

# Thermally Stable Maleimide Copolymer for Second-Order Nonlinear Optics

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## SYNOPSIS

Second-order nonlinear optical copolymer containing *p*-hydroxyphenyl maleimide as a comonomer was newly synthesized. Second-order nonlinear optical properties of the poled films were investigated in terms of the second harmonic generation (SHG) and linear electrooptic (EO) coefficient measurement. SHG coefficient,  $d_{33}$  was found to be 14 pm/V at the fundamental wavelength of 1064 nm and EO coefficient,  $r_{33}$  was found to be 25–30 pm/V at 633 nm wavelength. To prevent the orientational relaxation of poled polymer, the thermal crosslink reaction was induced using diisocyanate as a crosslinker between the side chains themselves. Temporal stabilities of second-order NLO coefficients of crosslinked polymer systems were proved much better than that of guest–host system or other side chain polymers. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Organic nonlinear optical (NLO) materials provide strong potential advantages for second harmonic generation and electrooptic applications.<sup>1–7</sup> Particularly, side-chain polymers have drawn remarkable interest in recent years as promising candidates for application in electrooptic and photonic devices.<sup>1–9</sup> This interest is partly from their large optical nonlinearity, relatively high damage threshold, fast response, and high optical transparency over a wide range of the wavelength.

Second-order NLO properties of poled polymers have been extensively studied in the past.<sup>10</sup> One difficulty with poled polymer has arisen from poor thermal and temporal stability of the NLO activity. The important issue for practical application with poled polymers is postulated that the temporal sta-

bility of dipolar alignment should be improved. For this purpose, two methods look quite promising; one is to synthesize the thermoplastic polymer whose glass transition temperature is very high and the other is to prepare the crosslinked polymer system.<sup>11–13</sup>

In an attempt to improve both the second-order NLO effect and its temporal stability, we designed and synthesized the copolymer that has a high  $T_g$  and a high chromophore concentration in copolymer structure. This polymer is easy to synthesize and quite soluble in common organic solvents. In addition to the inherent backbone rigidity, the copolymer possesses a carbamate group in the side chain, which would promote interactions between the polymer chains or side chain chromophores through inter- or intramolecular hydrogen bonding and therefore were expected to show a great enhancement of temporal stability of NLO activity. Also, we adopted the method of crosslink reaction between the side chains themselves using the diisocyanate. After we have synthesized novel copolymer, containing the piperazyl nitrostilbene NLO chromophore in the side chain, the second-order NLO properties of new copolymer and crosslinked polymer were investigated by virtue of the second harmonic generation and linear electrooptic coefficient measurement.

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## EXPERIMENTAL

### Synthesis of Monomer and Polymer

*p*-Hydroxyphenyl maleimide (HPMI) was obtained from the reaction with maleic anhydride and *p*-aminophenol by the literature method.<sup>14</sup>

### [1-[4-(*N*-Ethylenepiperazyl)-4'-nitrostilbene]-*N*-[(1,1-dimethyl-*m*-isopropenyl)benzyl]] carbamate

4-[*N*-(2-Hydroxyethyl)piperazyl]-4'-nitrostilbene (2.9 g, 8.21 mmol)<sup>15</sup> was dissolved in dry dimethyl formamide (DMF, 200 mL) at 25°C under nitrogen atmosphere. Then, a trace of dibutyltin dilaurate (0.15 mol %) was added to the mixture. This was followed by dropwise addition of *m*-isopropenyl- $\alpha,\alpha$ -dimethylbenzyl-isocyanate (*m*-TMI, 1.65 g, 8.21 mmol) which was diluted in DMF (10 mL) over a period of 15 min. The mixture was heated at 70°C for 8 h. After cooling, the resultant solution was poured into the excess amount of cold water (1 L). Precipitated red solid was collected and dried under vacuum at 70°C for 24 h. It was dissolved into chloroform and the solution was dried over sodium sulfate. After concentrating the final solution, it was recrystallized into ethanol. Percent yield, 70% (wt.) m.p. 120–121°C <sup>1</sup>H-NMR (DMSO-*d*<sup>6</sup>):  $\delta$  8.19 (d, 2H), 7.78 (d, 2H), 7.40 (s, 1H), 7.27 (s, 1H), 7.45 (d, 2H), 6.95 (d, 2H), 4.01 (s, 2H), 3.35 (s, 4H), 2.08 (9H), 1.54 (s, 6H), 5.06, 5.36 (s, 2H), 7.55 (s, 1H), 7.37 (s, 3H). Anal. Calcd for C<sub>33</sub>H<sub>38</sub>N<sub>4</sub>O<sub>4</sub> (554.69): C, 71.46; H, 6.91; N, 10.10. Found: C, 71.10; H, 6.10; N, 9.95.

