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**Second-Order Nonlinear Optical Polymers: From Fundamentals To Applications**

by

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13. ABSTRACT (Maximum 200 Words) Successful development of materials for photonic applications requires an understanding of the nonlinear optical process, chemistry and processing of materials, and technologies for device fabrications. We are able to successfully use different chemistries to develop several types of crosslinked and networked systems. Significant progress in improving material properties has been accomplished. Promising results have been observed in several materials developed. A prototype frequency doubling device has been prepared; second harmonic Cerenkov radiation emitting green and blue light have been observed. Relevant chemical modifications to fine-tune or enhance the desired properties will need to be iteratively performed to obtain optimized properties for practical applications.			
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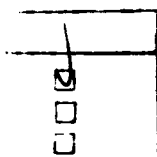
## SECOND-ORDER NONLINEAR OPTICAL POLYMERS: FROM FUNDAMENTALS TO APPLICATIONS

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A considerable volume of work has been reported in the area of second-order nonlinear optical (NLO) polymeric materials in the past decade.<sup>1</sup> A number of organic single crystals and polymers have been reported to surpass both the second harmonic and linear electro-optic (EO) coefficients of the traditional inorganic NLO materials such as lithium niobate and potassium dihydrogen phosphate.<sup>2,3</sup> The appropriately designed organic molecular and polymeric systems consistently have higher second harmonic coefficients because the origin of the nonlinearity is primarily *electronic*. The large dielectric constants (almost an order of magnitude larger than those of organics) of the inorganic materials lead to the large capacitance associated with the electrodes and severely limit the bandwidth for EO modulation. The lower dielectric constant of polymers also makes it easier to design traveling wave EO modulators due to the close match between the microwave and optical dielectric constants. The dielectric constant difference alone even with all other characteristics being equal gives the second-order organic NLO materials an edge over the inorganics for high speed EO modulation.

In order to impart second-order NLO properties, polymeric materials are incorporated with NLO chromophores. The NLO chromophores usually possess donor-acceptor groups attached to an aromatic ring system for increased charge transfer through  $\pi$ -electron delocalization.<sup>4</sup> These chromophores are characterized by intramolecular charge transfer giving rise to large ground and excited state dipole moments ( $\mu$ ) and second-order molecular hyperpolarizability ( $\beta$ ). These NLO chromophores have to be aligned in a noncentrosymmetric fashion so that the individual molecular susceptibilities do not cancel out and the




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system exhibits second-order nonlinearity. The alignment of dipoles are usually achieved by the poling technique.

The poling process is usually carried out by applying an external electric field across the polymer film at temperatures near the glass transition temperature ( $T_g$ ) of the polymer matrix.<sup>5,6</sup> The active moieties are subsequently "frozen" in the poled phase by cooling the matrix below its  $T_g$  in the presence of a poling field. However, this type of chromophore orientation is not in a state of thermodynamic equilibrium. Thus the poled polymer tends to relax to its original random order resulting in the cancellation of the second-order nonlinearity.

For the second-order polymeric material to be useful in most practical applications, it is necessary that the poled polymer is able to maintain a substantial degree of poled order and associated bulk nonlinearity at operating temperatures at least as high as 80 °C for years and at processing temperatures that may exceed 250 °C for short periods of time.<sup>7</sup> Therefore, such a relaxation of the poled order in the polymer has to be minimized. The stabilization of the poled order has been enhanced in polymeric films by different approaches as reported in a large volume of literature over the past few years.<sup>1</sup> In guest/host systems where NLO chromophores are dissolved in polymer matrices, the matrix needs to possess high  $T_g$  to obtain good stability. This is due to the fact that the relaxation of the poled order is closely related to the  $T_g$  of the polymer.<sup>7</sup> Covalent attachment of the NLO chromophores to the main chain or side chain of the polymers has also been reported to enhance the temporal stability of the poled systems.<sup>1,8-11</sup> Another approach is to employ crosslinking reactions to enhance stability of the second-order NLO properties in several poled polymer systems.<sup>12-17</sup> The resulting crosslinked polymer has a higher  $T_g$  and a network structure which restrict the mobility of the polymer chains. These features are able to efficiently prevent the aligned NLO chromophores from relaxing to a random orientation.

Other important properties of materials for photonic applications are large second-order optical nonlinearity, and low optical losses. NLO chromophores that exhibit large second-order susceptibilities often possess longer cutoff wavelengths (visible or near IR regions). This leads to substantial loss from absorption when the doubled frequency is in this region. For frequency doubling application, this problem must be avoided because the optical power density in most practical NLO waveguide devices is quite large. Therefore, even small

absorption can cause intolerable damage to the material.<sup>3</sup> For EO applications, waveguide optical loss should be low enough to allow sufficient signal transmission and processing. As some of the largest second-order nonlinearities are associated with highly delocalized NLO chromophores, one must contend with a trade-off between optical nonlinearities and cutoff wavelengths.

