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Nonlinear optical crosslinked polymers and interpenetrating polymer networks containing azo-benzothiazole chromophore groups

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Two kinds of crosslinked polymers and one kind of interpenetrating polymer network (IPN) containing phenylazo-benzothiazole (BT) chromophore groups were synthesized. Crosslinked polyurethane was obtained by the reaction between (2-hydroxypropyl acrylate-BT-1 methacrylate) copolymer and phenol-capped NCO-terminated BT-2, whereas crosslinked epoxy-based polymer was formed by reaction between epoxy-containing BT and BT-containing aniline. IPNs based on crosslinked polyurethane/epoxy-based polymer were obtained by carrying out the above two reactions simultaneously. The crosslinked polymers and IPNs were characterized by gel content, IR spectra and differential scanning calorimetry. The crosslinked polyurethane and the epoxy-based polymer exhibit glass transition temperatures at 140 and 178°C, respectively, whereas the IPN shows two T_g at 142 and 170°C. Thin, transparent poled films of the crosslinked polymers and IPN were prepared by spin-coating, followed by thermal curing and corona poling at 160°C for 1 h. The second-order non-linear optical properties of the poled films were studied by a visible light absorbance measurement according to the one-dimensional rigid oriented gas model. Long-term stability of the dipole alignment at 120°C was demonstrated for the three polymers.

(Keywords: crosslinked polymer; interpenetrating polymer network; nonlinear optical material)

INTRODUCTION

Interest in nonlinear optical (NLO) materials, both inorganic and organic, has grown tremendously in recent years, primarily because of their potential application in electro-optic devices. It is known that organic NLO materials possess several advantages over inorganic materials, such as large second-order susceptibility, ultrafast optical response, high laser damage threshold, ease of processing and especially the unlimited architectural flexibility for optimizing optical nonlinearities. Hence a great deal of research effort has been focused on organic materials, among which the NLO polymer systems are especially attractive because they possess good optical properties, wide variety, easy processing and low cost.

It has been known that dipolar molecules consisting of electron donating and accepting groups terminating pi-electron systems exhibit large second-order optical nonlinearities[1]. Incorporating these molecules into polymer materials for second-order nonlinear optics have become the subject of keen interest. In order to exhibit second-order nonlinear optical effects, normally amorphous centrosymmetric polymer must be subject to an electric field poling process. In this process dipolar nonlinear optical moieties, which are incorporated in the polymer, rotate through the coupling of the dipole to the electric field when the polymer is in a state allowing the rotation. After the dipoles are aligned, the polymer must be put into a state where the dipole rotation is inhibited in order to minimize the orientation decay.

To date, many studies have been performed to optimize one or some required properties by (1) the design and synthesis of more efficient NLO chromophores; (2) the incorporation of efficient NLO chromophores into thermally stable and processible polymers; (3) improving the alignment stability of poled NLO polymer films[2]. In order to be useful in integrated optical device applications, second-order NLO polymers should also maintain a significant bulk nonlinearity at elevated working temperature that can reach 80°C or higher[3]. These practical considerations have led investigators to search for new polymeric systems which exhibit better temporal and thermal NLO stability.

To reduce the relaxation or decay of the dipole alignment, crosslinking of the polymer containing the chromophores groups has been used to retard the mobility of the polymer segments, thereby preventing the aligned NLO chromophores from relaxing to a random orientation. Chen *et al.*[4] obtained new polymers containing dispersed red dye as an NLO active chromophore in conjunction with photo-crosslinkable groups. The NLO coefficient of the crosslinked polymer was stable for 1000 h after poling. Jeng *et al.*[5] studied a crosslinked second-order NLO polymer based on an alkoxysilane dye and a multifunctional phenoxy molecule, and showed that after a small initial decay the NLO coefficient remained essentially constant at 105°C for over 168 h. White and co-workers[6] produced NLO films by incorporating a rhodamine-based dye into a polyurea–polyurethane network via reaction with an isocyanate crosslinker. They observed a decay in the second-order susceptibility at 100°C. Later they prepared a polyurea–polyurethane network containing azo-benzimidazole NLO dye[7]. However, the NLO coefficient of the poled film

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decreased to about 80% of its initial value within 400 h at 100°C. Levenson *et al.*[8] synthesized a polyurethane containing both epoxy groups and COOH-substituted DR-1 which was then crosslinked by reaction between the epoxy and COOH groups; the poled crosslinked polymer was found to maintain its electro-optical coefficient for several weeks at 85°C.

