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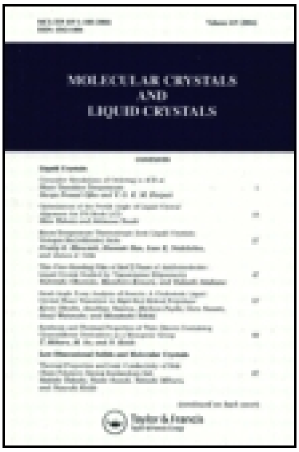

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Self-Crosslinkable Side-Chain Nonlinear Optical Copolymer

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SELF-CROSSLINKABLE SIDE-CHAIN NONLINEAR OPTICAL COPOLYMER

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ABSTRACT A self-crosslinkable second-order nonlinear optical copolymer with thermal stability at 100°C was prepared by the copolymerization of methacrylic nonlinear optical monomer with glycidyl methacrylate. The nonlinear optical property of this copolymer was compared with that of well-known side-chain polymer P2ANS. Electro-optic coefficient and second harmonic generation measurements showed a r_{33} value of 57 pm/V at 632.8 nm and a d_{33} value of 45.5 pm/V at 1064 nm. Moreover, self-crosslinking during poling was observed between the epoxy groups in the copolymer without adding any crosslinking agent and thus the copolymer showed an excellent thermal stability of aligned chromophores at 100°C. It is thought that the crosslinking was performed between the epoxy groups due to the catalytic basicity of tertiary amine groups in the NLO monomer.

INTRODUCTION

Second-order nonlinear optical (NLO) polymers are of great interest for application in integrated optical devices such as electro-optic (EO) switches, modulator, and frequency doubler. Polymeric materials offer additional advantages in device fabrication since they are easily soluble in common organic solvents, which is important for waveguide formation. The problem of second-order NLO polymers for practical device application is the gradual decay of second-order NLO coefficient resulted from the thermal relaxation of the non-centrosymmetric dipolar structure.[1] Generally, two different methods have been adopted to improve the temporal instability. First, polymers with high T_g like polyimides and polymaleimides have been used to prepare NLO polymers which are thermally stable at elevated device working temperatures (60~125°C).[2] Second method is related to the formation of a chemically crosslinked network during or after poling. Although fore-mentioned methods have been proven to be effective in preventing the dipolar relaxation, it should be pointed out that achieving a higher level of moleular alignment, namely a high NLO coefficient, is very difficult or limited with these methods. In the past study, NLO polymer with high T_g requires very high poling temperature and high electric field. Under

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this severe condition, NLO chromophore can be degraded and polymer matrix be subjected to dielectric breakdown. On the other hand, the crosslinking method is also limited by the restricted rotational alignment of dipoles by the crosslinking itself if the poling and curing processes were not precisely regulated.

In this paper, we are to demonstrate a novel and effective way of designing NLO polymers that exhibit good temporal stability, high degree of dipolar orientation, and good processability. We approached to use the NLO copolymer with crosslinkable covalent-bond unit in the side chain. Since electric-field poling is carried out at the vicinity of T_g, this polymer is simply the side-chain NLO polymer providing a high level of dipolar alignment after which the electric field and temperature are increased simultaneously to the formation of crosslinked structure resulting in the effective *fixation* of non-centrosymmetric dipolar structure.

EXPERIMENTAL

Copolymerization

The monomer containing NLO chromophore in its side chain, 4-(*N*'-methacroyloxyethyl-*N*-methyl-amino]-4'-nitrostilbene was prepared according to the literature method.[3] The copolymerization was carried out via free radical polymerization. 0.81 g (5.7 mmol) of glycidyl methacrylate (GMA) and 2.1 g, (5.7 mmol) of 4-(*N*'-methacroyloxyethyl-*N*-methyl-amino]-4'-nitrostilbene were dissolved in 25 ml of freshly distilled dimethylformamide (DMF). 1 mol% of azobisisobutyronitrile (AIBN) was also added in a vacuum ampoule. The mixed solution was thoroughly degassed by freeze-vacuum-thaw cycle and the ampoule was sealed. And then the polymerization was carried out at 80 °C for 72 hours. The resulting solution was cooled and poured into ethyl ether. The precipitate was filtered and purified by reprecipitation from tetrahydrofuran (THF) into ethyl ether and from THF into *n*-hexane repeatedly. The copolymer product was dried *in vacuo* at 60 °C for 72 hours. The copolymer (P2ANS) of methyl methacrylate (MMA) and 4-(*N*'-methacroyloxyethyl-*N*-methyl-amino]-4'-nitrostilbene was also prepared according to the literature method[3] to compare the EO properties with the GMA copolymer.

Film Preparation and Poling

The thin film of copolymer was obtained on indium-tin oxide (ITO) precoated glass by spin coating method. The solvent of copolymer used in spin coating was

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THF/cyclohexanone mixed solvent (conc. 10 wt%). The spin-coated film was dried *in vacuo* at 60 °C for 72 hours. For second harmonic generation (SHG) experiment, we poled the film on microslide glass using the corona poling technique in a wire-to-plane geometry. For linear EO coefficient measurement, we deposited the gold electrode on the top of the film and did electrode poling.

