

Self-Crosslinkable Side-Chain Copolymer for Nonlinear Optical Application

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2-Tetrahydropyranyl methacrylate with a self-crosslinkable moiety was copolymerized with methyl methacrylate and 4-[(2-methacryloxyethyl)methylamino]-4'-nitrostilbene or 4-[(2-methacryloxyethyl)ethylamino]-4'-nitroazobenzene to provide second-order nonlinear optical property. Glass transition temperatures (T_g) of the copolymers are around 140 °C. The copolymers were soluble in common organic solvents such as tetrahydrofuran (THF), cyclohexanone, and N,N-dimethylformamide (DMF). Poling was carried out at 140 °C for 20 min and identified with UV-Vis spectroscopy. Electro-optic coefficient (r_{33}) of copolymer was 62 pm/V for polymer 2 at 633 nm, and relaxation did not remarkably occur due to the formation of a crosslinked network at 200 °C for 15 min.

Introduction

There have been considerable interests and researches on the second-order nonlinear optical (NLO) polymers because they have potential advantages for electro-optic and photonic applications.^{1,2} The most critical consideration in the developments of NLO polymers for actual device applications is the stabilization of the electrically-induced dipole alignment, especially at elevated temperature. It was reported that the gradual decay of electro-optic coefficient occurs by the thermal relaxation of the non-centrosymmetric dipolar structure.³ Generally, there are two approaches to improve the temporal stability of the NLO polymers. One is to use crosslinking (thermally or photochemically) method^{4,5} and the other is to use high glass transition temperature (T_g) matrix polymers such as polyimides and polyquinolines.^{6,7} Polyimides have been widely used to prepare NLO polymers which are thermally stable at elevated device working temperature (60-125 °C). However, high T_g may give rise to the deterioration of NLO properties due to thermal decomposition of the chromophore during the poling process. In this respect, crosslinking method would be better suited for high degree of dipolar orientation and its stability, if crosslinking reaction could occur after the orientation at lower temperature.

In this study, our goal was to prepare NLO active copolymer with good thermal stability and high degree of dipolar orientation, and with good processibility. We demonstrate the novel thermal crosslinking system using 2-tetrahydropyranyl methacrylate. Pyran moiety, which has been utilized in a deep-UV photoresist chemistry for micro-lithography, was used for blocking a crosslinkable moiety in order to suppress efficiently the crosslinking reaction during poling. The approach used herein was to synthesize self-crosslinkable, NLO active side-chain copolymers and estimate the electro-optical and temporal stability of the copolymers.

Experimental

Synthesis of Monomers

2-Tetrahydropyranyl Methacrylate⁸. 12.5 mL of 3, 4-dihydro-2H-pyran and 2 drops of 50% sulfuric acid were

added to a 250 mL, four-necked flask equipped with a reflux condenser, addition funnel, thermocouple well, and nitrogen gas inlet. The mixture containing 11.6 mL of methacrylic acid, 12.5 mL of 3,4-dihydro-2H-pyran, and 1g of phenothiazine was then introduced to the reactor through a dropping funnel. The reaction temperature was increased to 80 °C and maintained at 50 °C for 25 h. After cooling to room temperature, 2 g of solid sodium bicarbonate and 8 g of anhydrous sodium sulfate were added. After stirring, the mixture was filtered. The filtrate was treated with 0.1 g of calcium hydride, and the excess dihydropyran was removed under reduced pressure. After addition of another 0.5 g of calcium hydride, 1 g of phenothiazine, and 0.2 g of 2,2-diphenyl-1-picrylhydrazyl, double distillation yielded 16.5 g of 2-tetrahydropyranyl methacrylate [bp 67 °C (0.35 Torr), 71%]. ¹H NMR (CDCl₃, 200 MHz, ppm, *J* in Hz): 1.56-1.9 (m, 6H, CH₂); 1.97 (m, *J*=1, 3H, CH₃); 3.71 and 3.93 (m, 2H, CH₂O); 5.62 (m, 1H, =CH); 6.05 (dd, *J*=3.0 and 2.75, 1H, OCHO); 6.18 (m, 1H, =CH).

