Phenoxysilicon Polymer with Stable Second-Order Optical Nonlinearity

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ABSTRACT: A new cross-linked second-order nonlinear optical material based on an alkoxysilane dye and a multifunctional phenoxyl molecule has been investigated. The design approach to this polymer system is also discussed. The nonlinear optical chromophore can be directly bound to an aryl-bridged network during the curing process. After cross-linking at 200 °C for 30 min, the cross-linked polymeric material was found to be amorphous with a T_g of 110 °C and a degradation temperature of 278 °C. The poled and cross-linked sample exhibits a second-order nonlinear optical coefficient, d_{33}, of 77 pm/V. After being subjected to thermal treatment at 105 °C for 24 h, a reduction of only 19% of d_{33} was observed for the poled and cured sample. This d_{33} value remained unchanged at 105 °C for another 144 h, to which measurements were carried out. Detailed characteristics of the cross-linked material are discussed.

I. Introduction

Background. Polymeric materials have become competitive with inorganics for nonlinear optical (NLO) applications such as fast waveguide electrooptic modulation and frequency doubling devices.[1] The noncentrosymmetric alignment of the NLO chromophores that results from the poling process tends to randomize in the absence of a poling field. In order to prevent the randomization of the poled molecules, the NLO chromophores are usually incorporated in a polymer which has a high glass transition temperature (T_g). This is due to the fact that the molecular motion of the NLO chromophore is closely associated with the T_g of the polymer.[2] Furthermore, enhanced temporal stability of second-order NLO properties in a poled polymer system can be obtained when a certain degree of cross-linking is introduced. In the cross-linked polymer, the NLO moieties are either incorporated or covalently bound into a rigid polymer network and are much less likely to relax to a random orientation. The polymers can be cross-linked by thermal means[3] or by photochemical means.[4] The stability of the poled order is strongly dependent on the cross-link density.[3e]

Sol–gel technology provides an attractive route to the preparation of a three-dimensional inorganic network.[5] The basic sol–gel process involves the sequential hydrolysis and polycondensation of silicon alkoxide at temperatures that are commonly used to process polymeric materials.[6] At low temperatures the condensation requires many hours or days; higher temperatures (>150 °C) shorten the curing time.[6a] Curing at higher temperatures leads to further cross-linking of the inorganic matrix but results in degradation and complete elimination of the organic component. Numerous chromophores have been incorporated into glassy materials, for instance, laser dyes, π-conjugated NLO polymers, and NLO dyes.[3f,7] There also have been other reports on the NLO sol–gel process, where large concentrations of NLO chromophores have been chemically bonded to the silicon oxide backbone of the inorganic network by attaching the NLO chromophore directly to the silicon atom.[6b,8]

Recently, a cross-linked system based on an alkoxysilane dye and phenylsiloxane polymer was reported.[9] Upon heating to high temperatures, the phenylsiloxane polymer containing hydroxyl and ethoxyl groups and the alkoxysilane dye form a cross-linked network. Phenylsiloxane polymers have been processed at high temperatures (to 425 °C) to lead to optically clear, low loss glasses (thin film sol–gel waveguides with optical losses of 1.5–2.5 dB/cm at λ = 0.5145 μm have been reported by Roncone et al.).[10] The samples can be poled and cured simultaneously. This ensures that the NLO dye will be locked in the three-dimensional network of the glass matrix in a noncentrosymmetric manner with acceptably slow relaxation even at elevated temperatures. The second-order NLO properties of the poled and cured sample showed no measurable decay at room temperature for an extended period of time. However, a slow decay of the second-order NLO properties was observed at 100 °C.

A second-order NLO organic/inorganic composite based on an alkoxysilane dye and a polyimide also has been reported by Jeng et al.[11] It was postulated that the sol-gel reaction took place in the polymer matrix aided by the curing of poly(amic acid).[12] The poled film of this polyimide/inorganic composite showed a large second-order NLO effect and excellent temporal stability at 120 °C measured over a period of 168 h.

