

Organically Modified Inorganic Sol-Gel Materials for Second-Order Nonlinear Optics

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ABSTRACT: A series of the organically modified inorganic NLO sol-gel materials based on the prepolymer of alkoxy silanes and an alkoxy silane dye (ASD) have been investigated. Optically clear samples exhibit large second-order optical nonlinearity ($d_{33} = \sim 10.8\text{--}54.0$ pm/V at 1064 nm) after poling and curing at 220°C for 1 h. The thermal behavior of these NLO sol-gel materials was studied by temperature-dependent dielectric relaxation. The results indicate that the crosslinking density of cured NLO sol-gel materials was increased with increasing alkoxy silane content. Subsequently, better temporal stabilities were obtained for the poled/cured NLO sol-gel materials with a higher alkoxy silane content. Moreover, the structural influence of alkoxy silanes on the thermal behavior and second-order nonlinearity was also studied for these NLO sol-gel materials. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1852–1859, 2001

Key words: second-order nonlinear optical; sol-gel material; alkoxy silane; dielectric relaxation; temporal stability

INTRODUCTION

Second-order nonlinear optical (NLO) polymers have been extensively studied for applications in photonic devices, such as frequency doubling and electro-optical (EO) modulation, because of their large optical nonlinearity, excellent processibility, low dielectric constants, and high laser damage thresholds.¹ Over the past few years, different approaches have been investigated to prepare NLO polymers with excellent NLO properties. They include the guest-host systems, side chain types, main chain types, and crosslinked-type NLO polymers.^{2–9}

Using sol-gel process for the development of NLO material has received increasing attention.^{6–9} Organically modified inorganic NLO sol-gel materials are obtained via incorporation of the organic NLO-active chromophore into an alkoxy silane-based inorganic network. Second-order NLO properties are present in the polymer when the NLO chromophores are aligned in a noncentrosymmetric manner by the poling technique.¹⁰ Moreover, the formation of three-dimensional silicon oxide networks via sol-gel process would prevent the randomization of poled NLO chromophore in the absence of a poling field. In addition, NLO sol-gel materials with low-temperature-processing capability, excellent optical quality, good thermal stabilities, refractive index control of films, and ease of device fabrication are promising for applications in photonic devices.^{6–9}

A sol-gel matrix doped with NLO chromophores was previously reported by Jeng et al.⁶

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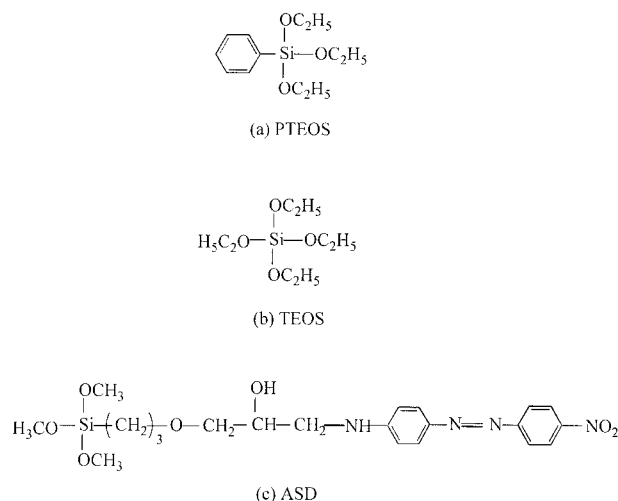


Figure 1 Chemical structures of (a) PTEOS, (b) TEOS, and (c) ASD, respectively.