Copolymerization was conducted under the general radical polymerization: 661 mg of HPMI (3.50 mmol) and 3.80 g of NLO monomer (7.00 mmol) were introduced into the vacuum ampoule. Freshly distilled dimethylformamide (38 mL) and azobisisobutyronitrile (AIBN, 17.1 mg) were added to the ampoule. The solution was degassed by freeze–vacuum–thaw technique repeatedly and sealed. The polymerization was carried out at 70°C for 24 h. Then, the resulting solution was poured into hot methanol to precipitate the copolymer. The copolymer was purified by reprecipitation from tetrahydrofuran into ethyl ether and dried *in vacuo* at 100°C for 48 h.

### Characterization

The chemical structure of the copolymer was identified and analyzed by FT-IR (Alpha Centauri) and

NMR (Bruker AM 200) spectrometer. Absorption spectra of the copolymer were recorded with a Shimadzu UV-3101 PC spectrophotometer. Differential scanning calorimeter (DSC, Perkin-Elmer DSC 7) was used to investigate the glass transition temperature of the copolymer. Elemental analysis was performed at Advanced Analytical Lab. in KIST.

### Material Processing

For thin film fabrication, the synthesized copolymer was dissolved in tetrahydrofuran (THF)/cyclohexanone. Polymer film was spin coated at 2000 rpm either on indium tin oxide (ITO)-precoated glass or normal microslide glass using filtered solution (10 wt %). When *m*-tetramethylxylene diisocyanate (*m*-TMXDI) of the crosslinker was mixed into the polymer solution, the mole ratio of copolymer and crosslinker was set at 4 : 1. The thickness of the film was measured using a stylus instrument Tencor P10. The refractive index of the copolymer coated on silicon wafer was measured with Rudolph Auto ELII ellipsometer (Rudolph Research Co.). The wavelength used for this measurement was 632.8 nm and the incident angle was 70°.

For SHG experiment, we poled the films on microslide glass using the corona poling technique in a wire-to-plane geometry.<sup>16,17</sup> For linear electrooptic coefficient measurement, we deposited the gold electrode on the top of the film and did electrode poling to apply the electric field directly to both gold and ITO electrode.

### Measurement of the Second-Order NLO Coefficient $d_{33}$

The second harmonic generation (SHG) measurements of poled samples were carried out with a Q-switched mode locked, Nd<sup>3+</sup>:YAG laser operating in the TEM<sub>00</sub> mode. We followed the standard Maker fringe technique, which was already well understood.<sup>18</sup> Assuming the Kleinman's symmetry rule, we used the p–p fringe to calculate the  $d_{33}$  value. The second harmonic signal was normalized with respect to that from a calibrated quartz crystal for which value of  $d_{11} = 0.5$  pm/V was assumed.<sup>19</sup>

### Measurement of Electrooptic Coefficient, $r_{33}$

We measured the linear electrooptic coefficients by way of simple reflection technique proposed by Teng and Mann.<sup>20</sup> The He-Ne laser (wavelength: 632.8 nm) was used for this measurement. In this measurement, the sine wave modulating voltage (10 V

at 8 kHz) was applied to each sample. The linear electrooptic coefficient “ $r_{33}$ ” could be calculated by following equation:

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{(n^2 - \sin^2 \theta)^{1/2}}{\sin^2 \theta} \quad (1)$$

where  $I_m$  is the amplitude of modulation,  $V_m$  is the modulating voltage applied to the sample, and  $I_c$  is half the maximum intensity of modulation. The refractive index of the new copolymer was determined to be 1.684 at 632 nm wavelength. The value determined will correspond to  $r_{33}$  provided that the electrooptic coefficient is dispersionless and the poled polymer belongs to the point group  $(\alpha, \infty, \infty)$ .