Design of a New Second-Order Nonlinear Optical Material. The approaches discussed earlier mainly dealt with incorporation of organic dyes or polymers into a typical sol–gel polymerization scheme. In this work we have extended the sol–gel concept to the polymerization of a multifunctional organic compound and an alkoxysilane dye. We have provided a general approach to the design of the multifunctional alkoxysilane dye for second-order nonlinear optics in which the NLO chromophore can be covalently incorporated in an alkoxysilane. For example, 4-[(4′-nitrophenyl)azo]phenylamine (Disperse Orange 3) was covalently coupled with (3-glycidoxypropyl)trimethoxysilane.[9,11] This scheme allows control of the absorption characteristics by appropriate choice of the NLO chromophore. For example, instead of Disperse Orange 3 as the NLO chromophore in the previous case, a 4-nitroaniline can be substituted in order to blue-shift the absorption characteristics. A second approach to synthesize the alkoxysilane dye is to take advantage of urethane chemistry.[13] For example, (3-isocyanatopropyl)triethoxysilane can be covalently coupled with 4-[ethyl(2-hydroxyethyl)-amino]-4′-nitroazobenzene (Disperse Red 1) to form an

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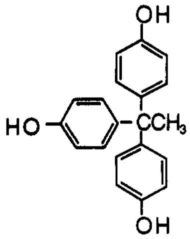
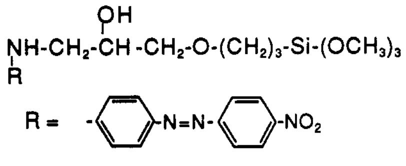


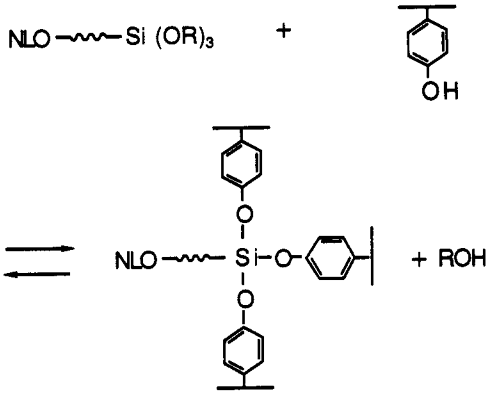
(a) 1, 1, 1,-Tris(4-hydroxyphenyl)ethane



(b) Alkoxysilane dye

Figure 1. Chemical structures of (a) 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) and (b) alkoxysilane dye (ASD).

Scheme I. Formation of Phenoxysilicon



alkoxysilane dye. A general formulation is illustrated as follows:

$NLO\sim\sim Si\ (OR)_3$

R: methyl or ethyl groups

Alkoxysilane reacts with phenol groups to form a phenoxysilicon compound.[14] This type of phenoxysilicon material has been shown to possess excellent thermal stability.[15] In addition, the phenol compound can also be an NLO chromophore, such as [(4-nitrophenyl)azo]resorcinol or 4-nitrocatechol, as well as polymers, such as poly(4-hydroxystyrene) or 2-methylresorcinol Novolac. The relative size and functionality of the phenol compound will have a direct bearing on the cross-link density in the cured system. In this investigation, we report the properties of an alkoxysilane covalently bonded to an NLO chromophore, which was reacted with 1,1,1-tris(4-hydroxyphenyl)ethane to form a cross-linked phenoxysilicon material. Upon heating to high temperatures, the rigid multiphenoxyl molecule containing three phenol groups and alkoxysilane with three methoxyl groups lead to a highly cross-linked network (Scheme I).

II. Experimental Section

Materials. The multifunctional phenoxyl molecule, 1,1,1-tris(4-hydroxyphenyl)ethane (THPE; Figure 1), is available from Aldrich Chemical and was used as received. The alkoxysilane dye (ASD; Figure 1) was synthesized by the coupling of a monoepoxy of (3-glycidoxypropyl)trimethoxysilane and a monoamine of 4-[(4′-nitrophenyl)azo]phenylamine (Disperse Orange 3).[16] ASD has a T_m of 36.6 °C.

ASD (0.200 g) and THPE (0.150 g) (molar ratio 1.00:1.17) were dissolved in 3 g of a mixed solvent (propylene glycol methyl ether acetate:1,4-dioxane = 3:1 by volume). The mixed solvent also contained 30 mg of *N*,*N*-dimethylbenzylamine and 30 mg of water, to aid in the hydrolysis of alkoxysilane.[5a] This solution was stirred by a magnetic stirrer for 4 h before spin-coating. Films were prepared by spin-coating the ASD/THPE solutions onto 1-mm-thick transparent microscope slides (Fisher Premium), fully frosted microscope slides, and KBr plates. Typical thickness obtained was approximately 615 nm for the cured ASD/THPE. Indices of refraction at two different wavelengths (532 and 1064 nm) were measured using an ellipsometer. They were 1.744 and 1.638 for 532 and 1064 nm, respectively.