Moreover, NLO-active dyes were covalently bonded with alkoxy silanes. Subsequently, organically modified inorganic NLO sol-gel materials were obtained.^{7,8} In addition, an alkoxy silane dye (TDP) has been incorporated into the alkoxy silane (TEOS and TMOS)-based inorganic network for the enhancement of temporal stability.⁹ However, the relationship among the composition, thermal behavior, and second-order nonlinearity has not been thoroughly examined. In this study, an alkoxy silane dye (ASD) was incorporated into the tetraethoxysilane (TEOS)- and phenyltriethoxysilane (PTEOS)-based prepolymers in different weight ratios. Subsequently, a series of the organically modified inorganic NLO sol-gel materials with different ASD contents were obtained. The rigid aromatic ring of PTEOS results in a favorable enhancement of the inorganic network rigidity. Moreover, the crosslinking density of NLO sol-gel materials is also affected by the number of reaction sites of the alkoxy silane. The structural influence of alkoxy silanes on the thermal behavior and second-order nonlinearity of NLO materials was studied.

EXPERIMENTAL

The prepolymers of PTEOS and TEOS (Fig. 1) were prepared by heating the monomer at 60°C for 5 h in the presence of an acetic acid, water, and tetrahydrofuran (THF). The alkoxy silane dye (ASD; Fig. 1) was synthesized by the coupling of a monoepoxy of (3-glycidoxypropyl) trimethoxysi-

lane and a monoamine of 4-[(4'-nitrophenyl)azophenylamine (Disperse Orange 3).¹¹ Moreover, a prepolymer solution containing ASD and alkoxy silane-based prepolymer (PTEOS and TEOS) was prepared for the spin-coating. In one example, the ASD (0.1 g) and alkoxy silane-based prepolymer (0.1 g) (1 : 1 w/w) were dissolved in THF, containing 20 mg of water and 20 mg of acetic acid to aid the hydrolysis of ASD and alkoxy silane-based prepolymer. The prepolymer solutions were each stirred at room temperature for 4 h. Thin films were prepared by spin-coating the polymer solution onto an indium tin oxide (ITO) glass substrate.

The curing behavior of the materials was determined by differential scanning calorimetry (DSC; Seiko SSC/5200) at a heating rate of 10°C/min. Degradation temperatures (T_d) were measured on a Seiko Exstar 6000 thermogravimetric analyzer (TGA) at 10°C/min under air. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 2S spectrophotometer (Perkin-Elmer, Palo Alto, CA). Crosslinking was characterized by FTIR (Bio-Rad FTS155 FTIR; Bio-Rad, Richmond, CA). Dielectric relaxation behavior was studied by dielectric spectroscopy (DEA; Nover-control GmbH). Measurements were performed using a Schlumberger SI 1260 impedance/gain-phase analyzer with a Quator temperature controller. For the dielectric measurements, prepolymer solutions were prepared in the same manner as for spin-coating. The solutions were cast onto DEA cell and dried at 60°C for 3 h, followed by curing at 220°C for 1 h. Dielectric measurements were made from -100°C to 250°C. The frequency scan range covered 10⁻¹ to 10⁶ Hz.

The poling process for the second-order NLO polymer films were carried out using an *in situ* poling technique. The details of the corona poling setup were previously reported.¹² The poling process was started at room temperature and increased to 220°C at a heating rate of 15°C/min. The corona current was maintained at 1 μA with a potential of 4.5 kV while maintaining the poling temperature at 220°C for 1 h. The formation of the network and the molecular alignment of the poled order proceeded simultaneously during this period. Upon saturation of the second-harmonic-generation (SHG) signal intensity, the sample was then cooled down to room temperature in the presence of the poling field, at which point the poling field was terminated. The thickness and indices of refraction for the NLO polymer films were measured by prism coupling (Metricon