## RESULTS AND DISCUSSION

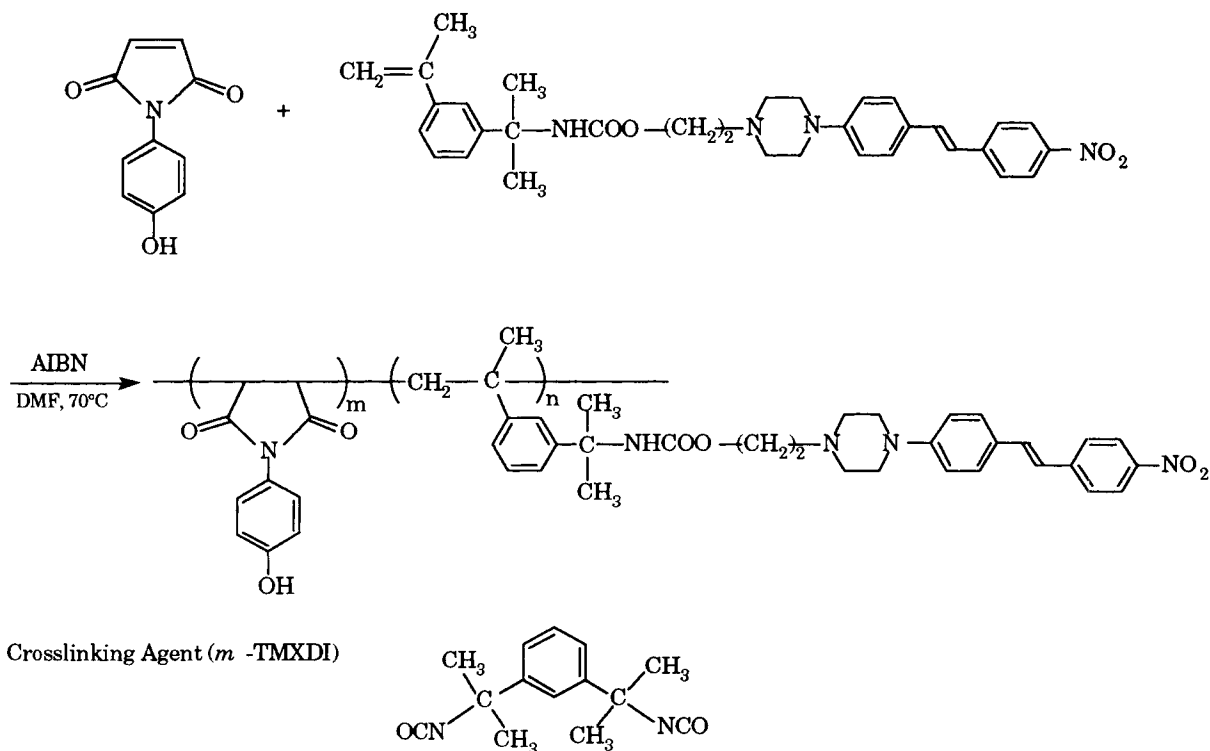
{1-[4-(*N*-Ethylenepiperazyl)-4'-nitrostilbene]-*N*-[(1,1-dimethylisopropenyl)benzyl]} carbamate was synthesized by a reaction of 4-[*N*-(2-hydroxyethyl)piperazyl]-4'-nitrostilbene with *m*-isopropenyl- $\alpha,\alpha$ -dimethylbenzyl-isocyanate (*m*-TMI) in the presence of catalyst. High reaction yield could be achieved around 70%.