Instruments. The glass transition temperatures, T_g, and the reaction behavior of the materials were obtained from differential scanning calorimetry using a TA instrument DSC2910 at a heating rate of 10 °C/min. The isotrack technique of DSC was applied to obtain the optimum curing conditions. The thermal degradation temperatures (T_d) of the polymers were determined on a TA Instrument TGA2950 with a heating rate of 10 °C/min under air. UV–Vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 1760X FTIR spectrometer.

Dielectric analysis was carried out using a TA Instrument dielectric analyzer DEA2970. A ceramic single surface sensor containing a coplanar interdigitated-comb electrode design was used for this study. For dielectric analysis of the polymer films, the depositing solution was prepared by dissolving ASD (0.200 g) and THPE (0.150 g) in THF (1.500 g), containing 30 mg of dimethylbenzylamine and 30 mg of water. The solution was cast onto the sensor and dried at 55 °C under vacuum for 12 h. Dielectric measurements were performed from −150 to +250 °C at a heating rate of 2 °C/min. The frequency scan range was from 10 to 100 000 Hz.

To fabricate the second-order NLO polymer films, poling was carried out using the corona discharge method. The details of the corona poling setup have been reported earlier.[17] The poling was started at 60 °C, and then the sample temperature was increased at the rate of 2 °C/min. The cross-linking reaction proceeds reasonably fast only at temperatures above 180 °C. The strength of the effective electric field used for poling was estimated to be approximately 5 MV/cm according to the literature.[18] The strength of the effective electric field is estimated from the order parameter, and it is important to realize that the chromophores are "measuring" the local field. Thin films were heated to a temperature at which the cross-linking is fast (approximately 200 °C) with the electric field left on. After a sufficient time to achieve maximum cross-linking of the material (30 min), the sample was cooled down to room temperature with the poling field on. The curing temperature was chosen to be 200 °C partly due to the fact that the thermal decomposition temperature of the ASD was determined to be approximately 237 °C by a thermogravimetric analyzer.

The second-order NLO properties of the poled ASD/THPE samples were measured by second-harmonic generation (SHG) from 1064-nm laser radiation. The relaxation behavior of the second-order nonlinear optical properties was studied by the decay of the second-order nonlinear optical coefficient (d_{33}) as a function of time both at room temperature (25 °C) and at 105 °C. The polarized Q-switched Nd:YAG laser with a 10-ns pulse width and a 20-Hz repetition rate was used as the light source. The typical energy per pulse of the laser was 15 mJ. The fundamental laser beam after passing through the sample was blocked by $CuSO_4$ solution and a 532-nm interference filter. The second-harmonic signal was detected by a photomultiplier tube and averaged over 300 pulses in a boxcar integrator. The SH intensity of a Y-cut single crystal of quartz with known thickness and d_{11} value (d_{11} = 0.5 pm/V)[19] was used as a reference mounted at the same position as that of the sample. The calculations of the second-order NLO coefficient d_{33} have been previously discussed.[20] In addition, the d_{33} values were corrected for absorption.[4a]

III. Results and Discussion

Thermal Analysis. A TGA scan at 10 °C/min of the cured ASD/THPE (molar ratio 1.00:1.17) is shown in

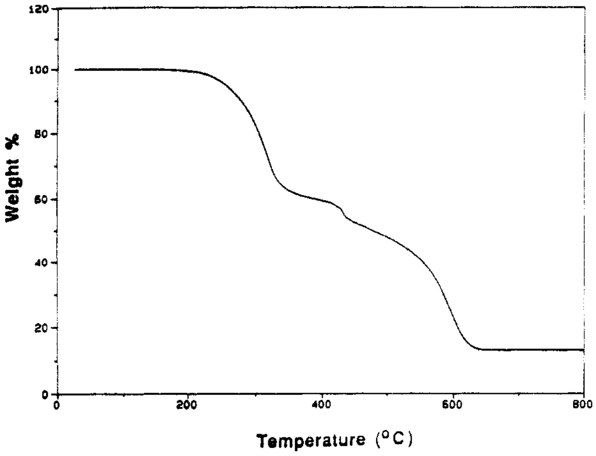


Figure 2. Thermal degradation behavior of the cured ASD/THPE.

