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## Thermally Stable Polymaleimide and Poly[maleimide-*co*-(methyl methacrylate)] Containing N-(4-Nitrophenyl)-L-prolinol Units for Second-order Nonlinear Optics

Ji Young Chang*, Chang Wuk Yeo, Man Jung Han, Dong Hoon Choi†, Soo Young Park†, and Nakjoong Kim†

*Department of Applied Chemistry, Ajou University, Suwon 441-749, Korea*
*†Frontier Polymer Laboratory, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 131-650, Korea*

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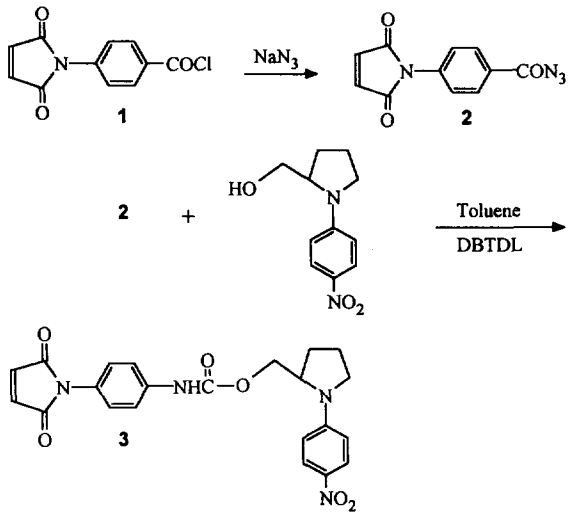
Side chain polymers with nonlinear optical properties have been intensively studied in recent years as potential candidates for application in electro-optic (EO) and photonic devices.[1-3] Ease of processability, high damage threshold, fast response, and large nonlinear optical (NLO) coefficients are the advantages to utilize them in NLO devices such as frequency doubler, light modulators, and logic gates. A number of new polymers and the related fabrication technology to realize the practical NLO devices have been developed so far. However, the fast relaxation of the poled dipolar alignment of the NLO chromophores is still a problem with these second-order NLO polymers and recent research efforts are more concentrated on the enhancement of the thermal stability.

In this work, we prepared N-phenyl maleimide coupled with N-(4-nitrophenyl)-L-prolinol (NPP) through a urethane linkage as a monomer (**3**). Monomer **3** was polymerized and copolymerized with methylmethacrylate (MMA). The polymers of N-phenyl maleimide and its derivatives have been known to exhibit high glass transition temperatures ($T_g$) due to the rigid imide rings in the backbones.[4,5] In addition to their inherent backbone rigidity, the polymers of monomer **3** possess urethane bonds, which would promote interactions between the polymer chains or the side chain chromophores through inter- or intramolecular hydrogen bondings, and therefore were expected to show a great enhancement of thermal stability of EO activity.

This synthesis of monomer **3** was carried out according to Scheme 1. Compound **1** was prepared by following the procedures in the literature.[6] To a solution of compound **1** (2.08 g, 8.8 mmol) in methylene chloride (35 mL) was added dropwise a solution of sodium azide (0.72 g, 10 mmol) in




**Scheme 1.**

water (25 mL) at 0℃. After stirring for 4h at the same temperature, the solution was washed with ice water three times and then dried over anhydrous $MgSO_4$. After filtration and evaporation, the product was isolated by column chromatography on silica gel (methylene chloride) to give N-(4-azidocarbonylphenyl)maleimide (**2**), mp. 120-121℃ (43% yield).[7] The azide of the acid is known to decompose thermally to the corresponding isocyanato compound. A solution of compound **2** (5 g, 20.6 mmol) and NPP (4 g, 18.0 mmol) in toluene (150 mL) was refluxed for 48h in the presence of dibutyltin dilaurate (DBTDL) (0.1 mL). In the reaction, the isocyanato compound formed was not isolated and subjected to react *in situ* with NPP. The precipitates were collected by filtration and purified by recrystallization from methanol to yield monomer **3**, mp 201-202℃ (46% yield).[7]