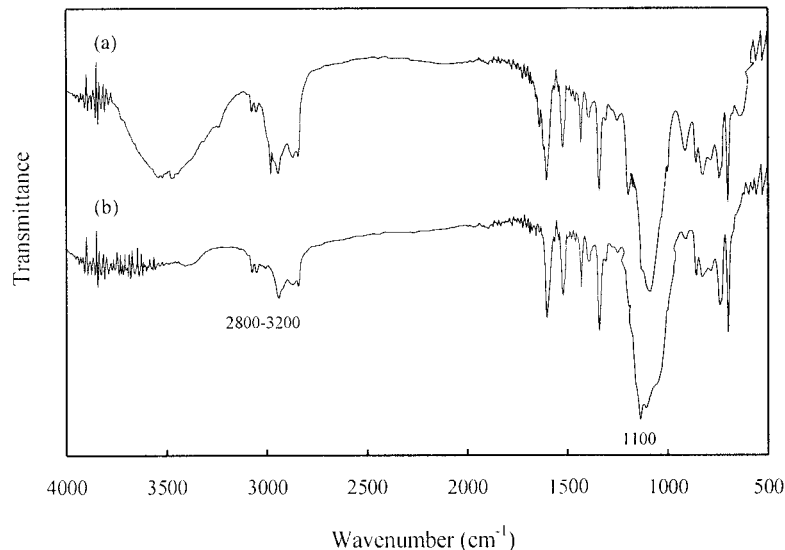


Figure 2 Infrared spectra of (a) PTEOS/ASD50 and (b) cured PTEOS/ASD50, respectively.

2010). SHG measurements were carried out using a Q-switched Nd : YAG laser operating at 1064 nm, and at 1542 nm by using a Raman cell.¹³ Measurement of the second-harmonic coefficient d_{33} was previously discussed,¹⁴ and the d_{33} values were corrected for absorption.¹⁵

RESULTS AND DISCUSSION

After curing the organically modified inorganic NLO sol-gel material PTEOS/ASD50 (PTEOS : ASD = 50 : 50) at 220°C for 1 h, the formation of the Si—O—Si was evidenced by the FTIR spectroscopy (Fig. 2). An appreciable decrease of the C—H vibrational stretching of the O—CH₃ groups at around 2800–3000 cm⁻¹ was observed, resulting from the condensation of the methoxymethyl groups. Moreover, the absorption peak at around 1100 cm⁻¹ became broader after curing, suggesting Si—O—Si formation.¹⁶

T_d 's of the sol-gel materials were measured on a thermogravimetric analyzer under air after curing at 220°C for 1 h. T_d was determined at the temperature corresponding to a weight loss of 5%. Compositions of the sol-gel materials and their T_d 's are summarized in Table I. The results indicate that T_d 's of the cured NLO sol-gel materials are increased with increasing alkoxy silane content, because of a higher content of inorganic component. Moreover, the cured PTEOS/ASD samples show higher T_d 's than those of the cured

TEOS/ASD samples, a result of the fact that the phenyl group present in PTEOS plays a role of filler in the sol-gel system.¹⁷ The thermal behavior of PTEOS and TEOS was further studied using ²⁹Si solid-state NMR, since it was closely associated with the structure and crosslinking density of materials. The ²⁹Si solid-state NMR spectra of cured TEOS and PTEOS are shown in Figure 3. In the spectra, the peaks of Q¹, Q², Q³, and Q⁴, indicative of T₁, T₂, T₃, and T₄ groups, respectively, show that a significant amount of silicate condensation has occurred.¹⁸ This indicates that most of the silicons are bounded to three other silicons through the oxygen bridges

Table I Thermal Behavior of the Organically Modified Inorganic NLO Sol-Gel Materials

Samples ^a	ASD Content (wt %)	T_d ^b (°C)
ASD	100	293.0
PTEOS	0	525.0
TEOS	0	350.0
PTEOS/ASD75	75	294.5
PTEOS/ASD50	50	311.0
PTEOS/ASD25	25	339.3
TEOS/ASD75	75	292.3
TEOS/ASD50	50	304.3
TEOS/ASD25	25	308.2

^a Samples were cured at 220°C for 1 h.

^b T_d was determined at the temperature corresponding to 5% weight loss.