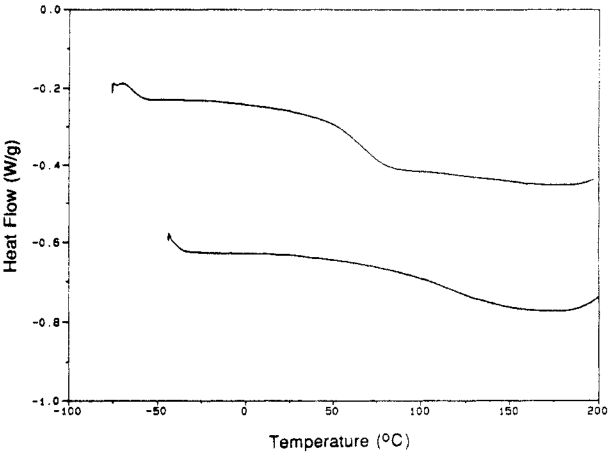


Figure 3. DSC thermographs of the cured ASD/THPE.

Figure 2. The degradation temperature, as taken from the onset point of the step transition, is 278 °C (9.3% weight loss).

A DSC scan at 10 °C/min of ASD/THPE (molar ratio 1.00:1.17) was performed. The sample was prepared by drying a small amount of the solution on the DSC pan. The exothermic reaction (curing) starts at approximately 180 °C. The DSC isotrack technique permits good control of the sample temperature and is used to optimize the curing condition. A higher curing temperature is necessary for high T_g systems because of low reaction rates after vitrification. However, curing and thermal degradation often compete at such high temperatures.[21] Moreover, to fabricate the second-order NLO polymer thin films, curing and poling are required to proceed simultaneously. When the poling temperature is high, thermal fluctuation (kT) would affect the noncentrosymmetric alignment of the NLO chromophores negatively.[22] These three factors were taken into consideration in our search for the optimum curing condition. When the sample of ASD/THPE was heated at 200 °C for 10 min, its T_g appeared at 65 °C (top of Figure 3). A thin film of the ASD/THPE sample subsequent to the above thermal treatment was soaked in THF (a good solvent for both ASD and THPE) for 2 h. The solvent did not extract any measurable concentration of dye from the cured sample. This implies that the NLO dye is already firmly locked in the phenoxysilicon network.

On heating for 30 min at 200 °C, the T_g of the ASD/THPE system advanced to 110 °C with a much smaller ΔC_p (T_g) (bottom of Figure 3) compared to the sample cured for 10 min. The rise of T_g and the decrease of ΔC_p (T_g) of the cured ASD/THPE indicate a net decrease in chain mobility and significant suppression of a number of phonon modes. This is considered to be a consequence of the formation of additional cross-links.[23] Curing of the sample of ASD/THPE at 200 °C for 85 min did not lead to a decrease in ΔC_p (T_g) or an increase in T_g (110 °C). On the other hand, upon heating the ASD/THPE system for 10 min at 220 °C, its T_g emerged at 73 °C. When the sample of ASD/THPE was cured at 220 °C for 30 min, its T_g advanced only to 105 °C. This suggests that thermal degradation outweighed curing at this stage. In order to limit this degradation and thermal fluctuation of the NLO chromophores, 220 °C was considered to be the upper limit for the curing temperature.

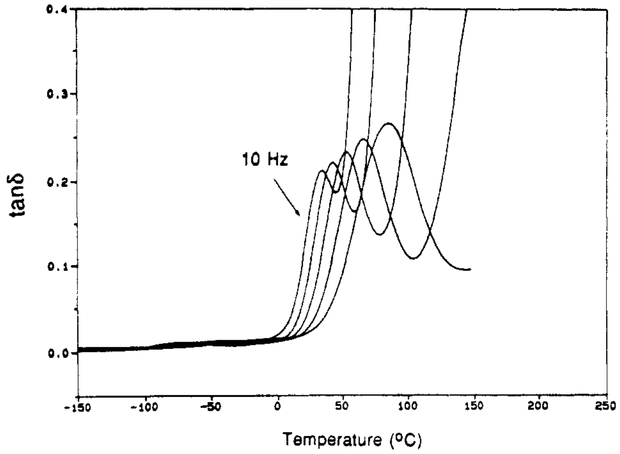


Figure 4. Tangent of the loss angle of the pristine ASD/THPE as a function of temperature measured at various frequencies. (from left: 10, 100, 1000, 10 000, and 100 000 Hz).