A mixture of monomer **3** (0.2 g, 0.5 mmol) and AIBN (1.6 mg) in N,N-dimethylformamide (DMF) (0.35 mL) was charged into a polymerization tube (5 mL). After freeze-thaw treatments under nitrogen, the tube was sealed. The polymerization was carried out at 80℃ for 24h. The resulting polymer was isolated by precipitation into methylene chloride and purified by reprecipitation from DMF into methylene chloride twice (76% yield). The copolymer was obtained in a similar manner. From monomer **3** (0.2 g, 0.46 mmol) and MMA (0.05 mL, 0.46 mmol) was obtained 0.12 g of the polymer (48% yield). The mole ratio of MMA units to maleimide units in the copolymer was determined to be 65 : 35 by $^1$H-NMR spectroscopy.[8]

Intrinsic viscosities of the homopolymer and the copolymer were measured in DMF at 30℃ to be 0.14 and 0.20 dL/g, respectively.

DSC thermograms were recorded under nitrogen atmosphere in order to investigate the glass transition temperature ($T_g$) of each polymer. In the case of the copolymer, very weak transition was observed around 160-163℃. The homopolymer did not show any distinctive transition below 250℃.

The filtered polymer solutions in dimethylformamide were spincoated at 1500 rpm onto indium tin oxide glass and dried overnight in a vacuum oven to give optically transparent films. The films were poled using the corona poling technique in a wire-plane geometry.[9,10] During poling, the polymer films

**Table 1.** Measured $r_{33}$ Values of the Polymers

| Polymer | $T_g$ (℃)[b] | Absorption maximum (nm)[c] | Cut off wavelength (nm) | $r_{33}$ (pm/V)[d] |
|---|---|---|---|---|
| Copolymer[a] | 162 | 390 | 500 | 10.6[e] |
| Homopolymer | – | 393 | 540 | 11.6[f] |

[a]Mole ratio of MMA to maleimide units was 65 : 35; [b]Measured by Perkin Elmer 7 DSC on the second run; [c]UV spectra were recorded on a Shimazu UV 240 spectrometer; [d]Measured by using the simple reflection method; [e]Poling temperature, 160℃; Corona electric field, 5 kV; [f]Poling temperature, 160℃; Corona electric field, 6 kV.

were heated to 160℃ and kept for 10 min. Subsequently, the samples were slowly cooled down to room temperature in the presence of the applied electric field.

In order to investigate the extent of molecular orientation under poling process, UV-VIS spectra of the poled and the unpoled films were compared. The thin film (about 1 μm thickness) was fabricated on the borosilicate glass. The absorption maximum of the copolymer was observed around 390 nm with a cutoff (100% transmission) at 500 nm prior to poling. In the case of the homopolymer, the absorption maximum appeared around 393 nm and the cutoff was at about 540 nm. After poling, the intensities of absorption maxima decreased by about 15% in accord with a general tendency.[11] Then, the linear electro-optic coefficient, $r_{33}$ was measured by a simple reflection technique.

The EO coefficient, $r_{33}$ was calculated from the difference of the phase retardation in transverse electric and transverse magnetic mode. The nonresonant linear EO coefficients, $r_{33}$ values were found to be in excess of 10 pm/V when measured at 632.8 nm. Overall data for two polymer samples are given in Table 1.

The long term stability and thermal stability for poled polymers are of critical importance for all nonlinear optical device applications. We examined the relaxation behavior of the EO coefficient, $r_{33}$ with the variation of time at 80℃ (Figure 1). The homopolymer showed the excellent thermal stability of the EO coefficient, which retained 85% of its original value when aged at 80℃ for 200 min. In copolymer, the NLO chromophores are much diluted with MMA to minimize the side chain interaction. The EO coefficient, $r_{33}$ of the copolymer was 52% of its original value after 200 min at 80℃. At room temperature, no decay of $r_{33}$ values of two polymers was observed over the period of 1 month. For comparison, the thermal relaxation behavior of guest-host polymer system [10 wt% NPP doped polymethylmethacrylate (PMMA)] is also plotted in Figure 1. Even after 10 min at 80℃, the EO signal decay rapidly. After 20 min annealing, the EO signal falls to almost zero, indicating that the molecular alignment of the poled film was completely disrupted at the vicinity of the $T_g$ of PMMA.