4-[(2-Methacryloxyethyl)ethylamino]-4'-nitroazobenzene⁹. 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 (CDCl₃, 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

2 mmol of the monomer containing NLO chromophore, 1 mmol of methyl methacrylate, 1 mmol of 2-tetrahydropyranyl methacrylate and azobisisobutyronitrile (AIBN) (0.65 wt.% to monomer) were dissolved in NMP (500 wt.% to monomer) in an ampoule. In order to remove any traces of oxygen, the mixed solution was freeze-thawed at least 3 cycles and then 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 eliminate the residual monomer and AIBN. The copolymer was then dried under reduced pressure at 60 °C for 48 h.

Film preparation, poling, and curing

0.1 g of copolymer was dissolved in 1 mL of tetrahydrofuran (THF). After filtered through 0.2 μm Teflon filter, the solution was spread onto either indium tin oxide (ITO) pre-coated glass or microslide glass and spin-coated at 1500 rpm. Films were dried *in vacuo* at 60 °C for 48 h.

The alignment of the NLO chromophore in the copolymers was achieved by corona poling method. 6 kV of corona voltage was applied as the temperature was raised to 140 °C and held at this temperature for 20 min. The sample was then cooled to room temperature with the corona voltage applied. For thermal crosslinking, the film was heated to 200 °C and maintained for 15 min at this temperature, and then cooled to room temperature with the corona voltage applied.

Measurements

A Midac FT-IR spectrophotometer and Varian Gemini 200 were used to analyze the chemical structures and compositions of the copolymers. The glass transition temperature (T_g) of the copolymers was obtained on a Perkin-Elmer DSC7 at a heating rate of 10 °C/min under nitrogen atmosphere. A Jasco V-530 spectrophotometer was used for ultraviolet-visible (UV-Vis) measurements. The molecular weights and molecular weight distributions of the copolymers were measured by Waters 490 gel permeation chromatography (GPC) using polystyrenes as a standard. The electro-optic coefficient, r_{33} , of the corona poled film was measured by simple reflection technique proposed by Teng *et al.*¹⁰

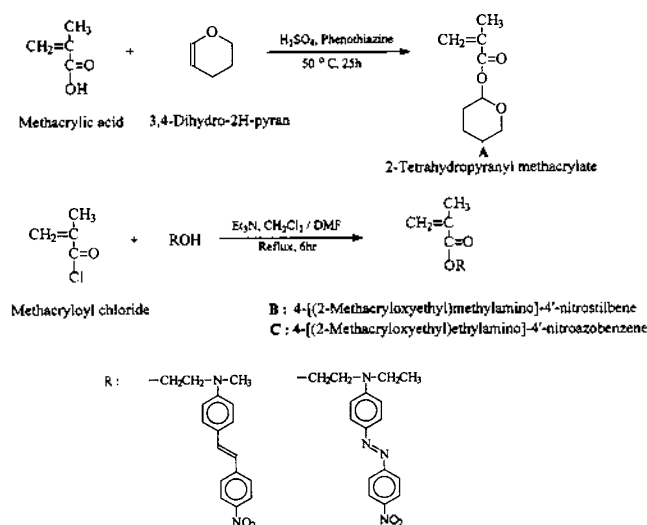
Temporal stability of r_{33} of the crosslinked films was investigated at 100 °C to monitor the variation of r_{33} with elapsed time.

Results and Discussion

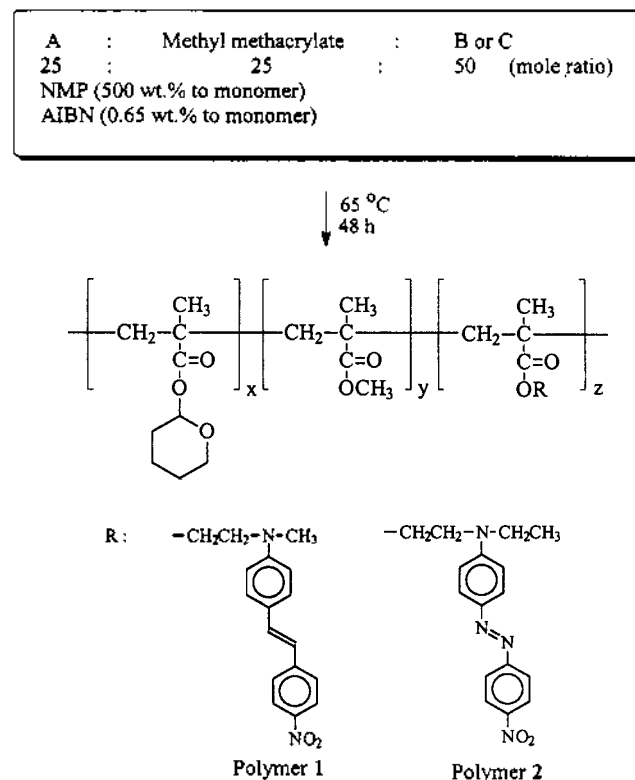
In order to enhance temporal stability, high T_g polymer such as polyimide has been used as NLO polymer backbone.⁶ In this system, a low level of molecular alignment is expected owing to the thermal decomposition of the NLO chromophore during the poling process. To overcome this problem, we have used the inter-chain reaction, namely crosslinking reaction, between polymer chains to increase the T_g of polymer after poling. Because the crosslinking reaction may occur during poling, which leads to the de-