Curing at a temperature lower than 200 °C, even for several hours, does not lead to a T_g as high as 105 °C. On the basis of the above observation, isothermal heating of the sample at 200 °C for 30 min was chosen as the optimum curing condition (unless otherwise stated, this curing condition was used throughout the study). This conclusion is also further confirmed by dielectric analysis. The ion conductivity of the ASD/THPE decreased gradually from the beginning of the curing cycle (200 °C) and then leveled off at the end of 30 min. This implies that the maximum degree of cross-linking without serious degradation of the ASD/THPE system can be obtained from this optimum curing condition.

Dielectric Analysis. The NLO chromophore mobility related to the orientation and stability of the poled state is temperature-dependent. The relaxation behavior can be studied by dielectric relaxation spectroscopy.[24] Figures 4 and 5 show the loss tan δ values for the pristine and the cured ASD/THPE, respectively, as a function of temperature at various frequencies. For pristine ASD/THPE, the tan δ peaks appeared in the range of 0–100 °C. After curing the sample at 200 °C for 30 min, the tan δ peaks shifted to a temperature range higher than 110 °C. The mobility of the NLO chromophore is expected to be restricted at temperatures lower than 110 °C, as implied by the extremely small tan δ values observed between −150 and +110 °C for cured ASD/THPE. As mentioned in the previous paragraph, the T_g of the optimally cured ASD/THPE is 110 °C. These results further confirm that the onset of relaxation of the NLO chromophore is directly related to the T_g of this polymer.

IR Study of the Chemical Reactions. Upon heating, the ASD/THPE undergoes reactions that can be analyzed by IR spectroscopy. As shown in Figure 6, after 30 min of heating at 200 °C, an appreciable change of absorbance in the IR spectra was observed due to the emergence of

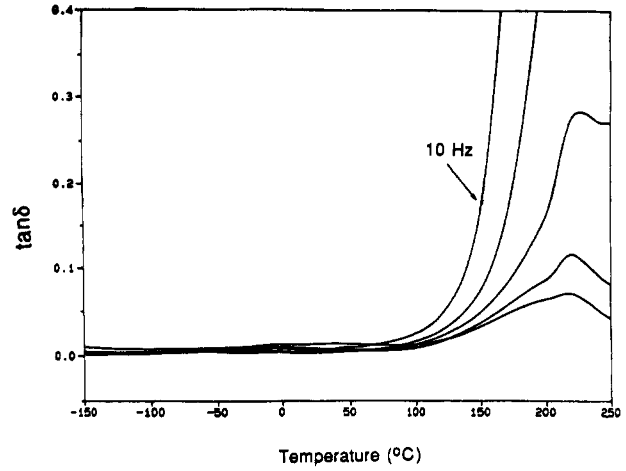


Figure 5. Tangent of the loss angle of the cured ASD/THPE as a function of temperature measured at various frequencies. (from left: 10, 100, 1000, 10 000, and 100 000 Hz).

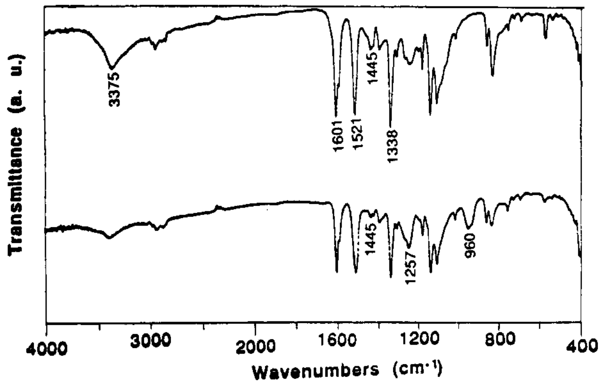


Figure 6. Infrared spectra of ASD/THPE (top) pristine, (bottom) cured.

the phenoxysilicon absorption at 1257 and 960 cm^{-1}. Moreover, the absorption peak of hydroxyl stretching around 3400 cm^{-1} and methyl asymmetric bending vibration (attached to the oxygen atom) at 1445 cm^{-1} decreased drastically after curing. This suggests that the phenoxysilicon has formed.[25] The absorption peaks of the NLO chromophore, such as the nitro group (1521 and 1338 cm^{-1}), using the absorption peak of the phenyl group (1601 cm^{-1}) as the standard, remained almost unchanged in intensity during the process of curing. It is, therefore, concluded that thermal degradation of the NLO chromophores was negligible during curing at these conditions.