In summary, we have synthesized a new class of second-order NLO maleimide polymers and studied their linear EO properties. The fairly large EO coefficients, $r_{33}$ values were observed ranging from 10-11 pm/V at 632.8 nm wavelength. We also observed the much improved thermal stabilities of the dipolar alignment in these polymers.

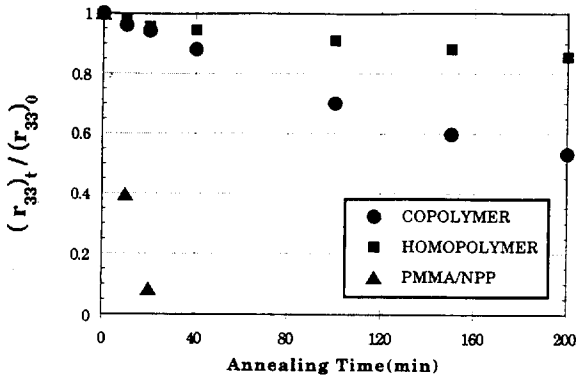



**Figure 1.** Relaxation behavior of $r_{33}$ of the polymers at 80℃.

We are now pursuing the synthesis of new chromophores with high molecular hyperpolarizability (β) followed by anchoring to maleimide polymer backbone.

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7. Compounds **2** and **3** were identified by elemental analysis and $^1$H-MMR spectroscopy. Compound **2**: Anal. Calcd for $C_{11}H_6N_4O_3$: C, 54.55; H, 2.50; N, 23.13. Found: C, 54.50; H, 2.44; N, 23.10. $^1$H-NMR (200 MHz, DMSO-$d_6$) δ (ppm)=7.25 (s, 2H, vinyl protons), 7.60 and 8.10 (dd, 4H, phenyl protons). Compound **3**: Anal. Calcd for $C_{22}H_{20}N_4O_6$: C, 60.55; H, 4.62; N, 12.84. Found: C, 60.40; H, 4.58; N, 12.70. $^1$H-NMR (200 MHz, DMSO-$d_6$) δ (ppm)= 9.90 (s, 1H, NH), 8.10, 7.60, 7.27 and 6.85 (4d, 8H, phenyl protons), 7.20 (s, 2H, vinyl protons), 4.30 (m, 2H, $OCH_2$), 4.05 (m, 1H, CH), 3.60 and 3.30 (m, 2H, $NCH_2$), 2.10 (m, 4H, $CH_2CH_2$).
8. In the $^1$H-NMR spectrum of the homopolymer (DMSO-$d_6$), a broad peak corresponding to the polymer backbone protons (CHCH) appeared at 3.7-4.5 ppm, which were overlapped with other peaks. The peaks for the other protons were observed at almost same positions as the peaks for the relevant protons of the monomer. In the $^1$H-NMR spectrum of the copolymer (DMSO-$d_6$), the peaks from MMA units appeared at 3.6 ppm ($OCH_3$), 1.7-2.1 ppm ($CH_2$), and 0.7-1.6 ppm ($CCH_3$). The peaks from maleimide units were observed at the same posi-

tions as those of the homopolymers. In the IR spectrum of the copolymer (film), the strong bands around 1718 $cm^{-1}$ (C=O stretching of ester and imide groups), 1670 $cm^{-1}$ (C=O stretching of urethane groups), 1600 $cm^{-1}$ (benzene rings), and 1518 $cm^{-1}$ (nitro groups) were observed.

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