Stable Second-Order Nonlinear Optical Polymer Network Based on an Organosoluble Polyimide

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Polymeric materials with large and stable second-order nonlinear optical (NLO) coefficients are of interest for their potential use in electrooptic applications.[1] To prevent the randomization of the aligned (poled) molecules, NLO chromophores are usually incorporated into either high-T_g polymers and/or cross-linked polymer networks.[2-14]

Aromatic polyimides are well-known for their high-temperature stability and high glass transition temperatures (T_g).[15] One approach to improve NLO stability at elevated temperatures is to dissolve NLO chromophores in polyimide matrices.[13,16] The orientation of the chromophores is preserved due to the decreased mobility of the host polymer and the chromophores. However, high loading of chromophores (20–30%) can lower the T_g considerably, and diffusion of the chromophores may also cause long-term stability problems.[17] In addition, high-T_g polyimides are usually obtained via thermal imidization of polyamic acids at high temperatures (250–400 °C).[18] Only a few organic NLO chromophores are capable of withstanding such harsh processing conditions during thermal imidization.[19] These factors are a hindrance in attaining stable second-order NLO active polyimide systems.

Several approaches have been reported to enhance the stability and processability of NLO materials based on polyimides. Jeng *et al.* have reported a second-order NLO organic/inorganic composite based on an alkoxysilane dye and an aromatic polyimide.[7,20] The formation of the inorganic network in the polyimide enhances the T_g of the composite material.[20] Lin *et al.* have reported the synthesis of a maleimide based NLO main-chain polymer.[21] More recently, Tapolsky *et al.* have reported maleimide based cross-linked NLO polymers.[22] These approaches were carried out at relatively low processing temperatures (150–220 °C). The resulting materials exhibited excellent temporal stability at elevated temperatures as well as large second-order nonlinearities.

On the basis of the above considerations, polyimides possessing both high T_g and a cross-linked network seem to be a reasonable approach to enhance the stability. Organosoluble polyimides may be used to circumvent the need for thermal imidization. Improved processability is achieved without sacrificing useful properties, such as excellent thermal stability and mechanical properties.[23-27] These organosoluble polyimides have been shown to possess T_g's ranging from 140 to 400 °C. Recently, Lakshmanan *et al.* have synthesized a series of aromatic hydroxyl-terminated organosoluble polyimides.[23] The molecular weights and T_g's were controlled by changing the feed ratio of an end-capper and the monomers. Moreover, the hydroxyl functionalities at the chain ends provide the possibility for further chemical incorporation of various moieties. In this paper, we have adoped similar chemistry to prepare an NLO polymer network based on organosoluble polyimides by taking advantage of the reactive end groups. An NLO-active alkoxysilane dye (ASD), serving as a cross-linking agent, was added to an organosoluble polyimide. The ASD was reacted with the aromatic hydroxyl end groups to form a cross-linked NLO-active polyimide (Scheme 1).

α,α'-Bis(4-aminophenyl)-1,4-diisopropylbenzene (Bis-P), 4,4'-oxydiphthalic anhydride (ODPA), and *p*-aminophenol (Figure 1) were obtained from Aldrich Chemical Co. and were used as received. The molar ratio of the two monomers, Bis-P and ODPA, was 1:1, and *p*-aminophenol

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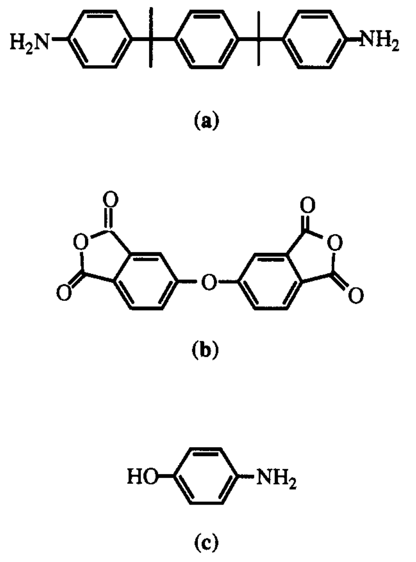


Figure 1. Chemical structures of (a) Bis-P, (b) ODPA, and (c) *p*-aminophenol.