In our laboratory, approaches to stable second-order NLO polymers have included multicomponent and multifunctional crosslinked networks. Several crosslinked systems have been achieved via photochemical, thermal or sol-gel reactions. The well known 2+2 cycloaddition reaction of the cinnamoyl groups was first utilized to stabilize the second-order nonlinearity in a photocrosslinkable guest/host system.<sup>13,14</sup> This system is based on a polyvinylcinnamate host and an active dye guest, CNNB-R, functionalized with cinnamoyl groups. The chromophores and polymer host undergo intermolecular crosslinking reaction upon UV irradiation subsequent to corona poling (Figure 1), resulting in enhancement of the temporal stability. In addition, the processing of this photocrosslinked system is compatible with photolithographic techniques, thus integrated optical device structures can be patterned directly in the material with the use of a mask aligner.

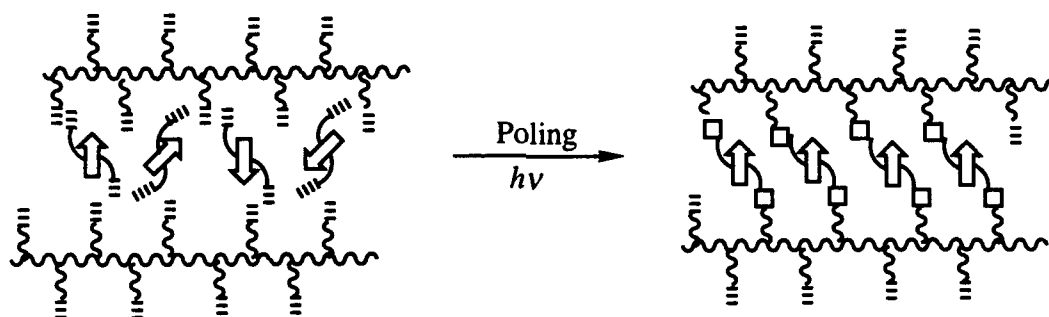


Figure 1. Schematic diagram for the network formation of the photocrosslinkable guest/host system.

Other types of photocrosslinked systems based on epoxy prepolymers have also been developed.<sup>16</sup> Epoxy polymers of diglycidyl ether of bisphenol A and NLO chromophores, such as Disperse Orange 3 (DGEBA-DO3C) or 4-nitroaniline (DGEBA-NAC), have been synthesized and subsequently functionalized with cinnamoyl groups. This UV curable epoxy based polymer has a higher molar concentration of the NLO chromophores compared to the

PVCN/CNNB-R system, because the NLO chromophores are covalently bonded onto the main chain of this polymer. DGEBA-DO3C exhibits large second-order NLO effects subsequent to poling. In a poled uncrosslinked thin film of DGEBA-DO3C, second harmonic coefficient,  $d_{33}$ , of 48 pm/V was observed at 1.064  $\mu\text{m}$ . As the sample was poled and photocrosslinked at 254 nm (Figure 2), a  $d_{33}$  of 31 pm/V was observed. This  $d_{33}$  value is less than that of the poled and uncrosslinked film sample due to photo-induced cis-trans isomerization and partial degradation of the NLO chromophores. Nevertheless, the poled and crosslinked film shows a more stable second-order optical nonlinearity than that of the uncrosslinked sample at room temperature.

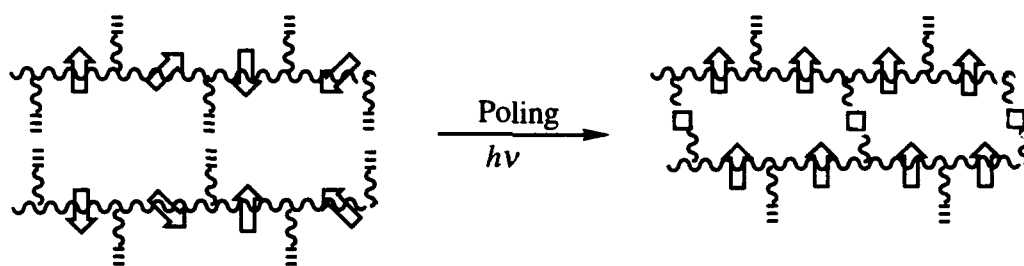
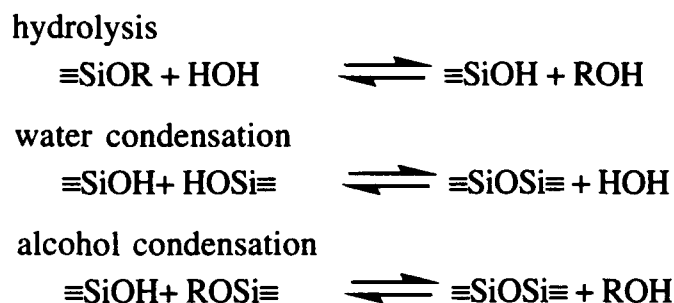


Figure 2. Schematic for the formation of network of the UV-curable epoxy polymer.

