

Figure 3. Temporal stability of the electro-optic coefficient of polymer **2** stored at 100 °C.

It means that the temporal stability of electro-optic coefficient of the copolymers was improved due to the formation of a crosslinked network.

Conclusion

We synthesized new self-crosslinkable NLO side-chain copolymers. The copolymers were soluble in common organic solvents and exhibited suitable T_g 's, around 140 °C, to be poled under a moderate condition. EO polymer with highly oriented dipolar alignment was obtained by corona

poling. Since carboxylic acid, a functional group for the crosslinking, in the copolymer was blocked with 3,4-dihydro-2H-pyran, it was thought that the possibility of the formation of crosslinking during poling decreased. The temporal stability of the electro-optic coefficients of the copolymers were improved due to the crosslinked network, which was successfully obtained by the thermal treatment.

References

1. Prasad, P. N.; Williams, D. J. In *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, U. S. A., 1991.
2. Prasad, P. N.; Ulrich, D. R. In *Nonlinear Optical and Electroactive Polymers*; Plenum Press: New York, U. S. A., 1988.
3. Hampsh, H. L.; Yang, J.; Wongand, G. K.; Torkelson, J. M. *Macromolecules* **1988**, *21*, 526.
4. Williams, D. J. In *Nonlinear Optical Properties of Organic and Polymeric Materials*; ACS Sym. Ser. 233, 1983.
5. Chemla, D. S.; Zyss, J. In *Nonlinear Optical Properties of Organic molecules and Crystals*; Academic Press: Orlando, U. S. A., 1987.
6. Becker, M. W.; Sapochak, L. S.; Ghosen, R.; Xu, C.; Dalton, L. R. *Chem. Mater.* **1994**, *6*, 104.
7. Morgan, R. J. In *Advances in Polymer Science*; Springer-Verlag: Berlin, 1985; p. 72.
8. Hubbard, M. A.; Minami, N.; Ye, C. T.; Marks, J.; Yang, J.; Wong, G. K. *SPIE Proc. Nonlinear Opt. Mat.* **1988**, *971*, 136.
9. USP 4,808,332, 1989.
10. Teng, C. C.; Mann, H. T. *Appl. Phys. Lett.* **1990**, *56*, 30.

Thermally Crosslinkable Second-Order Nonlinear Optical Polymer Using Pentaerythritol tetrakis(2-mercaptoacetate) as Crosslinker

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Two kinds of second-order nonlinear optical copolymers were prepared by the copolymerization of the vinyl monomers containing NLO chromophore, methacrylic acid, and methyl methacrylate or butyl methacrylate. Glass transition temperatures (T_g) of copolymers were around 130 °C. The copolymers were soluble in common organic solvents such as tetrahydrofuran (THF), cyclohexanone, and N,N-dimethylformamide (DMF). The crosslinked copolymer was obtained by thermal treatment using pentaerythritol tetrakis(2-mercaptoacetate) as a crosslinker and became insoluble in tetrahydrofuran (THF) and N,N-dimethylformamide (DMF). Poling was carried out at 120 °C for 20 min and identified with UV-Vis spectroscopy. Electro-optic coefficient (r_{33}) measurement showed a value of 35 pm/V for polymer **2** at 633 nm. Temporal stability of copolymers was improved owing to the crosslinked network, which was successfully obtained at 170 °C for 30 min after poling.

Introduction

Second-order organic nonlinear optical (NLO) polymers

are of great interest for application in integrated optical devices such as electro-optic (EO) switches, modulators and frequency doublers partially due to low cost and ease of

processing compared with inorganic material such as LiNbO_3 .¹⁻⁴ Although these materials have potential advantages for second harmonic generation and electro-optical application, there are some problems that should be overcome for practical devices. One of the critical problems in the developments of second-order NLO polymers is to stabilize the electrically-induced dipole alignment, especially at elevated device working temperature.⁵ One approach for solving this problem is the formation of a crosslinked network (thermally or photochemically) during or after poling.⁶⁻⁸ Various thermally crosslinkable NLO polymers have been reported using the crosslinking reactions via epoxy or urethane chemistry. Although these systems led to an improvement of temporal stability of dipolar alignment, it is expected that these NLO polymers show strong absorption at 1.3 μm and 1.5 μm which are used in the commercial telecommunication due to O-H and N-H bonds. Since it is reported that S-H bond has no absorption at 1.3 μm and 1.5 μm ,⁹ usage of crosslinker containing thiol group may yield thermally curable NLO polymers with improved temporal stability without sacrificing the optical properties for practical applications.

