as received. Melamine-based NLO prepolymers of M1DO320 and M2DO320 (Melamine / DO3: 80 / 20 wt%) were prepared by heating the melamines and DO3 at 140 ℃ for 3 h in the presence of an acetic acid, water, and tetrahydrofuran (THF) mixture$^{6)}$. The alkoxysilane-based prepolymer of phenyltriethoxysilane (PTEOS; Figure 1(d)) was prepared by heating the monomer at 60 ℃ for 5 h in the presence of an acetic acid, water, and THF. A prepolymer solution containing the prepolymer of PTEOS and melamine-based NLO-active prepolymer was prepared for spin-coating. In one example, the PTEOS (0.1 g) and M1DO320 (0.1 g) were dissolved in THF, containing 20 mg of water and 20 mg of acetic acid to aid the hydrolysis of the prepolymers. Degradation temperatures (T_d) were measured on a Seiko Exstar 6000 thermogravimetric analyzer (TGA) at 10 ℃/min under air. The curing reaction state was monitored by FTIR (Bio-Rad FTS155 FTIR). Dielectric relaxation behavior was studied by dielectric spectroscopy (DEA; Novercontrol GmbH). The poling process for the second-order NLO polymer films were carried out using an in-situ poling technique. The poling process was started at room temperature and increased to 220 ℃ at a heating rate of 15 ℃/min. The corona current was maintained at 1 μA with a potential of 4.5 kV while maintaining the poling temperature at 220 ℃ for 1 h. Second-harmonic generation (SHG) measurements were carried out using a Q-switched Nd:YAG laser operating at 1064 nm, and 1542 nm (Raman shifting)9).


(a) HMM1 (b) HMM2

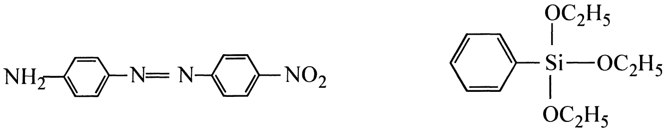

(c) DO3 (d) PTEOS

Fig. 1: Chemical structures of (a) HMM1, (b) HMM2, (c) DO3, and (d) PTEOS, respectively.

Results and Discussion

After curing of the organic-inorganic NLO sol-gel materials at 220 ℃for 1 h, the formation of the Si-O-Si was evidenced by the FTIR spectroscopy. An appreciable decrease of the C-H vibrational stretch of the O-CH_3 groups at around 2800-3000 cm^{-1} was observed, due to the condensation of the methoxymethyl groups. Moreover, the absorption peak at around 1100 cm^{-1} became broader after curing, suggesting Si-O-Si formation10). The composition and T_ds of the cured NLO sol-gel materials are summarized in Table 1. The results indicate that T_ds are increased with increasing alkoxysilane content, due to a higher content of inorganic component. Moreover, the cured PTEOS/M2DO320 samples show higher T_ds than the cured PTEOS/M1DO320 samples. The presence of phenyl ring in HMM2 may be plays the role of filler, thus enhances the thermal stability of the cured M2DO3206). In addition, the homogeneity of these organic-inorganic sol-gel materials was studied using SEM. The fractured surfaces of the cured PTEOS/M2DO320 samples are shown in Figure 2. No sign of any phase separation was observed when magnification was increased up to 4 K. The results supports that a high degree of uniform mixing between the organic and inorganic networks was obtained for these samples.

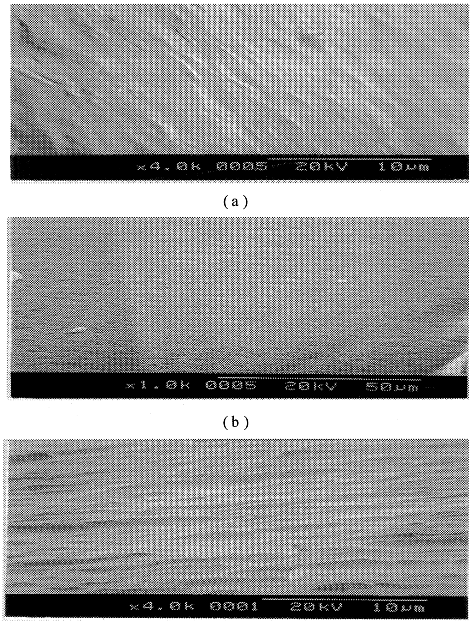
Table 1. Thermal behavior of a series of melamines and an alkoxysilane based organic-inorganic NLO sol-gel materials.