The IPN is known to be able to remarkably suppress the creep phenomenon in polymers. The motion of segments in the IPN is diminished by the entanglement between the networks. These properties of the IPN present the potential for restricting the mobility of the aligned NLO chromophores. Marturunkakul and co-workers[9–11] synthesized NLO IPNs based on epoxy resin/phenoxy-silicone polymer containing chromophore groups and reported that the poled IPN showed no change in its NLO activity after being heated at 110°C for 168 h but decreased apparently at 120°C. Recently, we reported two kinds of crosslinked polymers[12] and three kinds of IPNs based on polyacrylate/polyurethane[13], polyacrylate/epoxy resin and polyurethane/epoxy resin[14] all containing 4-(4′-nitrophenylazo) aniline chromophores as stable NLO polymers. The crosslinked polyacrylate and IPNs based on polyurethane/epoxy resin showed a good temporal stability of NLO properties at 100°C, whereas the crosslinked polyurethane and IPNs based on polyacrylate/polyurethane and polyurethane/epoxy resin exhibited a good temporal stability at 120°C.

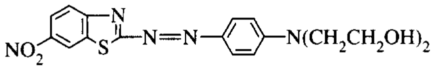
Since it was reported that phenylazo-benzothiazole (BT) chromophore possesses higher hyperpolarizability β_0 value than that of phenylazo-chromophore[15], this paper deals with the synthesis, corona poling and temporal stability of crosslinked polyurethane, epoxy-based polymer and IPN composed of the two polymers, all containing BT chromophore, in order to obtain a large second-order NLO effect.

EXPERIMENTAL

Synthesis of chromophore compounds

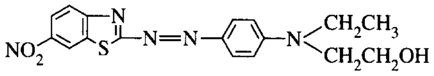
2-Amino-6-nitrobenzothiazole was synthesized as follows. To 150 ml glacial acetic acid containing 13.8 g (0.1 mol) 4-nitroaniline, 19.4 g (0.2 mol) potassium thiocyanate in an ice bath, 25 ml glacial acetic acid containing 16 g (0.1 mol) bromine was added dropwise during stirring for 0.5 h. The reaction temperature was kept below 10°C. The precipitate formed was filtered and dissolved in hot water. After being neutralized with alkali, the precipitate was filtered, dried and recrystallized from ethanol, and 10.6 g of purified product was obtained as yellow needle crystals with 54.3% yield and a m.p. of 247–249°C.

2-[4′-(*N*,*N*-Di-2-hydroxyethyl)amino-phenylazo]-6-nitrobenzothiazole represented by



(BT-2) was synthesized in the following way. To 320 ml glacial acid containing 7.8 g (0.04 mol) 2-amino-6-nitrobenzothiazole in an ice bath, 200 ml concentrated sulfuric acid containing 2.8 g $NaNO_2$ was added dropwise during stirring for 0.5 h. The reaction mixture was poured into crushed ice to obtain diazonium salt solution, which was then poured into 120 ml methanol/water (2/1 volume ratio) mixture contain 7.4 g (0.04 mol) *N*,*N*-di(2-hydroxyethyl) aniline in an ice bath during stirring for 1 h. Then the mixture was neutralized with ammonia water to pH 5–6, while stirring for 0.5 h. The precipitate was filtered, dried and recrystallized from acetone. The purified product was obtained as black powdered crystals with 34% yield (m.p. 220–221°C).

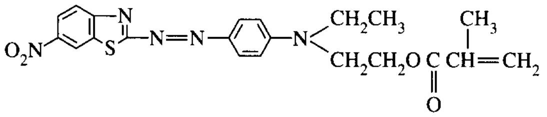
2-[4′-(*N*-Ethyl,*N*-2-hydroxyethyl)amino-phenylazo]-6-nitro-benzothiazole, given by



(BT-1) was synthesized in the same way as BT-2 except that *N*-ethyl,*N*-(2-hydroxyethyl) aniline was used instead of *N*,*N*-di(2-hydroxyethyl)aniline. The product was obtained as brown powder with 48.6% yield and a m.p. of 216–218°C.