In this study, we demonstrated the novel approach to designing NLO polymers that exhibit good temporal stability using thiol compound as crosslinker, and investigated the related properties. Vinyl monomer containing NLO active chromophore and methacrylic acid, in which acrylic acid moiety would be reacted with thiol group to form crosslinked network, were used as comonomers. Glass transition temperature (T_g) of the NLO copolymer was controlled by copolymerization of methyl methacrylate or butyl methacrylate with vinyl monomer containing NLO active chromophore and methacrylic acid to enhance the poling efficiency.

Experimental

Synthesis of monomers

4-[(2-Methacryloxyethyl)ethylamino]-4'-nitroazobenzene¹⁰. 8 g (25 mmol) of 4-[(2-hydroxyethyl)ethylamino]-4'-nitroazobenzene, 100 mL of dry tetrahydrofuran (THF), and 2.53 g (25 mmol) of triethylamine were added to a 250 mL, three-necked flask equipped with a reflux condenser, addition funnel, and nitrogen gas inlet. The THF solution containing 5.3 g (50 mmol) of methacryloyl chloride was then slowly introduced to the reactor through a dropping funnel with string. The reaction mixture was stirred for 3 h at 50 °C. After cooling to room temperature, the reaction mixture was poured into excess water and extracted with diethyl ether 3 times (3×100 mL). The organic phase was washed with saturated aqueous sodium chloride solution and water and then dried over magnesium sulfate. Diethyl ether was removed under reduced pressure and the resulting solid was recrystallized from hexane. This solid was further purified by column chromatography using dichloromethane as eluent (mp 73-76 °C, 70%).

¹H NMR (CDCl_3 , 200 MHz, ppm, J in Hz): 1.25 (t, 3H, $J=7.0$); 1.92 (s, 3H); 3.54 (q, 2H, $J=7.0$); 3.73 (t, 2H, $J=6.0$); 4.36 (q, 2H, $J=6.0$); 5.58 (s, 1H); 6.09 (s, 1H); 6.82 (d, 2H, $J=9.0$); 7.93 (d, 4H, $J=9.0$); 8.3 (d, 2H, $J=9.0$). 4-[(2-Methacryloxyethyl)methylamino]-4'-nitrostilbene was also synthesized from the reaction of 4-[(2-hydroxyethyl)methylamino]-4'-nitrostilbene with methacryloyl chloride as shown in

above manner.

Copolymerization

The monomers containing NLO chromophore were copolymerized with methacrylic acid and butyl methacrylate or methyl methacrylate via free radical copolymerization. 2 mmol of the monomer containing NLO chromophore, 1 mmol of butyl methacrylate or methyl methacrylate, 1 mmol of methacrylic acid and azobisisobutyronitrile (AIBN) (0.65 wt.% to monomer) were dissolved in NMP (500 wt.% to monomer) in the ampoule. The solution was freeze-degassed-thawed at least 3 cycles to remove any traces of oxygen and sealed off using a hand torch. The copolymerization was carried out at 65 °C for 48 h. The resulting solution was poured into methanol and the precipitate was filtered and washed with methanol to obtain the pure copolymer. The copolymer was then dried under reduced pressure at 60 °C for 48 h.

Film preparation, poling, and curing

A tetrahydrofuran (THF) (1 mL) solution of copolymer (0.1 g) and pentaerythritol tetrakis(2-mercaptoacetate) (PTMA) (0.01 g) was spread onto either indium tin oxide (ITO) pre-coated glass or microslide glass and was spin-coated at 1500 rpm. The spin-coated film was dried under vacuum at 60 °C for 48 h.