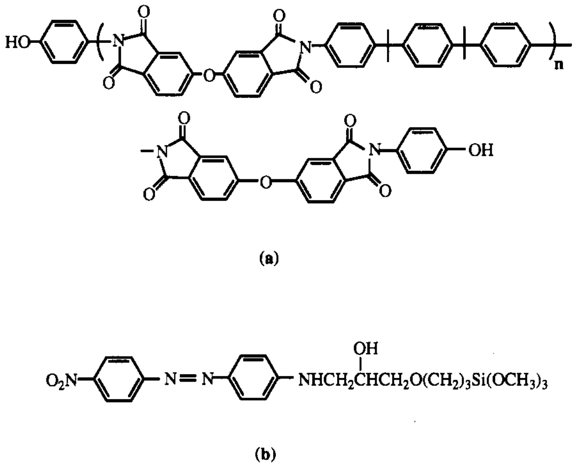
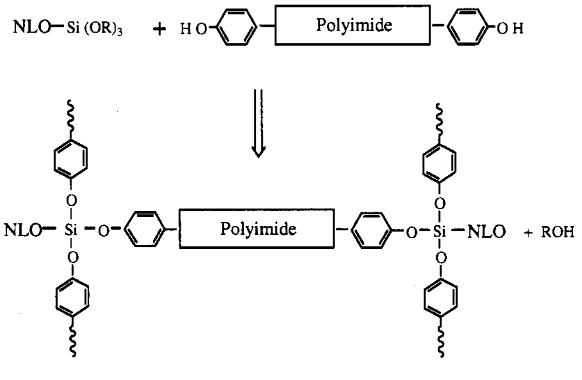


Figure 2. Chemical structures of (a) the aromatic hydroxyl-terminated polyimide and (b) DO3-based ASD.

Scheme 1. Formation of a Cross-Linked Polyimide Network



was used as the end-capper. Aromatic hydroxyl terminated organosoluble polyimides (Figure 2a) with various molecular weights were successfully synthesized by solution imidization techniques.[23] T_g's were determined using differential scanning calorimetry (DSC, Seiko SSC/5200) with a heating rate of 10 °C/min. An NLO chromophore, 4-((4′-nitrophenyl)azo)aniline (disperse orange 3, DO3) was coupled with (3-glycidoxypropyl)trimethoxysilane to form an ASD (Figure 2b).[12]

An organosoluble polyimide (Figure 2a) with a T_g of 208 °C (named 50P hereafter) doped with the ASD was chosen for further study. A polymer solution was prepared by dissolving 0.03 g of ASD and 0.07 g of polyimide 50P in 1.5 mL of chloroform. Thin films were prepared by spin-coating the polymer solution onto appropriate substrates. The isotrack technique of DSC was applied to obtain optimum curing conditions. The thermal degradation temperatures (T_d) of the materials were determined on a thermogravimetric analyzer (TA Instrument, TGA2950) with a heating rate of 10 °C/min under air.

Corona poling technique was used to impart the second-order NLO properties to the polymer films.[28] Poling field was applied when the temperature reached 60 °C. The temperature was then increased to 240 °C at a rate of 10 °C/min. The corona current was maintained at 3 μA with a potential of 4 kV while the poling temperature was kept at 240 °C for 10 min. The formation of the network and the alignment of chromophores proceeded simultaneously during this period. The sample was then cooled down to room temperature in the presence of the poling field. The typical thickness for the cured 50P/ASD samples was approximately 0.28 μm.

The second-order NLO properties of the poled 50P/ASD samples were measured by second harmonic generation at 1.06 μm. The relaxation behavior of the second-order NLO properties was studied by monitoring the decay of the effective second harmonic coefficient, d_{eff}, as a function of time at 110 °C. Measurements of the second harmonic coefficient, d_{33}, have been previously discussed,[4,12,29,30] and the d_{33} values were not corrected for absorption.

Hydroxyl-terminated ODPA/Bis-P polyimides were soluble in various solvents such as tetrahydrofuran, chloroform, *N*-methylpyrrolidinone, and dimethylacetamide. The T_g's of these polyimides were in the range 169–250 °C as the molar feed ratio of the end-capper to the monomers changed from 0.5 to 0.05.