Samples[a)]	Composition (weight ratio)	T_d [b)] (°C)
M1DO320	-------	272.2
PM1DO375	PTEOS/M1DO320 (25/75)	288.6
PM1DO350	PTEOS/M1DO320 (50/50)	313.2
PM1DO325	PTEOS/M1DO320 (75/25)	346.0
M2DO320	-------	299.8
PM2DO375	PTEOS/M2DO320 (25/75)	308.8
PM2DO350	PTEOS/M2DO320 (50/50)	313.3
PM2DO325	PTEOS/M2DO320 (75/25)	337.2

[a)] Samples were cured at 220 °Cfor 1 h.

[b)] T_d was read at the temperature corresponding to 5 % weight loss.

Temperature dependence of the dielectric loss tangent for the cured M1DO320 and PTEOS/M1DO320 samples is shown in Figure 3. For the cured M1DO320, the β-relaxation was observed in the temperature range of −100 ℃ to 50 ℃, which corresponds to the local motions of the dangling chains. Moreover, the rotational motions of NLO-active chromophores results in an σ-relaxation, observed in the temperature range of 0 ℃ to 125 ℃[6)]. The α-relaxation (associated with the glass transition) occurred at temperatures above 125 ℃ for this melamine-based sol-gel material. For the cured PM1DO375, the α and β-relaxations were observed clearly in the frequency range from 10 Hz to 100 KHz. Moreover, the σ-relaxation was suppressed and could not observed in comparison with the cured M1DO320. This implies that the local motion of NLO chromophore was restricted as blending with 25 wt % PTEOS. The entrapment of the NLO chromophores within the highly crosslinked organic-inorganic network led to the suppression of the σ-relaxation. However, the amplitudes of the α and σ-relaxations became more distinguished when the PTEOS content was increased up to 50 wt %. The relaxation temperatures shifted to a lower temperature range when the PTEOS content was further increased. This is possibly due to poorer miscibility for the cured PTEOS/M1DO320 samples containing higher PTEOS contents[11]. For the cured PTEOS/M2DO320 samples, the influence of the composition on the dielectric relaxation behavior was the same the cured PTEOS/M1 DO320 samples.



(a)

(b)

(c)

Fig 2: Scanning electron micrograph of the cured (a) PM2DO375, (b) PM2DO350, and (c) PM2DO325, respectively.

The second-harmonic coefficients, d_{33} and d_{31} of poled/cured PTEOS/M1DO320, and PTEOS/M2DO320 samples for incident light of 1064 nm and 1542 nm are shown in Figure 4. These organic-inorganic NLO materials show large second-order nonlinearity after poling and curing at 220 ℃ for 1 h. The second-harmonic coefficients increased each with increasing M1DO320, and M2DO320 contents, respectively. Larger second-harmonic coefficients were obtained for incident light of 1064 nm as compared to those obtained at 1542 nm, due to the resonant enhancement of the second-harmonic generation at wavelength near 532 nm[12].

The temporal characteristics of the second harmonic coefficient for the poled/cured NLO sol-gel polymer films at 100 ℃ are shown in Figure 5. The temporal stability of poled/cured M1DO320 and M2DO320 has been improved as blending with 25 wt% PTEOS. The dense and uniform packing of the organic and inorganic networks leads to better temporal