The NLO active monomer was copolymerized with HPMI through free radical polymerization as depicted in Scheme I. The yield was 44–45% and inherent viscosity was 0.32 dL/g in DMF at 25°C. The copolymer was quite soluble in common organic solvents such as DMF, THF, and cyclohexanone. With the feeding ratio of 1 : 2 (HPMI: NLO monomer), the resultant mole ratio of each component in the copolymer was determined to be 1 : 0.95, which was estimated by integration of NMR proton signals.

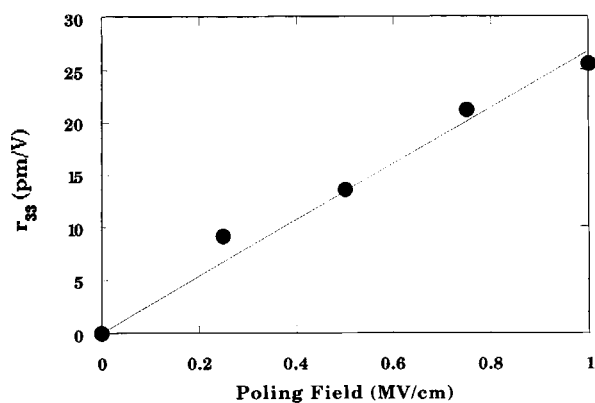
DSC was used to investigate the thermal transition behavior of the copolymer. DSC thermogram showed that this copolymer was amorphous judging from the absence of the melting transition and a high glass transition temperature appeared at 201–203°C due to the robust maleimide structure.

### Second-Order NLO Properties of Copolymer and Its Crosslinked Structure

We fabricated the thin film of copolymer and poled this film at 180°C with the change of poling field. The EO coefficient,  $r_{33}$  increased linearly with the electric field (see Fig. 1). The measured  $r_{33}$  value was in the range of 25–30 pm/V at 632.8 nm wavelength when the film was poled under 0.8–1 MV/



**Scheme 1** Synthetic procedure of maleimide copolymer and used crosslinking agent.

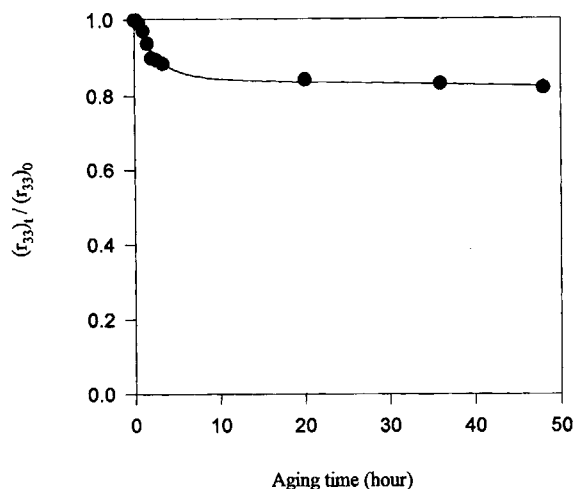


**Figure 1** Poling field dependence of  $r_{33}$  of maleimide copolymer. Poling temperature 180°C.

cm at 180°C. SHG measurement was performed to calculate the second-order NLO coefficient,  $d_{33}$  value of the poled film. The  $d_{33}$  value was determined to be 14 pm/V after corona poling under 5 kV at 180°C.

The temporal stability of NLO activity was investigated by monitoring the decay of NLO coefficient as a function of time at elevated temperatures. After being subjected to thermal aging at 80°C for 72 h, a reduction of only 20% in the  $r_{33}$  value was observed for the poled film. After exponential decay of  $r_{33}$  at first stage of relaxation, the  $r_{33}$  value did not vary at the level of 80% of the initial  $r_{33}$  value.