RESULTS & DISCUSSION

An NLO monomer, 4-(*N'*-methacroyloxyethyl-*N*-methyl-amino]-4'-nitrostilbene, was synthesized by reaction of 4-(*N'*-hydroxyethyl-*N*-methyl-amino]-4'-nitrostilbene with methacryloyl chloride. The structures of the GMA copolymer and P2ANS are shown at the FIGURE 1. The GMA copolymer had a good solubility in DMF, cyclohexanone, THF, and chloroform. We determined the resultant molar composition using the Kjeldahl's microanalysis method.[5] It was proved that the GMA copolymer contained 36 mol% of NLO chromophore. We used DSC analysis to study the thermal transition of the GMA copolymer, which would be an useful information to determine the poling temperature of the thin film. The poling and curing processes should be performed through two steps and the T_g of the pristine copolymer was observed at 118-120 °C. We, therefore, poled the polymer sample at 120 °C and raised the temperature gradually as self-crosslinking reaction proceeded during poling (FIGURE 2). The two step poling process was applied to this system : first the GMA copolymer was poled at 120°C to obtain maximum alignment of molecular dipoles ; second the poling temperature was increased to 140°C to obtain a crosslinked structure maintaining molecular dipoles oriented perpendicular to the substrate. UV-VIS spectra of poled and unpoled films of the GMA copolymer were compared to investigate the extent of molecular orientation along

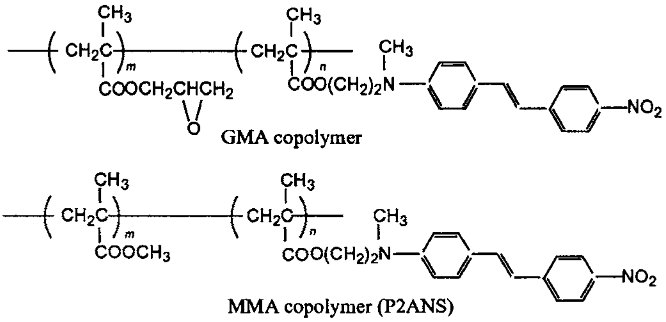

FIGURE 1 Chemical structures of NLO copolymers.

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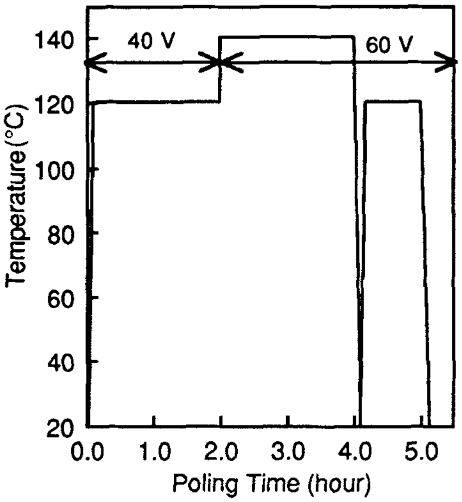

FIGURE 2 Electrode poling process.

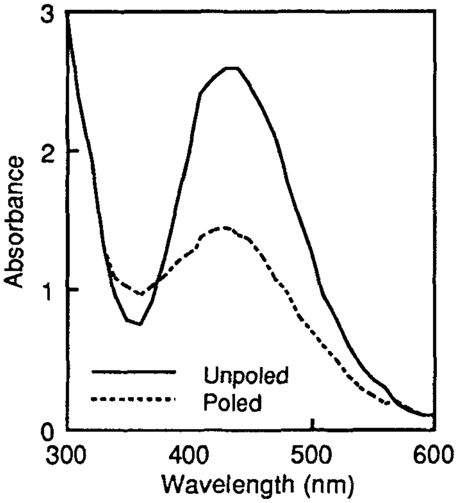

FIGURE 3. UV-VIS spectra of the GMA copolymer.

TABLE I Various properties of the GMA copolymer.

Absorption maximum λ_{max} (nm)	Cut-off (nm)	T_g(°C)[1]	Refractive index[2]	r_{33}[3] (pm/V)	d_{33}[4] (pm/V)
435	590	118-120	1.68	57	45.5

[1] determined by DSC
[2] determined by ellipsometry measurement (He-Ne laser wavelength)
[3] EO coefficient at the He-Ne laser wavelength (632.8 nm)
[4] SHG value at 1064 nm by Maker Fringe method

the direction of the poling electric field. The absorption maximum of the copolymer appeared around 430-440 nm (FIGURE 3). The absorption spectrum of poled film exhibited a decrease in the absorption intensity resulting from the molecular dipolar arrangement partially in the direction of the poling field. TABLE I summarizes the various properties of the GMA copolymer. Temporal stability of r_{33}'s of the poled films at 100°C is shown in FIGURE 4. We have normalized the r_{33} values obtained for the respective films to the initial r_{33} value $[(r_{33})_t/(r_{33})_0]$. A comparison of the two curves in this plot shown in FIGURE 4 indicates that the GMA copolymer has further improved long-term stability at 100°C rather than P2ANS. Thus it is seeing that a certain reaction might be performed at the epoxy groups in the GMA unit during the poling process. According to the recent report,[6] GMA has been also used as a comonomer in synthesis of NLO materal using its reactivity toward carboxylic acid group attached onto the NLO chromophore