An exothermic reaction was observed at approximately 180 °C using DSC indicating the formation of phenoxy-silicon bonds in a 50P/ASD sample.[12] Generally, a higher curing temperature is necessary for high-T_g systems due to a slow reaction rate after vitrification. Furthermore, curing and thermal degradation often compete at such high temperatures.[31] These two factors were taken into consideration to select polyimides with appropriate T_g's and further optimize the curing condition. Therefore, a polyimide, 50P, with a T_g of 208 °C (Figure 3) was selected for further study. The optimum curing condition of 50P/ASD samples was chosen to be at 240 °C for 10 min. The T_d of 50P, as taken from the first step transition, is 450 °C (Figure 4a), whereas the cured 50P/ASD sample showed a T_g of 252 °C (Figure 3b) and a T_d of 500 °C (Figure 4b). It is important to note that the polyimide 50P remained soluble even after being subjected to heating at 400 °C for 5 min. Its T_g remained unchanged after the thermal treatment. Therefore, the increase in T_g of the cured 50P/ASD sample is due to the formation of the network. In addition, ΔC_p (T_g) of the cured 50P/ASD sample is much smaller than that of the 50P. This indicates a net decrease

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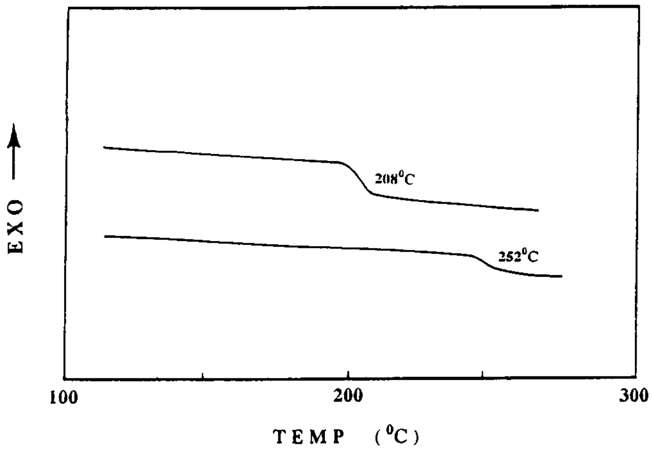

Figure 3. DSC thermographs of (a) polyimide 50P, top, and (b) cured 50P/ASD, bottom.

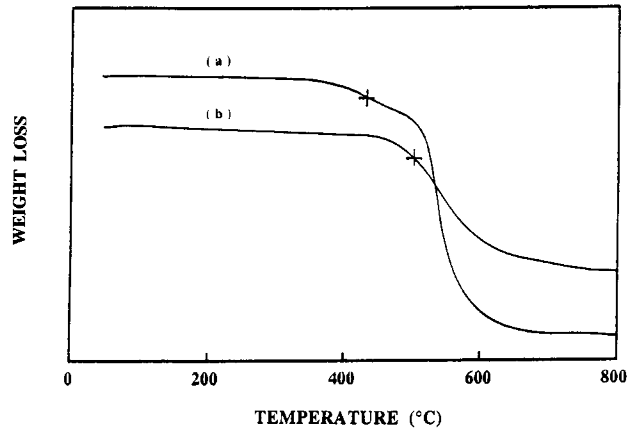

Figure 4. Thermal degradation behavior of (a) 50P and (b) cured 50P/ASD.

in both chain mobility and vibrational contributions to C_p as a result of the interchain cross-linking reactions.[32,33] A thin film of the cured 50P/ASD sample was soaked in tetrahydrofuran (a good solvent for both aromatic polyimides and ASD) for 8 h. The cured polymer film remained intact after the treatment. The solvent did not extract any measurable amount of dye from the cured sample as measured by UV-vis spectroscopy.