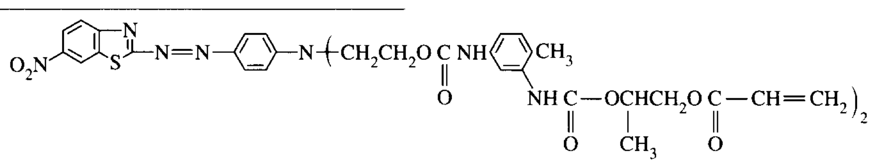
Synthesis of monomers

Methacrylate-terminated BT-1 (BT-1-MA) represented by



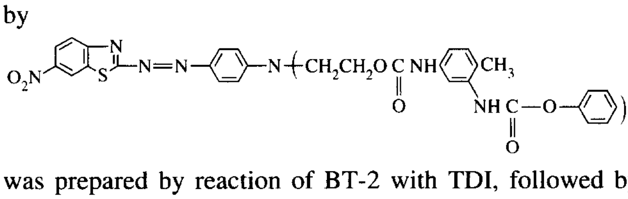
was prepared in the following way. To a mixture of 32 g BT-1, 100 mg, *p*-hydroxyphenol, 400 ml dried tetrahydrofuran (THF), and 13 ml triethylamine under a nitrogen atmosphere, 40 ml of a THF solution of 10 ml freshly prepared methacryloyl chloride was added dropwise with stirring at room temperature for 3 days. After filtration, the solvent was removed by distillation under reduced pressure. The residue was dissolved in $CHCl_3$ and washed with saturated $NaHCO_3$ solution and saturated NaCl solution successively, twice each. After drying with anhydrous $MgSO_4$ and evaporating off the solvent, the crude product was recrystallized with acetone/petroleum ether (b.p. 60–90°C). The purified product was obtained as a purple product with 78% yield (m.p. 160–161°C).

Acrylate-terminated BT-2 (BT-2-DA), given by



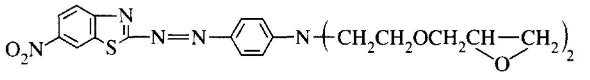
was synthesized as follows: stoichiometric amounts of BT-2 and chemically pure 2,4-toluene diisocyanate (TDI) were reacted in dimethylformamide (DMF) at 75°C for 1 h, then at 90°C for 2 h. After cooling down the mixture to 50°C, a small excess of 2-hydroxypropyl acrylate was added and the reaction was carried out at 60°C for 3 h until no isocyanate group was detected with aniline. The product was precipitated out with methanol and vacuum dried. Yield was 76.9%.

Phenol-capped isocyanate-terminated BT-2, represented by



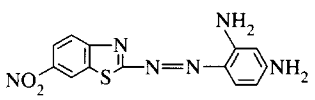
was prepared by reaction of BT-2 with TDI, followed by capping with phenol was as follows: stoichiometric amounts of BT-2 and TDI were reacted in DMF at 75°C for 1 h and then at 90°C for 2 h. A stoichiometric amount of phenol was then added to cap the isocyanate groups remaining, The capping reaction was carried out at 100°C for about 2 h, until no isocyanate groups could be detected by aniline. After cooling the mixture, the product was precipitated out with ethanol.

2-(4′(*N*,*N*-Di-glycidyloxyethyl)amino-phenylazo)-6-nitro-benzothiazole (BT-2-E0), given by



was synthesized in the following way: 6.2 g BT-2 and 0.7 g sodium were added to 200 ml purified 1,4-dioxane. The mixture was refluxed for 6 h to form sodium salt of BT-2. After removing the solvent by distillation under reduced pressure, 200 ml epichlorohydrin and a small amount of tetramethyl ammonium bromide was added and the reaction mixture was refluxed for 24 h and then washed with water. The unreacted, epichlorohydrin was removed by distillation. The product was obtained as a dark red semisolid. The epoxy group was detected by i.r. spectroscopy.

2-(2′,4′-Di-amino-phenylazo)-6-nitro-benzothiazole (DABT), represented by



was prepared as follows. Ice-cooled diazonium salt of benzothiazole, prepared as the synthetic procedure of BT-2, was added slowly to a solution containing 5.4 g 3-aminoaniline, 10 ml concentrated hydrochloric acid and 120 ml water during stirring for 0.5 h. After neutralization with ammonia water to pH 5–6, reaction was continued for 0.5 h. The precipitate was filtered, washed with water and dried. The product was obtained as a brown powder with 95% yield and a m.p. of 225–226°C.

Synthesis of prepolymers

Polyhydroxy polymer containing BT-1 chromophores was prepared by polymerization of BT-1-MA with 2-hydroxypropyl acrylate at weight ratio of 1/1 at 60°C using 2 mol% azobisisobutyronitrile as initiator and chlorobenzene as solvent under nitrogen atmosphere for 24 h. After removing most of the solvent, the prepolymer was precipitated with CH_3OH and purified by dissolving in CH_2Cl_2 and precipitated with CH_3OH again. The purified product was vacuum-dried at 80°C.

Epoxy-based prepolymer containing BT-2 chromophores was synthesized by first mixing BT-2-EO and DABT thoroughly with a molar ratio of $EO/NH_2 = 1$ at 130–140°C for 3 min to obtain uniform melt, followed by reaction at 110°C for 1 h and then at 120°C for 20 min. Finally DMF was added to stop the reaction and DMF solution of epoxy-based prepolymer was obtained.