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resulting in crosslinked structure. But the EO coefficient is somewhat low because the fast crosslink reaction hinders the molecular orientation during poling/curing process. They thought that the crosslink reaction occurred only between epoxy and carboxy groups. We, however, confirmed the occurrence of crosslink reaction between the epoxy groups in the copolymer by two reasons. One is the solubility of the poled and unpoled films. The poled film was not soluble in any solvent. The other is related to the measured epoxy group content by means of FT-IR study. The sample was poled at 140°C using corona poling method, taken out at convenient intervals. The intensity of the epoxy group at 907 cm^{-1} was observed to decrease with poling time that means decrease of the epoxy groups in the reaction system. The characteristic band of carbonyl group at 1730 cm^{-1} was used as a standard for this measurement, because its intensity did not change during thermal treatment. Indeed, IR absorbance ratio (A_{907}/A_{1730}) of poled films shows that the fraction of epoxy unreacted after poling was about 75 % (FIGURE 5). We also investigated the change of IR absorbance ratio in poly(glycidyl methacrylate) (PGMA) film at 140°C with various reaction times. The IR absorbance ratio, epoxy group and carbonyl group in copolymer did not decrease at a elapsed reaction time. This implies that the chemical reaction between epoxy groups in the polymer did not occurred. Tanaka[7] reported that self-crosslinkable polyepoxides could be obtained from the copolymerization

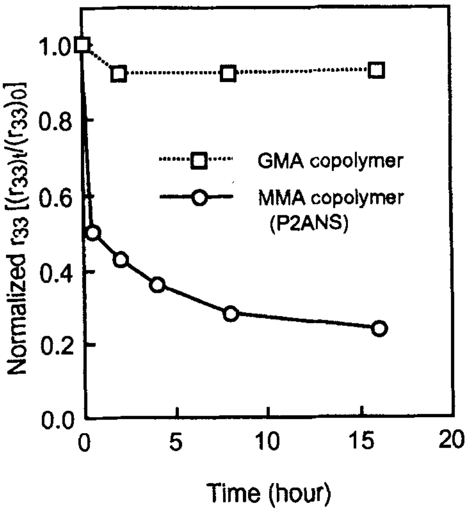

FIGURE 4 Thermal relaxation behavior of copolymers. (relaxation temperature =100 °C)

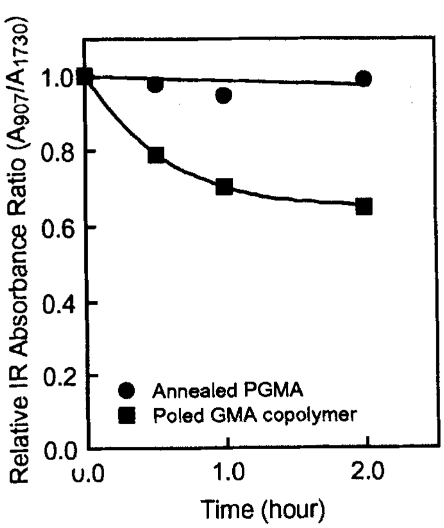

FIGURE 5 Epoxy groups remained after poling or heating. (poling & annealing temp.=140°C)

of 2,3-epoxy-1-propyl methacryalte and vinyl pyridine by means of catalytic activity of tertiary amine (pyridine group in vinyl pyridine). Many reports have revealed that the Lewis bases, e.g. tertiary amines are quite suitable for curing epoxy resins.[8,9] We have epoxy groups in the GMA unit and tertiary amine in NLO monomer. Therefore it is suggested that spontaneous self-crosslinking of the GMA copolymer occurred between the epoxy groups in the presence of tertiary amine in the solid state during the high temperature poling process .

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CONCLUSION

We designed and synthesized a new self-crosslinkable NLO side-chain copolymer. The GMA copolymer was stable up to T_g and could be self-crosslinked by thermal treatment. The GMA copolymer has a suitable T_g to be poled under a moderate condition which gave a EO polymer with highly oriented dipolar alignment. Moreover, self-crosslink reaction between the side-chains themselves occurred at higher temperature than T_g. Thus network structure was easily obtained by spontaneous crosslinking between epoxy groups during poling due to the catalytic basicity of tertiary amine in the copolymer. Two step poling process was adopted to obtain an effective NLO material which had both good NLO properties and excellent thermal stability. We obtained a r_{33} value of 57 pm/V at 632.8 nm and a d_{33} value of 45.5 pm/V at 1064 nm. We improved poling induced molecular alignment and long term stability at 100°C from our synthetic strategy.

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