The thermal cross-linking reaction of the 50P/ASD sample was analyzed by infrared (IR) spectroscopy. As shown in Figure 5, after being heated at 240 °C for 10 min, a change of absorbance in the IR spectra was observed due to the emergence of the phenoxysilicon absorption at 960 cm^{-1}. Moreover, the absorption peak of hydroxyl stretching around 3400 cm^{-1} decreased drastically after curing which further supports the formation of the phenoxysilicon bonds.[34] The hydrolysis of the phenoxysilicon bonds is expected to be negligible as there is no acid or base catalyst in the sample (as long as the experiment was carried out). This is confirmed by the stability of optical nonlinearities at 110 °C as described below. However, the intensity of the absorption peaks from some functional groups such as nitro (ν_{as}, 1521 cm^{-1}) and phenyl (1601 cm^{-1}) were found to have slightly decreased. This indicates that some degree of thermal degradation has occurred during curing. It is important to note that the formation of Si-O-Si bonds (reaction among ASD molecules) is insignificant as the absorption peaks at around 1100 cm^{-1} did not broaden after curing.[7,35,36]

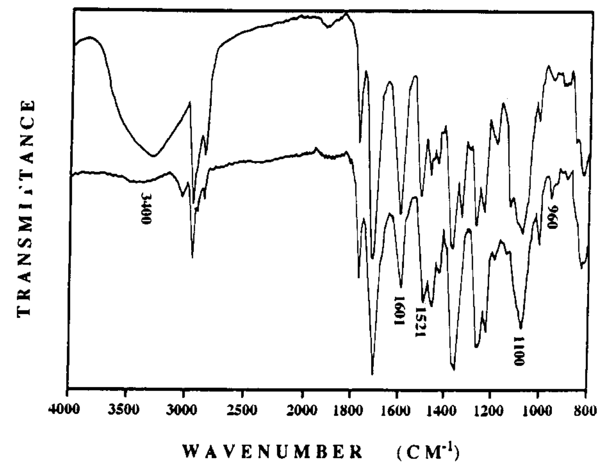

Figure 5. Infrared spectra of 50P/ASD, from top to bottom: pristine, cured.

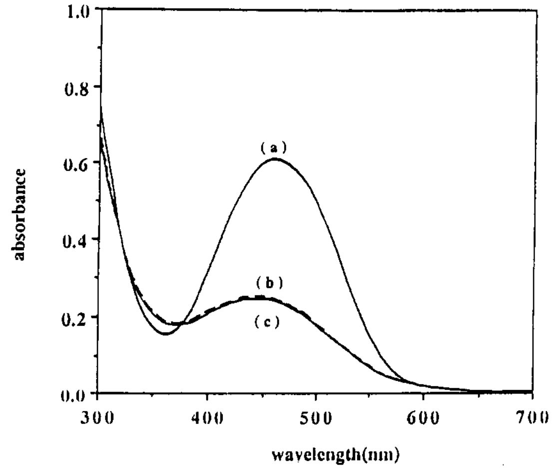

Figure 6. UV-vis absorption spectra of 50P/ASD, from top to bottom: (a) pristine; (b) immediately after poling and curing; (c) poled/cured sample, after thermal treatment at 110 °C for 122h.

The poled/cured film of 50P/ASD has a d_{33} value of 17.8 pm/V. The optical quality of the samples appears to be excellent under an optical microscope. After thermal treatment at 110 °C for 122 h, no sign of decay in the d_{eff} value was observed for the poled/cured sample. Excellent temporal stability at 110 °C is a direct consequence of the extensively cross-linked network and high T_g in this system. The d_{eff} of a poled/cured 50P/ASD sample decayed to 51% of its original value after being heated at 160 °C for 3 h.

To investigate the absorption behavior for the poled/cured sample at 110 °C as a function of time, the absorption spectra were taken at regular intervals over 122 h. Immediately after poling and curing, a decrease in absorbance was observed. This is due to some dye degradation and orientational dichroism.[28] The absorption peak of the chromophore shifted slightly toward shorter wavelength (Figure 6). This behavior is similar to that observed in other cross-linked NLO polymer systems.[9]

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During the next 122 h, the absorption spectra remained unchanged.

In conclusion, a new class of cross-linked polymer networks based on organosoluble polyimides for second-order nonlinear optics has been developed. The T_g's of these aromatic polyimides can be tailored to suit subsequent processing and reaction schemes. This approach demonstrated a convenient route to achieve hybrid character of both high T_g and network features. Excellent temporal stability of the nonlinearity at 110 °C is a result of this hybrid characteristics. Optimization of the curing cycle may further increase the optical nonlinearity. Future work involves the synthesis of thermally stable NLO-active ASD and the incorporation of these chromophores into organosoluble polyimide mainchains to further enhance the nonlinearity as well as temporal stability.

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