crease of poling efficiency, carboxylic acid moiety, the cross-linking part, was blocked by 3,4-dihydro-2H-pyran. Pyran moiety is decomposed at *ca.* 200 °C to generate carboxylic acid, a pendant group on the copolymer backbone. Elevated temperature may induce crosslinking by inter-molecular anhydride formation. T_g 's of the NLO copolymers used in this study were selected below 200 °C because the poling temperature should be under the pyran decomposition temperature.

The vinyl monomers containing NLO chromophore and self-crosslinkable moiety were synthesized as shown in Scheme 1. 4-[(2-Methacryloxyethyl)methylamino]-4'-nitrostil-



Scheme 1. Monomer syntheses.



Scheme 2. Polymer syntheses.

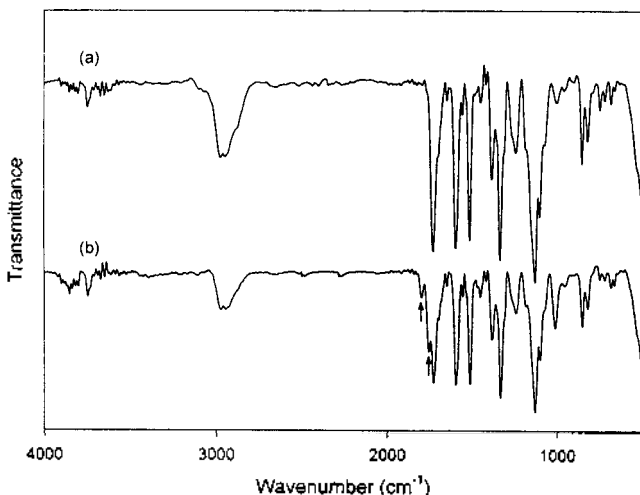
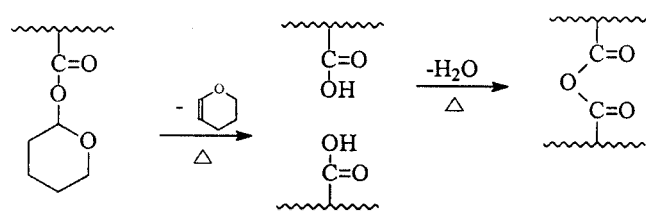
Table 1. Characterization of copolymers

	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	24	50	7.2	19.3	2.7	72	145
Polymer 2	23	33	44	5.7	10.7	1.9	40	142

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

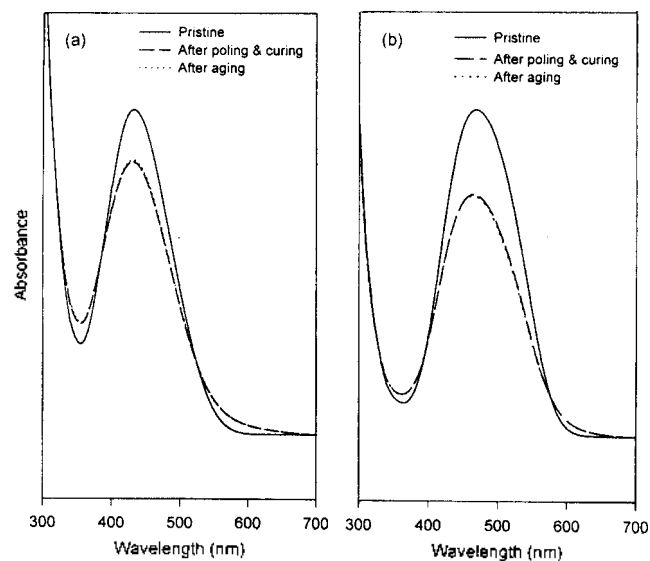
bene and 4-[(2-methacryloxyethyl)ethylamino]-4'-nitroazobenzene were further purified by column chromatography using dichloromethane as an eluent and the yield was 82 and 70%, respectively. 2-Tetrahydropyranyl methacrylate was purified by double distillation and the yield was 63%. These monomers were copolymerized with methyl methacrylate according to Scheme 2. The yield of polymer 1 and 2 was 70 and 42%, respectively. The resulting copolymer exhibited good solubility in common organic solvents such as THF, cyclohexanone, and DMF. The composition, molecular weights, and glass transition temperatures (T_g) of the copolymers are summarized in Table 1. T_g's of polymer 1 and 2 were measured as 145 and 142 °C, respectively, which gave useful information for determining the poling temperature. The resultant mole ratio of each component in the copolymers was estimated by integration of NMR proton signals. Molecular weights of the copolymers were good enough for film casting.