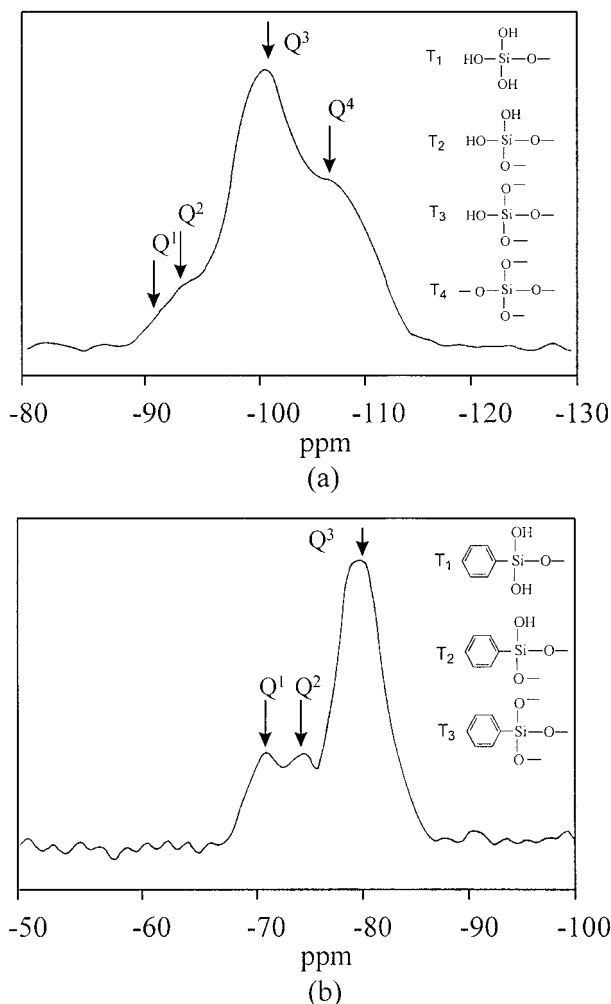


Figure 3 ^{29}Si solid-state NMR spectra of the cured (a) TEOS and (b) PTEOS, respectively.

for both the cured TEOS and PTEOS. This also provides evidence that the curing is more nearly complete for PTEOS than for TEOS, since the number of the reaction sites for PTEOS was less than that for TEOS. As a result, the T_d obtained for the cured PTEOS was higher than that obtained for the cured TEOS.

Glass transition temperatures (T_g 's) were not detectable via DSC for the cured NLO sol-gel materials as a result of the formation of a high crosslink density of the inorganic network.¹⁹ Dielectric relaxation is a useful technique for studying the dynamic behavior of the polymers, since it is sensitive to the motions of the ground-state dipole moments of the NLO chromophores. Moreover, the molecular mobility is determined by the rigidity and molecular packing of the inorganic network. The packing structure of the NLO sol-

gel material could be studied by the dielectric relaxation behavior. Temperature dependence of the dielectric loss tangent for the cured ASD and PTEOS is shown in Figure 4. In Figure 4(a), the β -relaxation was observed from -100°C to 50°C , which corresponds to the local motions of the dangling chains for the cured ASD.^{20,21} Moreover, the large amplitude of the α -relaxation occurred at a temperature above 50°C . The chromophores were grafted on the inorganic network via the flexible spacer, which led to the high mobility of the NLO-active chromophores. As a result, the high relaxation intensity was observed during the α -relaxation for the cured ASD. In Figure 4(b), the β -relaxation of the cured PTEOS was observed from -100°C to 25°C . The α -relaxation showed up at a temperature above 100°C . The amplitudes of α - and β -relaxations are insignificant for the cured PTEOS compared to those for the cured ASD.