Preparation of poled polymer films

Polyurethane film containing both BT-1 and BT-2 chromophores was prepared by dissolving weighed amounts of polyhydroxyl prepolymer and phenol-capped NCO-terminated BT-2 at a NCO/OH molar ratio of 1/1 in DMF to give a concentration of 10%, followed by filtration and spin-coating onto a clean glass slide at a rotation speed of 1500 rev min^{-1}, for 30 s at about 50°C. The film coated on the glass slide was vacuum dried for 48 h to remove the residual solvent.

Epoxy-based polymer film was obtained by filtering and spin-coating the DMF solution of the epoxy-based pre-polymer onto a clean glass slide. Then it was vacuum dried for 48 h.

For preparation of polyurethane/epoxy-based polymer IPN film, phenol-capped NCO-terminated BT-2, the polyhydroxyl prepolymer and DMF solution of epoxy prepolymer were weighed according to the composition of the IPN and the molar ratios of NCO/OH and $epoxy/NH_2 = 1$ and dissolved in DMF to make up a 10% concentration. After filtration the filtrate was spin-coated onto a clean glass slide with a rotation speed of 1500 rev min^{-1} for 30 s at 50°C. The film coated on the glass slide was vacuum dried for 24 h to remove the residual solvent.

Alignment of the chromophores and crosslinking of the films were carried out in a corona poling apparatus with a heating rate of 2°C min^{-1}. The apparatus consisted of a tungsten needle as positive electrode and a copper disc as negative electrode, the distance between the electrodes being 1.5 cm. The optimum conditions for poling and crosslinking were as follows. As the temperature was raised to 100°C, the corona field was applied until the temperature and electrode potential reached 160°C and 8.5 kV, respectively. After maintaining the temperature and potential for 1 h, the film was allowed to cool naturally to 100°C and then cooled quickly to room temperature by means of a water jacket. Finally the corona field was switched off. The whole poling procedure took 3 h. Another sample with the same composition and the same visible light absorption (difference of peak absorption $< 2\%$), spin-coated on to another glass slide, was crosslinked by heating in the same way but without corona poling and used as a reference.

Characterization of poled films

Visible light spectra of the polymers were taken using a Shimadzu UV-240 spectrophotometer. Infra-red spectra were recorded on a Shimadzu IR-435 spectrophotometer using KBr crystals spin-coated with polymerization mixture and cured at 160°C. Differential scanning calorimetry (d.s.c.) curves were obtained with a CDR-1 calorimeter (made by Shanghai Analytical Instrument Co.) at a heating rate of 10°C min^{-1}. Thickness and refractive index of the poled films were estimated by ellipsometric polarizing spectroscopy (TP-77 instrument, made by Beijing Apparatus Co.) using a wavelength of 632.8 nm. Gel content of the crosslinked polyurethane, epoxy-based polymer or IPN was determined by immersing a weighed film in DMF for 24 h, followed by filtering, drying and weighing the insoluble gel.

Temporal stability of the second-order NLO properties of the NLO polymers

The relaxation behaviour of the second-order NLO properties of the polymers was studied by monitoring the decay of the order parameter as a function of time at 120°C. The order parameter (ϕ) can be calculated according to the visible light absorbance value of a poled sample measured with electric fields polarized parallel (A_0) and perpendicular to the poling direction ($A_\perp$): $\phi = 1 - A_\perp/A_0$.

RESULTS AND DISCUSSION

Formation of crosslinked polymers and IPN

No gel was formed from the polymerization of BT-2-DA even in the presence of R_2O_2. The difficult formation of crosslinked polyacrylate is probably due to the steric hindrance of the large BT groups, which may also act as an inhibitor for the free radical polymerization.

Crosslinked polyurethane can be formed from the reaction between phenol-capped NCO-terminated BT-2 and the polyhydroxyl copolymer. The purpose of using phenol-capped NCO-terminated BT-2 is to avoid the reaction between NCO-terminated BT-2 and moisture. The phenol-capped chromophores began to decap at about 120°C and then reacted with the polyhydroxyl copolymer to form a polyurethane network. *Table 1* shows that the gel content of the polyurethane reached 96% after 30 min at 160°C and 99% after 60 min at 160°C. I.r. spectra showed that no absorption peaks for hydroxyl and NCO groups remained for the polyurethane formed at 160°C for 1 h. The gel content of the epoxy-based polymer reached 91 and 96% at 160°C for 30 min and 1 h, respectively. The i.r. spectra of the epoxy-based resin showed that no absorption peaks for epoxy groups remained for the epoxy-based polymer formed at 160°C for 1 h. The gel content of the two crosslinked polymers indicated that the formation rates of the two networks differ only slightly at 160°C.