Nonlinear Optical Properties. It is noted that when the poling temperature is high, thermal fluctuation (kT) will fight against the aligning torque of the poling field.[22] Nevertheless, the poled/cured film has a d_{33} value of 77 pm/V due to its high NLO chromophore concentration (approximately 30% by weight). After being subjected to thermal treatment at 105 °C for 24 h, a reduction of only 19% in the d_{33} value was observed for the poled and cured sample. This d_{33} value remained unchanged under the same thermal treatment for another 144 h (Figure 7). As mentioned in the Dielectric Analysis section, the relaxation of the NLO chromophore is directly related to the T_g (110 °C). The initial decay of a few percent in the d_{33} value at 105 °C is a result of the initial loss of orientation, perhaps of the un-cross-linked components. This is expected since the temperature of thermal treatment (105 °C) is so close to the T_g (110 °C) of the cross-linked polymer. Excellent long-term stability is a direct consequence of the extensively cross-linked network.[3e] The nonlinear optical coefficient (d_{33}) of the poled/cured sample remained unchanged under ambient condition for at least 168 h. It is important to point out that the condensation of the ASD and THPE may generate water or alcohol. However, no microscopic voids due to water or alcohol generation were observed in the cured polymer film.

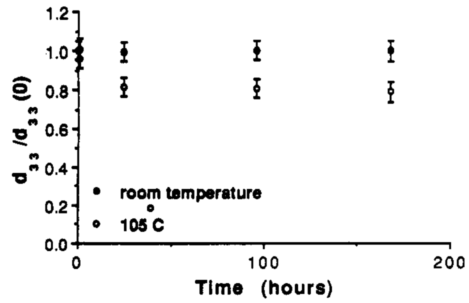


Figure 7. Time behavior of the second-harmonic coefficient of the poled/cured ASD/THPE.

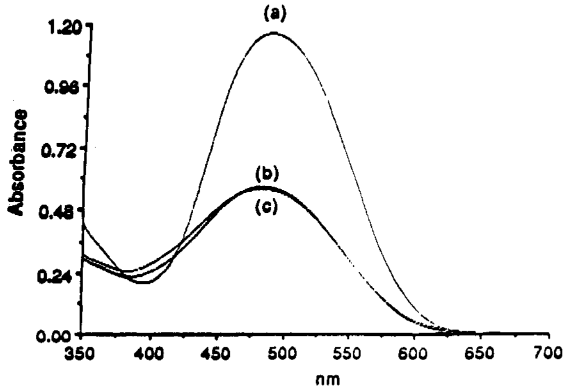


Figure 8. UV–vis absorption spectra of the ASD/THPE: (a) pristine; (b) right after poling/curing; (c) poled/cured samples, thermal treatment at 105 °C for 168 h.

UV–Vis Absorption Characteristics of the Poled Film. To investigate the absorption behavior as a function of time, the absorption spectrum was taken at regular intervals over 168 h for the poled/cured sample kept at 105 °C. Immediately after poling/curing, a decrease in absorbance was observed as expected. This is partially due to orientational dichroism.[26] The absorption peak of the Disperse Orange 3 chromophore shifted slightly toward shorter wavelength (Figure 8). This behavior is similar to that observed in other cross-linked NLO polymer systems.[4a,27] During the next 168 h, the absorption spectrum remained practically unchanged. This result suggests that the dye/polymer system did not degrade or sublime throughout the whole period of thermal treatment.

IV. Conclusion

A new class of cross-linked phenoxysilicon polymeric material for second-order nonlinear optics has been synthesized A very high NLO chromophore density can be achieved in this system. The UV–vis absorption characteristics can be controlled and tailored. In spite of poling at a relatively high temperature, the d_{33} of 77 pm/V was obtained. Highly stable second-order nonlinearity at 105 °C also has been achieved through this cross-linked phenoxysilicon polymer. After a small initial decay, the d_{33} value of the poled sample remains essentially constant even after it is subjected to thermal treatment at 105 °C for over 168 h. This is due to the tailored extensively cross-linked network structure generated.

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