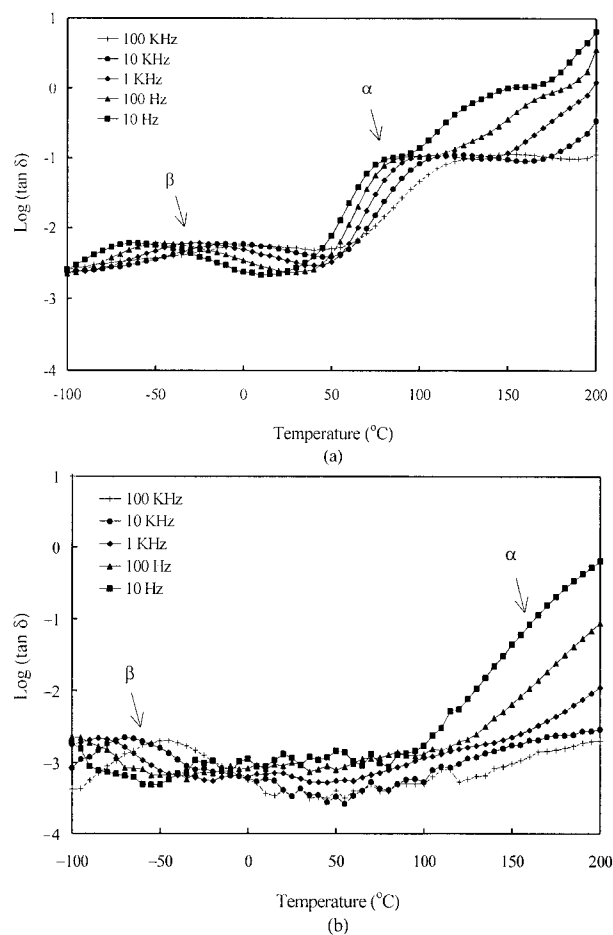


Figure 4 Temperature dependence of the dielectric loss tangent for the cured (a) ASD and (b) PTEOS, respectively.