In order to circumvent the photodegradation and photoisomerization effects, a thermally crosslinkable guest/host system based on epoxy polymer was developed.<sup>17</sup> Both the dye and the polymer are NLO active and are functionalized with the same reactive acryloyl groups. As the polymer film is subjected to heat as a part of the poling process, the inter- and intramolecular crosslinking reactions occur simultaneously. The  $T_g$  of the crosslinked polymer/dye network is lower than that of the polymer network perhaps due to some plasticizing effect of the dissolved dye. However, the temporal stability of the former is better than that of the latter at 100 °C as a direct result of the increased crosslinking density in the crosslinked guest/host system. Therefore, the addition of the thermally crosslinkable NLO chromophore not only helps in the increase of the NLO coefficient, but to enhance the temporal stability at elevated temperatures as well.

Sol-gel process has also been used to prepare a number of crosslinked network systems in our laboratory.<sup>18-21</sup> A typical sol-gel process involves a sequential hydrolysis and condensation reaction (Scheme 1). A crosslinked

guest/host system based on an organically modified alkoxy silane dye (ASD) and a phenyl siloxane polymer has been prepared.<sup>19</sup> By using this approach, NLO chromophores are successfully incorporated into an inorganic network (Figure 3). The second-order NLO property of this system is stable at room temperature and decay to 55 % after 40 h at 100 °C. A second system involves a sol-gel reaction of ASD and a multihydroxyl compound forming a phenoxysilicon network with a  $T_g$  of 110 °C.<sup>21</sup> This system exhibits excellent temporal stability as only a 10 % decay of the optical nonlinearity was observed after 168 h at 105 °C, only 5 °C below its  $T_g$ . These studies have demonstrated the design flexibility of utilizing sol-gel reactions for the development of NLO materials.



Scheme 1. The reaction mechanism of the sol-gel process.

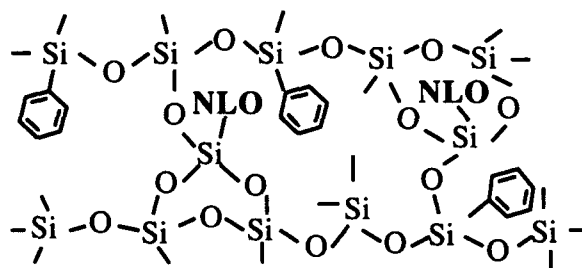


Figure 3. Inorganic network incorporating NLO chromophores.

NLO-active interpenetrating polymer network (IPN) samples were developed for enhanced temporal stability by realizing the potential of an IPN structure in improving the viscoelastic properties.<sup>22,23</sup> The combination of a thermally crosslinkable polymer and the sol-gel processable phenoxysilicon polymer forming an IPN (Figure 4) results in the synergistic enhancement of the temporal stability. No measurable decay of the SHG intensity of the IPN could be observed after the sample was treated at 110 °C for upto 1,000 h. The EO

coefficient,  $r_{33}$ , of this IPN is 17 pm/V and 5 pm/V at 633 nm and 1.3  $\mu\text{m}$ , respectively. Further investigation on the relaxation behavior shows that the stability of the IPN is superior to that of the guest/host and sidechain systems especially when the polymers are treated to the temperatures close to their  $T_{gs}$ .<sup>23</sup> The IPN system has been demonstrated to be a successful approach to stable NLO materials. Further developments can be built on this technique to obtain materials with optimized properties.