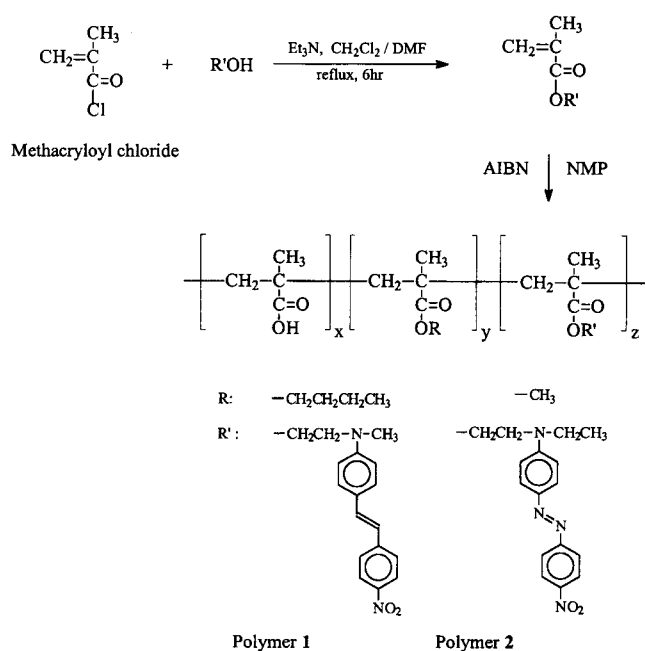
The alignment of the NLO chromophore was achieved by corona poling method. The 6 kV of corona voltage was applied as the temperature was raised to 120 °C and held at this temperature for 20 min. The film was then cooled to room temperature before the corona field was removed. For the crosslinking, the temperature was increased to 170 °C and maintained for 30 min with the corona voltage on. The sample was then cooled to room temperature without removing the field.

Measurements

IR spectra were recorded on a Midac FT-IR spectrophotometer. A Varian Gemini 200 was used for ¹H NMR measurements. A Jasco V-530 spectrophotometer was used for ultraviolet-visible (UV-Vis) measurements. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer DSC 7 at a heating rate of 10 °C/min to obtain the glass transition temperature (T_g) of the copolymers. The molecular weights and molecular weight distributions of the copolymers were measured by Waters 490 gel permeation chromatography (GPC) using polystyrene as a standard. The electro-optic coefficients, r_{33} of the corona poled film were measured by simple reflection technique proposed by Teng *et al.*¹¹ To identify the temporal stability of r_{33} of the crosslinked films, the change of r_{33} with time was monitored at 100 °C.

Results and Discussion

The most critical consideration in the development of NLO polymers for actual device applications is the stabilization of the electrically-induced dipole alignment, especially at the elevated temperature. It is reported that the gradual decay of electro-optic coefficient occurs from the thermal relaxation of the non-centrosymmetric dipolar alignment.



Scheme 1. Syntheses of monomers and copolymers.

Table 1. Characterization of copolymers

	Composition ^a (mol.%)			Molecular weight ^b (g/mole)			Yield (%)	T _g ^c (°C)
	x	y	z	M _n × 10 ⁻³	M _w × 10 ⁻³	M _w /M _n		
Polymer 1	26	30	44	5.9	13.6	2.3	65	130
Polymer 2	23	39	38	6.1	18.6	3.1	46	127

^a Determined by ¹H NMR. ^b Determined by GPC using polystyrenes as standard. ^c Determined by DSC (heating rate 10 °C/min.).

Generally, there are two approaches to improve the temporal stability of the NLO polymers. One is to use crosslinking (thermally or photochemically) method and the other is to use high glass transition temperature (T_g) matrix such as polyimides. The high T_g polymer matrix may lead to the deterioration of NLO properties due to the thermal decomposition of the chromophore during poling, however. The decrease in NLO properties and strong absorption at 1.3 μm and 1.5 μm, which are used in the commercial telecommunication, may occur in crosslinking system using epoxy or urethane chemistry due to occurrence of crosslinking during poling, and formation of hydroxy or amide bond after crosslinking reaction. In this respect, we tried to use pentaerythritol tetrakis(2-mercaptoacetate) (PTMA) as a crosslinker because S-H bond has no absorption at wavelengths mentioned above. In addition, methyl methacrylate or butyl methacrylate was used as a comonomer to control T_g of the NLO polymer.

The vinyl monomers containing NLO chromophore were synthesized and copolymerized with methacrylic acid and butyl methacrylate or methyl methacrylate according to Scheme 1. The yield of polymer 1 and 2 was 46 and 65%, respectively. The resulting copolymers exhibited good solubility in common organic solvents such as tetrahydrofuran (THF), acetone, and cyclohexanone. The NLO chromophore contents, molecular weights, and glass transition temper-