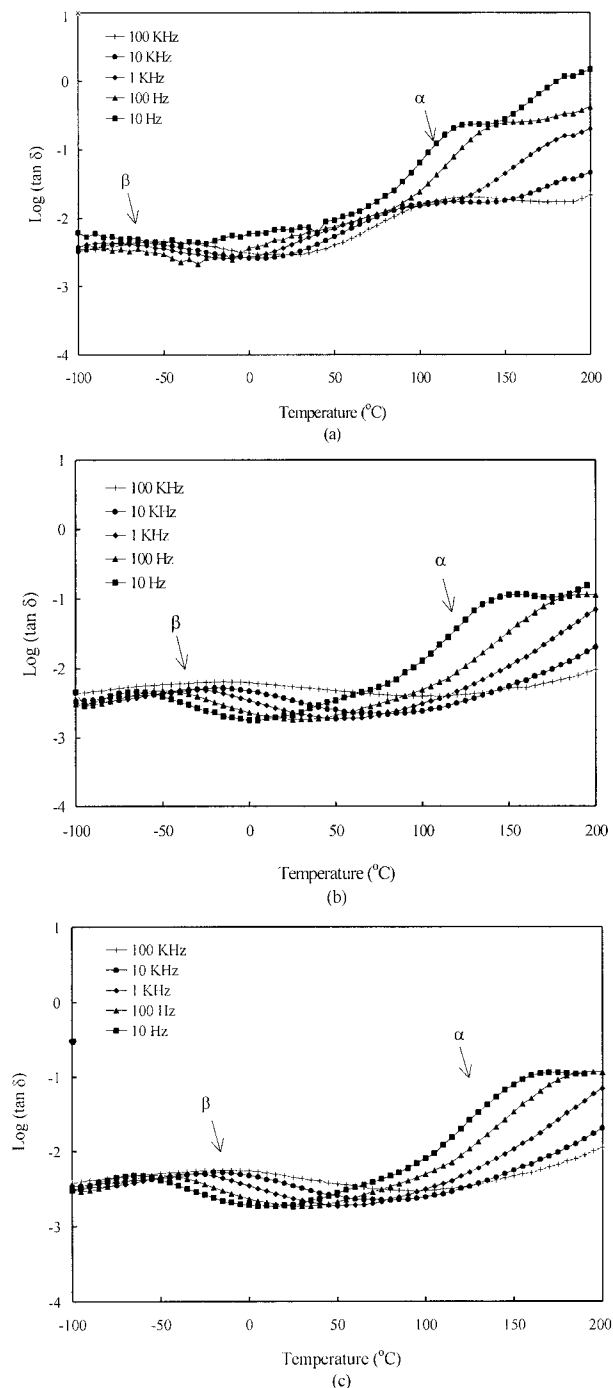


Figure 5 Temperature dependence of the dielectric loss tangent for the cured (a) PTEOS/ASD75, (b) PTEOS/ASD50, and (c) PTEOS/ASD25, respectively.

This implies that the cured PTEOS has a higher crosslinking density than the cured ASD.²² In addition, dielectric relaxation behavior of the cured TEOS could not be measured because of the relatively poor film formability on the DEA cell.

Temperature dependence of the dielectric loss tangent for the cured PTEOS/ASD samples is shown in Figure 5. For the cured PTEOS/ASD75, the amplitude of the α -relaxation was remarkably suppressed compared to that of the cured ASD. Suppression of the relaxation intensity provides evidence that the crosslinking density of ASD was enhanced as 25 wt % PTEOS was incorporated. Moreover, the α -relaxation temperature increased with increasing content of PTEOS for the cured PTEOS/ASD samples. The α -relaxation appeared at a temperature above 100°C for the cured PTEOS/ASD50 and PTEOS/ASD25. In addition, temperature dependence of the cured TEOS/ASD50 samples is shown in Figure 6. The amplitude of the α -relaxation was also suppressed for the cured TEOS/ASD50 compared to that of the cured ASD. This implies that the cured TEOS/ASD50 has a higher crosslinking density than that of the cured ASD. However, the amplitude of the α -relaxation was significant for the cured TEOS/ASD50 compared to that of the cured PTEOS/ASD50. The sol-gel material based on PTEOS suppresses the molecular motion during glass transition more effectively than the one based on TEOS, as a result of the higher crosslinking density of the cured PTEOS. In addition, the rigid aromatic ring also contributes to the suppression of the molecular motion for the PTEOS.²³

The poling effect on the absorption behavior of these NLO polymer films was measured by UV-Vis spectroscopy. The absorption spectra for the NLO polymer films before and after poling, and under thermal treatments at 100°C, are shown in

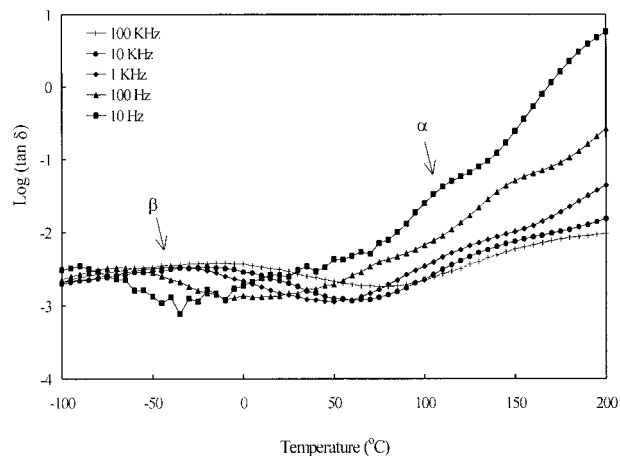


Figure 6 Temperature dependence of the dielectric loss tangent for cured TEOS/ASD50.