The decaying curve of polymer shows two different stages; at the first stage, EO coefficient rapidly decreased and then the value slowly decreased and approached a certain value ( $\sim 80\%$ ) asymptotically at second stage (see Fig. 2). Therefore, the elec-

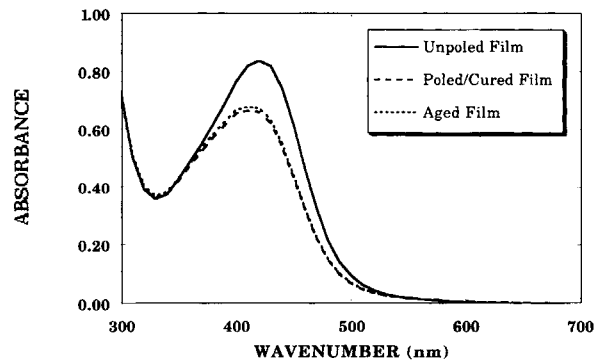


**Figure 2** Decay of  $r_{33}$  in an electrode-poled copolymer film with the temperature maintained at 80°C.

tropic effect of this copolymer was considered quite outstanding resulting from the fairly high EO coefficient and its thermal stability. Based on the theoretical approach, we can fit these data to a biexponential of the form,  $A \exp(-t/\tau_1) + (1 - A) \exp(-t/\tau_2)$ . For this case,  $A = 0.156$ ,  $\tau_1 = 159$  min, and  $\tau_2 = 120,000$  min. The experimental data cannot be fit to Kohlrausch-Williams-Watts stretched exponential function,  $\exp\{(-t/\tau)^\beta\}$ . Therefore, the  $r_{33}$  value of this polymer showed fast decay initially and then decreased very slowly.

Copolymer containing a hydroxyl group in the side chain can be crosslinkable with diisocyanate inter- or intramolecularly. Additionally, the NLO monomer used herein contains the carbamate group in the side chain. There is a secondary amine that can react with isocyanate to form biuret or allophanate. It was found that our copolymer with *p*-hydroxyphenyl maleimide could be thermally crosslinked in an atmosphere without deterioration of NLO activity around 140–150°C. The extent of crosslinking will be dependent on curing time and temperature. During poling, the crosslinking will be induced at the same period. This poling procedure also has a sequential temperature program to pole and then cure the film. We adopted two temperatures, 130 and 160°C. First, we poled the film at 130°C for 1 h and then raised the temperature to 160°C gradually in the presence of an electric field. After keeping that condition for 1 h, the poling was completed.

Using the corona poling method, the UV-VIS spectra of unpoled and poled film of crosslinked polymer were compared. In Figure 3, after two stage poling, the absorption intensity decreased and the absorption peak shifted slightly toward shorter wavelength. Then, the films were aged at 150°C for 1 h. Usually, the absorption intensity increases due