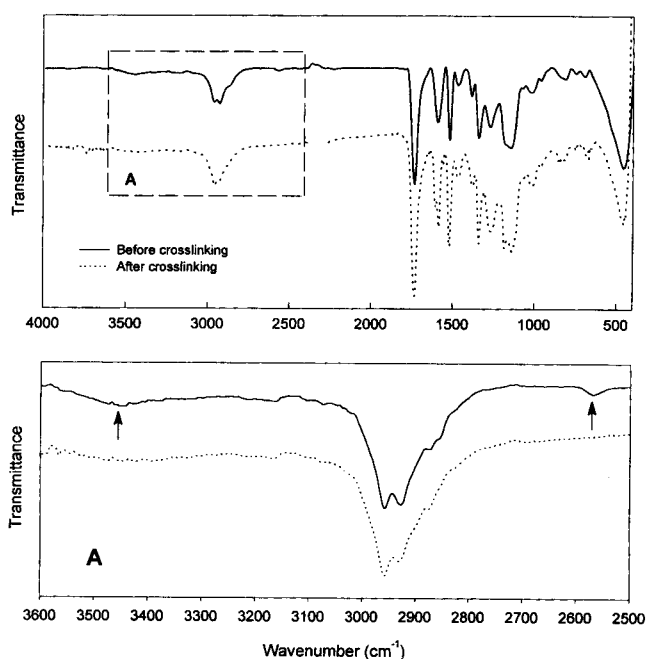
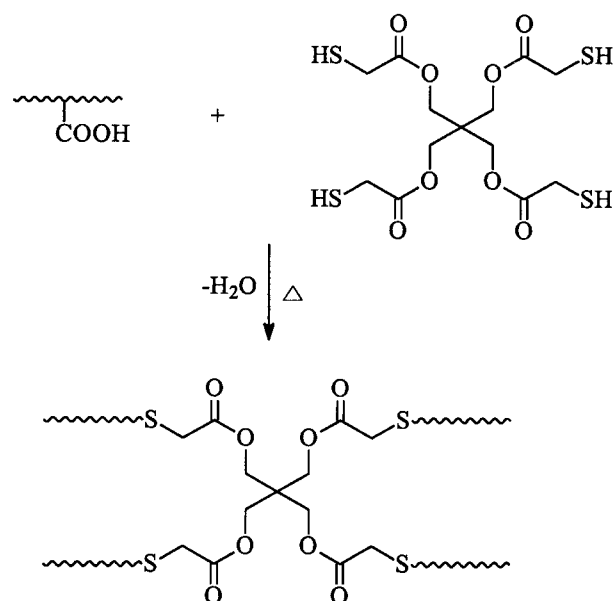


Figure 1. IR spectra of polymer 2 before and after crosslinking.

atures (T_g) of the copolymers were summarized in Table 1. Determination of T_g would give useful information for poling temperature of the thin film. T_g's of copolymers were observed at 127-130 °C by DSC analysis. From the result, we poled the copolymer films at 120 °C for 20 min. The NLO active chromophore would not be decomposed at this temperature. Molecular weights of the copolymers were good enough for film casting and PTMA was miscible with the copolymer solutions.

For the thermal crosslinking, the poled film containing crosslinker, PTMA, was heated to 170 °C, at which the crosslinking network was formed and the chromophore was not decomposed, with 6 kV of corona field applied. Thus, the formation of molecular alignment and networks were



Scheme 2. Crosslinking formation.

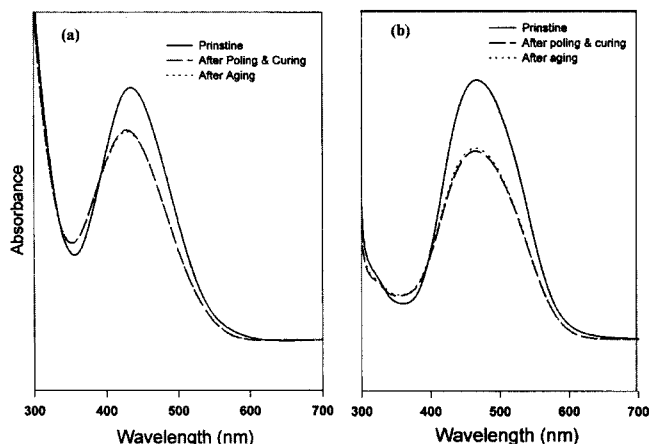


Figure 2. UV-Vis spectra of polymer 1 (a) and 2 (b) after poling, curing, and aging.