The copolymers were fabricated into thin films and poled under 6 kV at 140 °C, which is near to the DSC-measured glass transition temperatures of the copolymers. For thermal crosslinking, the films were poled and then heated to 200 °C with same corona voltage applied, which resulted in the formation of molecular alignment and networks in the films. The crosslinking temperature was as high as the chromophore's decomposition temperature, but the reaction time was short to decompose active NLO chromophore. IR spectra of polymer 2 before and after crosslinking are illustrated in Figure 1. The characteristic peaks for anhydride linkage, which was formed between the copolymer backbones after curing as shown in Scheme 3, appeared at 1750

**Figure 1.** IR spectra of polymer 2 before (a) and after (b) curing.**Scheme 3.** Crosslinking mechanism.

and 1820 cm⁻¹ corresponding to the asymmetric and symmetric stretching vibration. Since carboxylic acids in copolymer need to be formed preferentially for the crosslinking, the possibility of crosslinking during poling decreases, which in turn promotes the poling efficiency. Figure 2 shows the UV-Vis spectra of polymer 1 and 2 after poling, curing, and aging (100 °C, 1 h). 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 after curing. It means that the molecular dipole in NLO copolymer occurs by corona poling and is not disarranged at high temperature due to the formation of chemically crosslinked network. The absorption intensity of uncured, poled films was increased after the aging test at 100 °C for 1 h, however. This result indicated that maintaining dipolar orientation after poling requires an appreciable crosslinking reaction. No spectral change before and after aging indicated that this crosslinking reaction was successfully achieved by the thermal treatment. This crosslinking reaction was also confirmed by solubility test of two samples. While the uncured film was soluble in common organic solvents such as tetrahydrofuran (THF), cyclohexanone, and N,N-dimethylformamide (DMF), the cured film was not soluble in these solvents.

The r₃₃ value of polymer 2 was measured to be 62 pm/V for polymer 2 at 633 nm. To identify the thermal stability of electro-optic coefficient after curing, we have normalized the r₃₃ value, obtained for the respective films according to time, to the initial r₃₃ value, [(r₃₃)/(r₃₃)₀] for polymer 2 and showed the result in Figure 3. The ratio was maintained to ca. 65%.

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

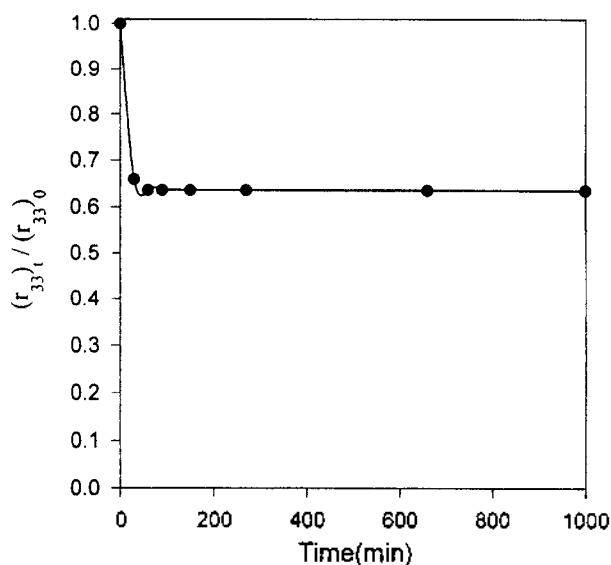


Figure 3. Temporal stability of the electro-optic coefficient of polymer 2 stored at 100 °C.

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 for 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