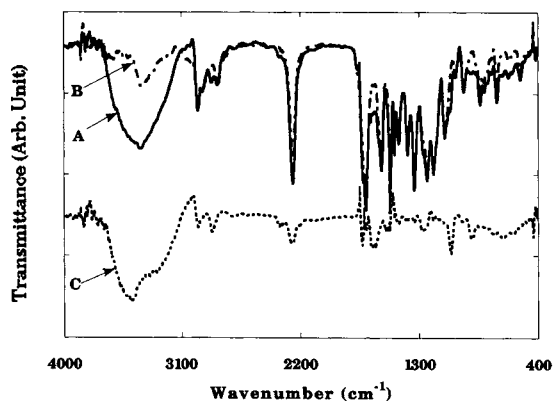


**Figure 3** UV-VIS spectra of unpoled, poled, and aged film of the crosslinked copolymer.

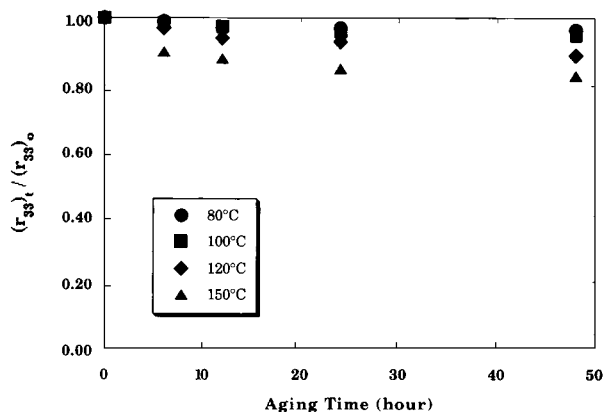
to randomization of dipolar molecules when aged at high temperature. The film with crosslinking agent showed no change of absorption intensity. Additionally, the solubility of the film was totally different from that before poling. We believe that the dipolar alignment to poling direction was completely locked up and the stability was quite good up to 150°C. Additionally, it was thought that the copolymer system did not degrade throughout the whole period of aging.

The FT-IR spectra showed that the crosslinking reaction between the isocyanate and hydroxyl group in the HPMI occurred. We recorded the FT-IR spectra before curing and after curing at 110°C. We also introduced the difference spectrum of the above two spectra. The IR peaks at 2270  $\text{cm}^{-1}$  from isocyanate and 3500  $\text{cm}^{-1}$  from hydroxyl group decreased after curing (see Fig. 4). This indicates the partial crosslinking reaction occurred through the isocyanate group and the hydroxyl group to form carbamate linkage between the side chains in *p*-hydroxyphenyl maleimide.

Similar to the copolymer film without crosslinker, the EO coefficient,  $r_{33}$  of the crosslinked polymer was observed around 25–30 pm/V, which depends on the poling field. In an attempt to investigate the temporal stabilities of the films with crosslinker, we aged the sample at elevated temperatures. Since the temporal stability of NLO activity should be considered to extend the period for device application, we performed the accelerating aging test at various high temperatures. Aging temperatures were selected 80, 100, 120, and 150°C. We traced the decay of  $r_{33}$  over 48 h at each temperature. The pure copolymer film showed 80% of the initial value of  $r_{33}$  after 2 day aging at 80°C whereas the crosslinked film



**Figure 4** FT-IR spectra of the copolymer with crosslinking agent. (A) Before curing, (B) after curing, (C) difference spectrum.



**Figure 5** Decay of  $r_{33}$  of the crosslinked copolymer under various temperatures.

maintains its  $r_{33}$  up to 98% of initial signal over the same period. The crosslinked copolymer showed quite outstanding temporal stability at 80°C compared to the copolymer itself. The crosslinked samples aged at 100°C, and 120°C for 48 h showed 95 and 90% of the initial EO signal, respectively. Even after 48 h at 150°C, 80% of the residual signal remained (see Fig. 5).

We finally compared our  $r_{33}$ ,  $d_{33}$ , and temporal stability of our crosslinked copolymer with those of known NLO polymers. The absolute second-order NLO coefficient is relatively high, however, the value can be varied under the different poling condition. The temporal stability itself at a high temperature was observed better than the others in our crosslinked copolymer.<sup>12,21–23</sup>

We observed good thermal stability of the second-order NLO properties up to 150°C using the highly crosslinked maleimide copolymer without degradation of the NLO chromophores.

## CONCLUSION

Thermally stable maleimide copolymer containing NLO chromophore in the side chain was synthesized and characterized. The polymer is thermoplastic in nature and can be crosslinked adding a crosslinking agent. We measured the linear EO coefficient of 25–30 pm/V at 632 nm and second-order NLO coefficient,  $d_{33}$  of 14 pm/V at 1064 nm. Due to the robust maleimide unit in the copolymer, the copolymer showed a good thermal stability of the EO activity at 80°C. In addition, we could prepare a crosslinked copolymer through a reaction between the side chains themselves. Thermal crosslink reaction further improved temporal stability of NLO activity.

The poling efficiency, hence the resulting second-order NLO activity, the film forming properties, and the temporal stability of poling-induced orientation of these copolymers, can be largely enhanced by our synthetic strategy.

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