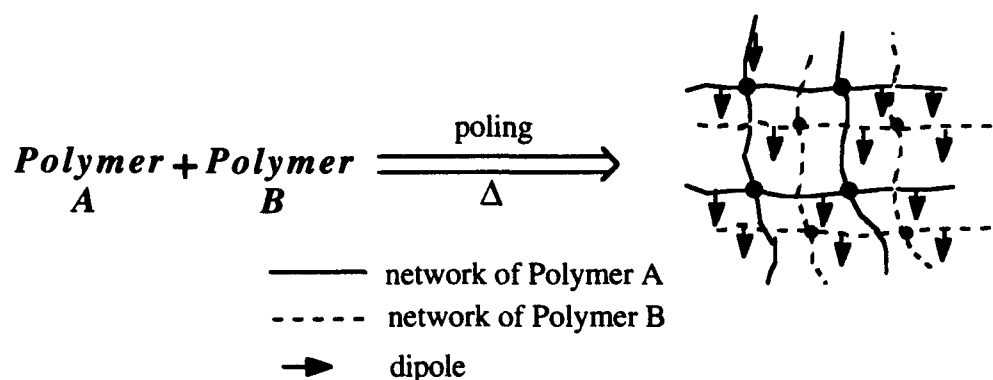


Figure 4. Schematic of the formation of an NLO-active IPN.

Prototype devices have been fabricated in our laboratory in parallel to the material development effort using the in-house polymers with suitable properties. Cerenkov second harmonic devices for frequency doubling applications have been fabricated using the aforementioned UV curable epoxy based polymer, DGEBA-NAC.<sup>24,25</sup> This type of polymers have exhibited a  $d_{33}$  of 13 pm/V at 1.064  $\mu\text{m}$ . Cerenkov second harmonic generation at 1.064  $\mu\text{m}$  and at 900 nm was carried out in the crosslinked poled polymer slab and channel waveguide structures. The schematic of a typical device configuration is shown in Figure 5. Green light was observed at 532 nm even with the Nd:YAG laser operating in a cw mode. Blue light at 450 nm was obtained with a fundamental beam of 900 nm from a cw Ti-Sapphire laser. These NLO polymer waveguides were characterized by fairly low optical losses. Yet, further optimization of the system, for example, increasing of the  $d_{33}$  coefficient and reduction of the absorptive losses, will be needed to enhance the output second harmonic intensity.

In summary, successful development of materials for photonic applications requires an understanding of the nonlinear optical process, chemistry and processing of materials, and technologies for device fabrications. We are able to

successfully use different chemistries to develop several types of crosslinked and networked systems. Significant progress in improving material properties has been accomplished. Promising results have been observed in several materials developed. A prototype frequency doubling device has been prepared; second harmonic Cerenkov radiation emitting green and blue light have been observed. Relevant chemical modifications to fine-tune or enhance the desired properties will need to be iteratively performed to obtain optimized properties for practical applications.

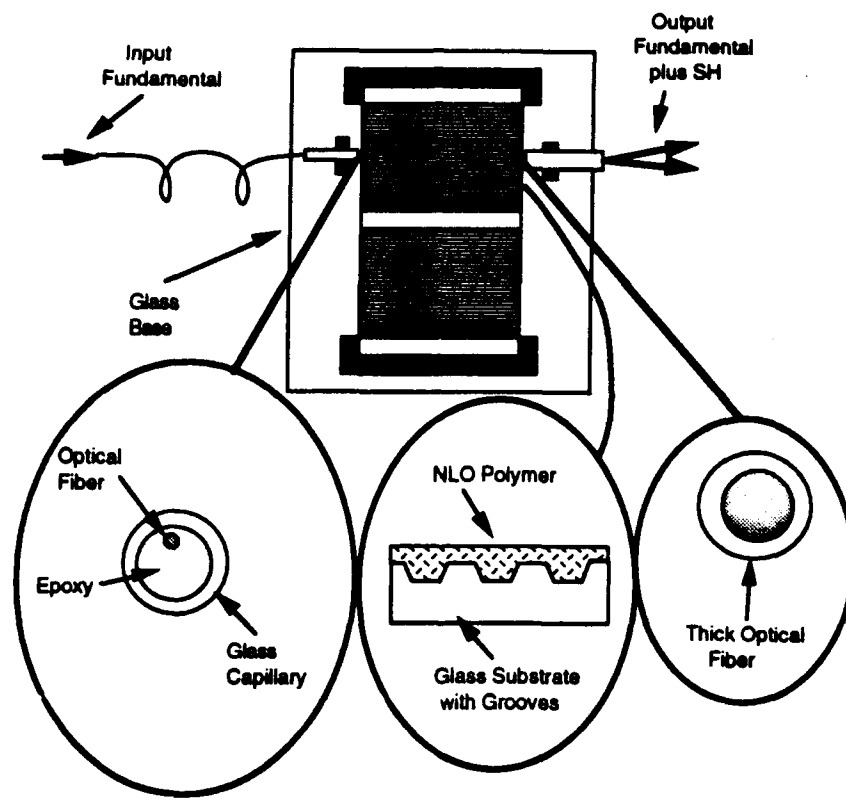


Figure 5. Diagram of a typical device for second harmonic generation based on Cerenkov radiation.

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