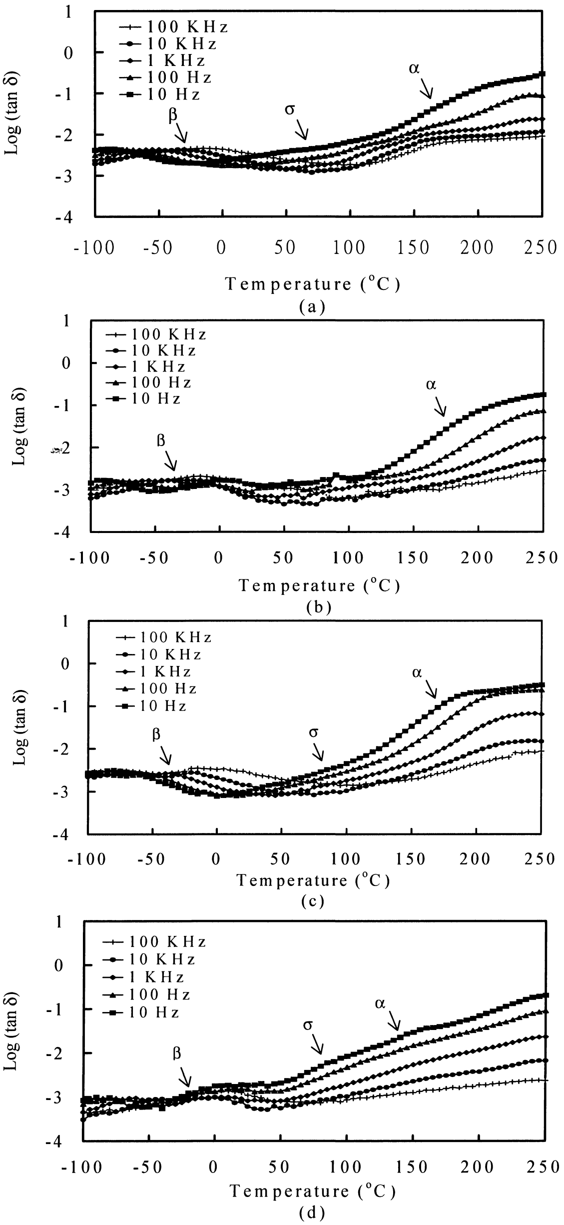


Fig. 3: Dielectric loss tangent versus temperature for the cured (a) M1DO320, (b) PM1DO375, (c) PM1DO350, and (d) PM1DO325, respectively.

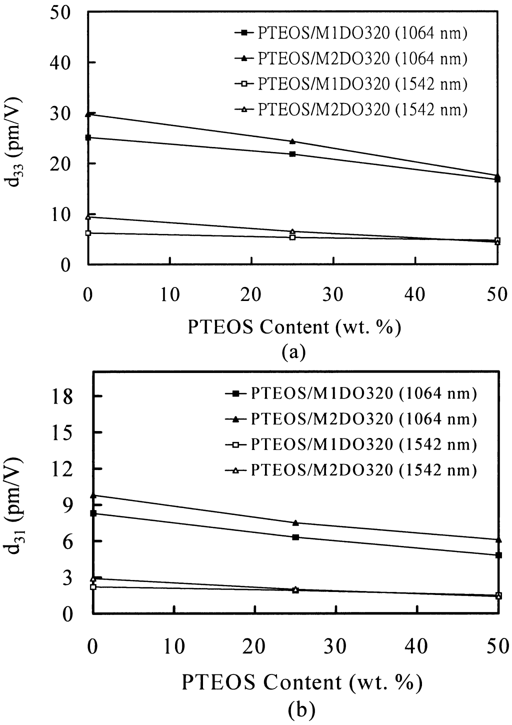


Fig. 4: Second harmonic coefficients of the poled/cured PTEOS/M1DO320 and PTEOS/M2DO320 samples for incident light of 1064 nm and 1542 nm wavelength.

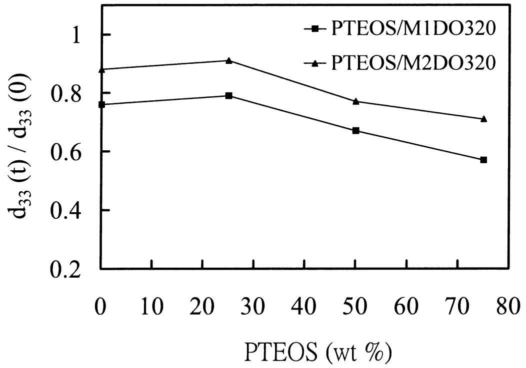


Fig. 5: Temporal behavior of the second-order NLO coefficient for the poled/cured PTEOS/M1DO320 and PTEOS/M2DO320 samples under 100 ℃ for 250 h.

stability of the organic-inorganic NLO sol-gel materials. However, the temporal stability was reduced when the PTEOS content was increased up to 50 wt%. The influence of the composition on the temporal stability behavior corroborates the dielectric relaxation study.

Conclusion

Novel organic-inorganic NLO sol-gel materials based on the melamine-based NLO prepolymers and an alkoxysilane prepolymer have been developed. Large second-order nonlineraity was obtained after poling and curing at 220 ℃ for 1 h. Dielectric results indicates that the thermal behavior of the melamine-based NLO material has been improved when blended with 25 wt% alkoxysilane prepolymer. Subsequently, a better temporal stability of second-order nonlinearity was obtained for these organic-inorganic NLO sol-gel materials. However, excessive PTEOS content was not favorable for temporal stability enhancement perhaps due to poorer miscibility.

Acknowledgment

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