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**Stable Second-Order Nonlinear Optical Materials  
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**by**

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## Stable Second-Order Nonlinear Optical Materials Based On Interpenetrating Polymer Networks

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### Introduction

Nonlinear optical (NLO) polymers have shown increased potential in practical applications, such as frequency doubling and electro-optic modulation, due to their large nonlinearity and ease of processing. A practical NLO polymer will need to possess large second-order nonlinearity, excellent temporal stability at elevated temperatures, and low optical loss.<sup>1</sup> A number of NLO polymers have been developed to exhibit large second-order NLO coefficients comparable to those of the inorganic NLO materials which are currently in use in devices.<sup>2,3</sup> However, the major drawback of NLO polymers is the decay of their electric field induced second-order optical nonlinearities. This decay is a result of the relaxation of the NLO chromophores from the induced noncentrosymmetric alignment to a random configuration. Numerous efforts have been made to minimize this decay through different approaches.<sup>4</sup>

Recently, we have reported on an approach to stable second-order NLO polymers using an interpenetrating polymer network (IPN) structure.<sup>5,6</sup> This IPN system, with the hybrid properties of a high glass transition temperature ( $T_g$ ), an extensively crosslinked network, and permanent entanglements, exhibited excellent temporal stability at elevated temperatures.<sup>6</sup> In this report, a new IPN system, modified from the one reported earlier,<sup>5</sup> with higher degree of crosslinking density and larger NLO chromophore density is investigated.

### Experimental

The IPN system in this study combines a network of an NLO-active epoxy-based polymer incorporating thermally crosslinkable NLO chromophores, and an NLO-active phenoxysilicon polymer network. The epoxy-based network is prepared from the epoxy prepolymer (namely Polymer-11, see Figure 1a) based on the diglycidyl ether of bisphenol A and 4-(4'-nitrophenylazo)aniline functionalized with crosslinkable methacryloyl groups. The crosslinkable NLO

chromophore, namely DRMA (Figure 1b, Disperse Red 19 functionalized with methacryloyl groups), is synthesized by coupling the corresponding acid chloride with the hydroxyl groups of Disperse Red 19. The phenoxysilicon polymer, incorporated in the previously reported IPN system,<sup>5</sup> is based on an alkoxy silane dye (ASD) of (3-glycidoxypropyl) trimethoxysilane and 4(4'-nitrophenylazo)aniline, and the multifunctional phenoxyl molecule 1,1,1 - tris (4-hydroxyphenyl) ethane (THPE). Figure 2 shows the structures of ASD and THPE.

Thin films were prepared according to the literature.<sup>5</sup> IPN samples containing 1:1 and 2:1 weight ratio of the phenoxysilicon to Polymer-11/DRMA, where the weight ratio of Polymer-11 to DRMA was 2:1, were obtained. The network of each prepolymer was formed simultaneously when the thin films were heated either at 200 °C or 220 °C on a hot stage.

The corona poling technique<sup>7,8</sup> was employed to align the NLO chromophores. The second-order NLO properties of the poled IPN samples were measured by second harmonic generation from 1.064 μm laser radiation. Electro-optic coefficients,  $r_{33}$ , of the IPN samples were measured at 633 nm and 1.3 μm, using the reflection method.<sup>9</sup> The relaxation behavior of the second-order NLO properties was studied by monitoring the decay of the second harmonic (SH) intensity as a function of time at 100 °C after poling and curing.

## Result and Discussion

The design rationale to incorporate the thermally crosslinkable methacryloyl group on the epoxy polymer, Polymer-11, is that a high degree of the functionalization is possible (close to 100%). In order to further increase the chromophore- and the crosslinking density of the IPN system, the thermally crosslinkable NLO chromophore, DRMA, is added. An onset point of an exotherm at 185 °C was observed for the methacryloyl groups from the Polymer-11 and the functionalized chromophore by differential calorimetric analysis. As the samples were heated at 200 °C for 1 h or at 220 °C for 30 min during the poling and curing process, the inter- and intramolecular crosslinking reactions between the polymer and the dye, DRMA, took place. This has been confirmed by the solubility test.

The poled and cured IPN samples showed excellent optical quality. The temporal stability of optical nonlinearity for the IPN sample containing 2:1 weight ratio of phenoxysilicon to Polymer-11/DRMA is shown in Figure 3. The

SH intensity of the sample is stable after a small initial decay as the sample is subjected to thermal treatment at 100 °C for upto 168 h. The second-order NLO coefficient,  $d_{33}$ , of the poled/cured IPN samples is summarized in Table 1. The IPN sample with 1:1 weight ratio of each network component exhibits a  $d_{33}$  of 32 pm/V at 1.064  $\mu\text{m}$ . The  $r_{33}$  values of this sample were determined to be 18 pm/V at 633 nm and 6.5 pm/V at 1.3  $\mu\text{m}$ .

Polymer 11 exhibits relatively low optical loss even when the processing conditions have not been optimized. Measurements on unclad slab waveguides gave values of 4.7 dB/cm at 830 nm and about 2 dB/cm at 1.3  $\mu\text{m}$ . Loss measurement on the IPN sample (2:1) was also performed at 830 nm indicating that waveguiding is possible in this IPN system.