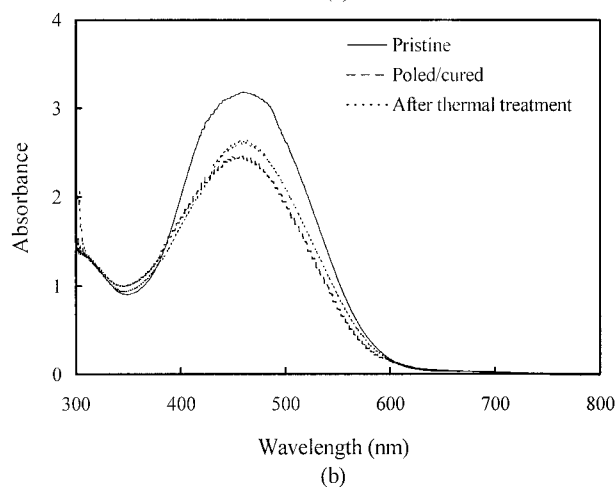
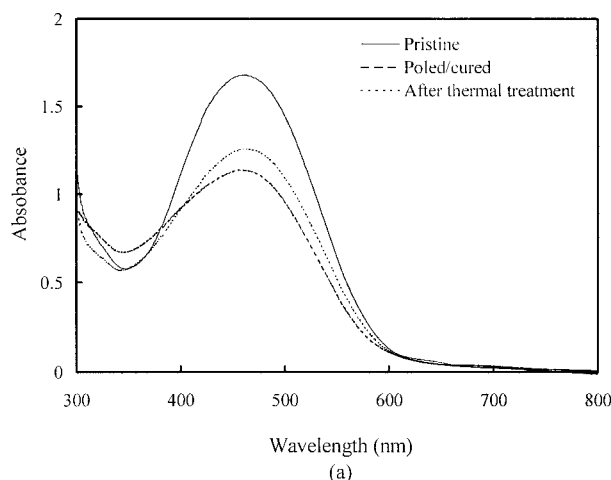


Figure 7 UV-Vis absorption spectra of (a) PTEOS/ASD50 and (b) TEOS/ASD50, respectively.

Figure 7. The absorption maximum occurred around 460 nm for these NLO sol-gel materials. Immediately after poling/curing, a decrease and a blue shift were observed in the spectrum, as a

Table III Second Harmonic Coefficients d_{33} and d_{31} (pm/V) of the Organically Modified Inorganic NLO Sol-Gel Materials for Incident Light of 1064- and 1542-nm Wavelength

Samples	$d_{33(1064)}$	$d_{31(1064)}$	$d_{33(1542)}$	$d_{31(1542)}$
ASD	54.0	19.2	16.6	6.4
PTEOS/ASD75	43.1	14.2	12.4	3.4
PTEOS/ASD50	34.5	9.7	10.7	3.5
PTEOS/ASD25	11.2	3.5	4.2	2.1
TEOS/ASD75	39.4	12.8	10.3	3.7
TEOS/ASD50	36.5	13.1	7.4	3.0
TEOS/ASD25	10.8	3.1	3.7	1.1

consequence of the dichroism and electrochromism that resulted from induced dipole alignment.²⁴ Moreover, the absorption of the poled/cured NLO materials increased after thermal treatment at 100°C for 250 h as a result of randomization of the induced dipole alignments. Refractive indices of these NLO sol-gel materials are listed in Table II. Film thicknesses ranged from 1.0 to 1.4 μm . Refraction indices are ranged from 1.54 to 1.75, and increase with increasing ASD content. The second-harmonic coefficients d_{33} and d_{31} of poled/cured ASD, PTEOS/ASD, and TEOS/ASD samples for the incident light of 1064 and 1542 nm are listed in Table III. These organically modified inorganic NLO materials showed large second-order nonlinearity after poling and curing at 220°C for 1 h. The second-harmonic coefficients increased with increasing ASD content. Larger second-harmonic coefficients were obtained for the incident light of 1064 nm compared to those obtained at 1542 nm, as a result of the resonant enhancement of the second-harmonic generation at a wavelength near 532 nm.²⁵

Table II Thickness and Refraction Indices of the Organically Modified Inorganic NLO Sol-Gel Materials