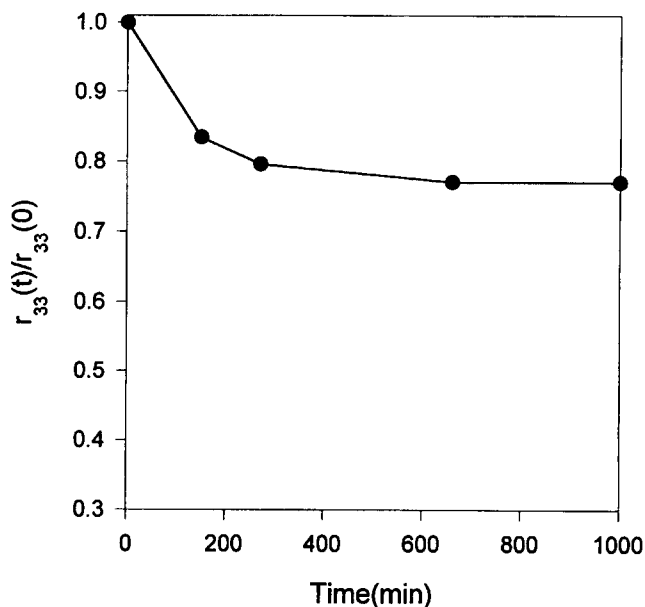


Figure 3. Temporal stability of the electro-optic coefficient of polymer 2 stored at 100 °C.

achieved in these procedures. IR spectra of polymer 2 before and after crosslinking are illustrated in Figure 1. O-H stretching peak in carboxylic acid in copolymer backbone and S-H stretching peak in PMTA were appeared at 3500 cm^{-1} and 2570 cm^{-1} , respectively. These peaks were disappeared after crosslinking, indicating that the network in copolymer was formed by the reaction of carboxylic acid with thiol group as shown in Scheme 2. The cured films were insoluble in common organic solvents such as tetrahydrofuran (THF) and N,N-dimethylformamide (DMF). UV-Vis spectra of polymer 1 and 2 after poling, curing, and aging were shown in Figure 2. The absorption intensity of unpoled films was decreased with poling due to molecular

alignment in the direction of the poling field and this decreased absorption intensity was not changed at 100 °C for 1 h after curing. The absorption intensity of uncured, poled films was increased after the aging test at 100 °C for 1 h, however. It means that the molecular dipole in NLO polymer was not disarranged at high temperature due to the crosslinked network, which was successfully achieved by reaction of carboxylic acids in copolymer and thiol functional group in crosslinker.

The r_{33} value of polymer 2 was measured to be 35 pm/V at 633 nm. To identify the temporal stability of r_{33} value of the respective film, we measured the ratio of $(r_{33})_t$ to $(r_{33})_0$ according to time for polymer 2 and showed the result in Figure 3. The ratio was maintained to ca. 80%, meaning that the temporal stability of copolymers was improved due to the formation of a crosslinking network.

Conclusion

We synthesized a new NLO side-chain copolymer in which pentaerythritol tetrakis(2-mercaptoacetate) could crosslink each backbone by thermal treatment. The copolymers have a suitable T_g to be poled under a moderate condition and are soluble in common solvents. After poling, the crosslinked network in copolymer containing the crosslinker was successfully obtained by thermal treatment and yield good temporal stability.

References

1. Prasad, P. N.; Williams, D. J. In *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, U. S. A., 1991.
2. Prasad, P. N.; Ulrich, D. R. In *Nonlinear Optical and Electroactive Polymers*; Plenum Press: New York, U. S. A., 1988.
3. Williams, D. J. In *Nonlinear Optical Properties of Organic and Polymeric Materials*; ACS Sym. Ser. 233, 1983.
4. Chemla, D. S.; Zyss, J. In *Nonlinear Optical Properties of Organic molecules and Crystals*; Academic Press: Orlando, U. S. A., 1987.
5. Becker, M. W.; Sapochak, L. S.; Ghosen, R.; Xu, C.; Dalton, L. R. *Chem. Mater.* **1994**, *6*, 104.
6. Morgan, R. J. In *Advances in Polymer Science*; Springer-Verlag: Berlin, 1985; p 72.
7. Hubbard, M. A.; Minami, N.; Ye, C. T.; Marks, J.; Yang, J.; Wong, G. K. *SPIE Proc. Nonlinear Opt. Mat.* **1988**, *971*, 136.
8. Chen, M.; Dalton, L. R.; Xu, L. P.; Shi, X. Q.; Steier, W. H. *Macromolecules* **1992**, *25*, 4032.
9. Wheeler, O. H. *Chem. Rev.* **1954**, *59*, 629.
10. USP 4,808,332 1989.
11. Teng, C. C.; Mann, H. T. *Appl. Phys. Lett.* **1990**, *56*, 30.