## Conclusion

A second-order NLO IPN system has been developed and the samples exhibit reasonably large and stable optical nonlinearities. The nonlinearity of this IPN system is affected by the compositions as well as the processing conditions. Waveguide optical loss measurement at 830 nm. was performed on this system. Further improvements of the linear and nonlinear optical properties of this class of materials is currently underway from the perspective of practical device applications.

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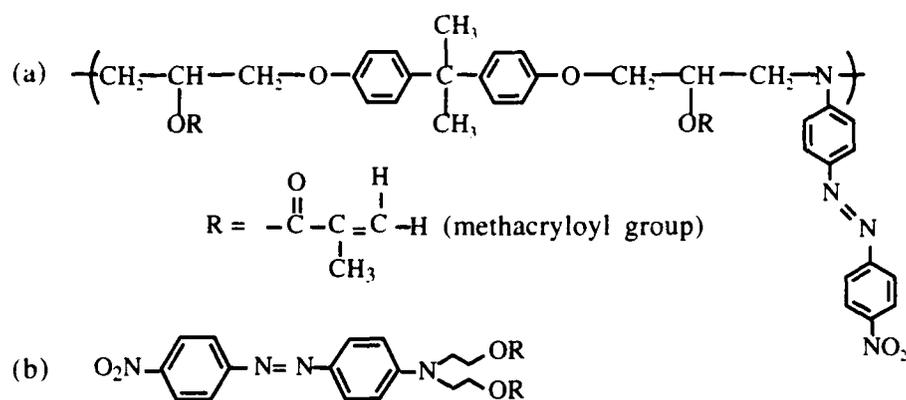


Figure 1. Chemical structures of (a) Polymer-11 and (b) DRMA.

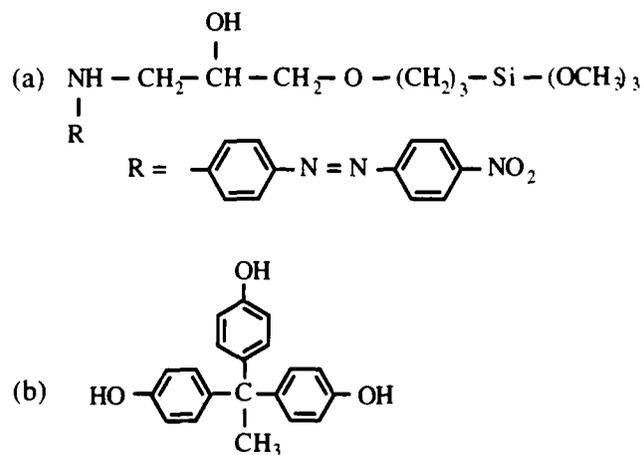


Figure 2. Chemical structures of (a) ASD and (b) THPE.

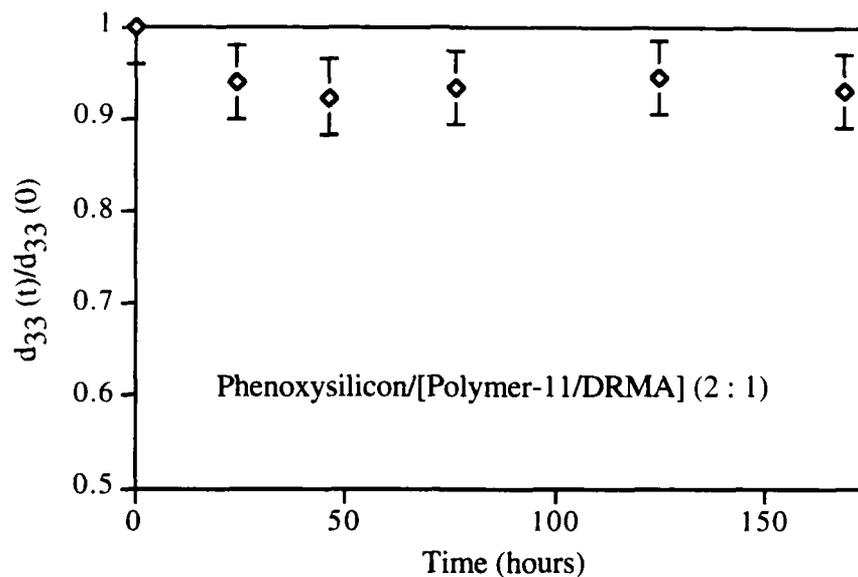


Figure 3. Temporal Stability of the IPN sample as subjected to thermal treatment at 100 °C.

Table 1. Optical properties of the poled and cured IPN samples processed at different conditions.

	Phenoxysilicon (ASD/THPE)	Polymer-11/DRMA (2:1 w/w)	Processing Conditions	$d_{33}$ at 1.064 $\mu\text{m}$
Weight ratio	1	1	1h @ 200 °C	32.0
	2	1	1h @ 200 °C	26.0
	1	1	0.5 h @ 220 °C	10.6
	2	1	0.5 h @ 220 °C	24.8