Samples	d^a (μm)	n_{532}^b	n_{771}^b	n_{1064}^b	n_{1542}^b
ASD	1.1	1.75	1.67	1.64	1.61
PTEOS/ASD75	1.2	1.71	1.67	1.64	1.61
PTEOS/ASD50	1.4	1.68	1.64	1.62	1.59
PTEOS/ASD25	1.0	1.65	1.62	1.59	1.58
TEOS/ASD75	1.1	1.70	1.65	1.63	1.60
TEOS/ASD50	1.3	1.67	1.64	1.62	1.59
TEOS/ASD25	0.9	1.65	1.61	1.59	1.58

^a d , the thickness of polymer film.

^b n_{532} , n_{771} , n_{1064} , n_{1542} : refraction indices at 532, 771, 1064, and 1542 nm, respectively.

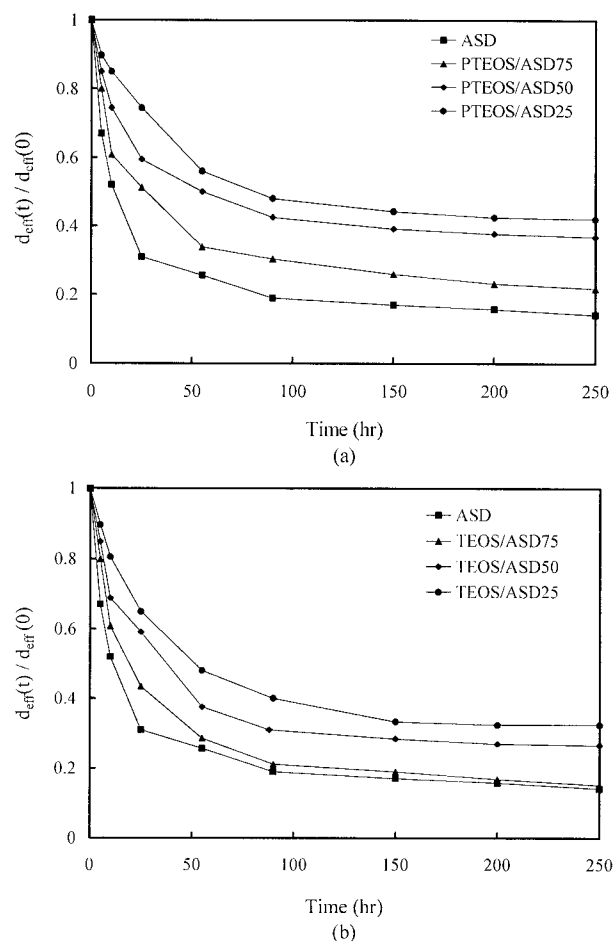


Figure 8 Temporal behavior of the second-order NLO coefficient for the poled/cured (a) PTEOS/ASD and (b) TEOS/ASD samples, respectively.

The temporal characteristics of the second-harmonic coefficient for the poled/cured NLO sol-gel polymer films at 100°C are shown in Figure 8. The result indicates that the poled/cured ASD exhibited a relatively poor temporal stability. The second-harmonic coefficient quickly decayed under 100°C at the beginning of 50 h. However, the temporal stability was improved by blending with different contents of PTEOS or TEOS. The temporal stability increased with increasing alkoxy silane content. Moreover, the poled/cured PTEOS/ASD samples possessed a better temporal stability than that of the poled/cured TEOS/ASD samples. The temporal stability behavior for various systems corroborates the dielectric relaxation study.

CONCLUSIONS

A series of organically modified inorganic NLO sol-gel materials based on the alkoxy silanes

and ASD have been developed. Large second-harmonic coefficients were obtained for these NLO sol-gel materials at the incident light of 1064 nm. Temporal stability of the poled/cured ASD could be improved as different alkoxy silane contents were incorporated. Moreover, the NLO sol-gel material based on PTEOS exhibits better temporal stability than the one based on TEOS as a result of the rigid aromatic ring of PTEOS.

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