The IPNs containing the polyurethane and epoxy-based polymer showed a gel content of 94 and 99%, when cured at 160°C for 30 min and 1 h, respectively. Both i.r. spectra and gel content demonstrated that the two networks formed simultaneously through two different mechanisms. However the isocyanate group may also react with the amino groups of DABT. Hence, there may occur some links between the two networks.

Properties of poled crosslinked polymers and IPN films

The surface of the poled polymer films appeared very even and smooth, and no change was evident after immersion in DMF or THF. Visible light absorption spectra of the reference films did not change after thermal crosslinking and i.r. spectra of the polymer films showed no change of absorption peaks after poling. These facts demonstrate that no evident decomposition or volatilization of the polymer film occurred during heating at 160°C or corona poling.

The poled films exhibited good transparency. *Table 2* showed some properties of the poled crosslinked polyurethane, epoxy-based polymer and the IPN. Both the density and the refractive index of the polyurethane are higher than those of the epoxy-based polymer. D.s.c. curves showed that the glass transition temperatures (T_g) for the crosslinked polyurethane and epoxy-based polymer are 140 and 178°C, respectively. The decomposition temperature (T_d) of polyurethane is higher than that of epoxy-based polymer. It is of interest to note that both the density and the refractive index of the IPN are higher than those of the two crosslinked polymers, but the T_d and N values of the IPN are about the average values of the two networks. The IPN exhibits two T_g values which shift inward from the T_g values of the two networks. This may be attributed to some enhanced compatibility of the two networks caused by the interpenetrating networks.

Table 1 Gel content of the two crosslinked polymers and IPN cured at 160°C for different times

Polymer	Gel content (%)	
	30 min	60 min
Polyurethane[a]	96	99
Epoxy-based polymer	91	96
IPN[b]	94	99

[a] BT-1-MA/2-hydroxypropyl acrylate = 1/1 (wt. ratio)
[b] Polyurethane/epoxy-based polymer = 1/1 (wt. ratio)

In order to obtain a large second-order NLO effect, it is necessary to increase the density of chromophores in the polymer and to select a chromophore with a large β value and a large dipole moment μ. The β_0 and μ values of the BT chromophore used in this work are 60×10^{-30} e.s.u. and 9.47 D, respectively. Both values of the BT chromophore are higher than those of 4-(4′-nitrophenylazo)aniline chromophore. The density of chromophores (N) of the crosslinked polyurethane, epoxy-based polymer and IPN were found through absorbance measurements to be 9.99×10^{20}, 19.0×10^{20} and 15.9×10^{20} molecules cm^{-3}, respectively, as shown in *Table 2*.

The macroscopic second-order NLO polarizability can be calculated according to a one-dimensional, rigid oriented gas model[16] as follows:

$$\chi^2 = N\beta F(\cos^3\theta) \qquad (1)$$

where N is the density of the chromophore molecules, and F the local field factor, and $(\cos^3\theta)$ is the average alignment factor which can be estimated according to the approximate relationship between $(\cos^3\theta)$ and the order parameter (ϕ): $(\cos^3\theta) = (0.6\phi)^{1/2}$. ϕ can be calculated according to the visible light absorbance value of a poled sample.

Figures 1–3 illustrate the visible light absorbance spectra of the crosslinked polymers and IPN films before and after corona poling, respectively. During corona poling under high voltage field and heating, the chromophore groups of the crosslinked polymer align along the field direction, resulting in a decrease of peak absorbance of the incident light perpendicular to the film. The order parameters of the poled polyurethane epoxy resin and IPN films can reach 0.23, 0.19 and 0.32, as shown in *Table 3*. The second-order NLO coefficients χ^2were approximately calculated to be 1.10×10^{-7}, 1.59×10^{-7} and 2.18×10^{-7} e.s.u., respectively, according to equation (1). The exact value of χ^2 should be determined with second harmonic generation in our future work.

Relaxation of chromophore alignment in the poled films

The order parameter was used to describe the chromophore alignment which correlates to the NLO properties of the polymers. *Table 4* shows the temporal behavior of the

Table 2 Some properties of the poled crosslinked polymers and IPN

Polymer	Density at 20°C (g cm^{-3})	Refractive index at 632.8 nm	T_g(°C)	T_d(°C)	$N \times 10^{-20}$ (molecules cm^{-3})
Polyurethane[a]	1.38	1.762	140	295	9.99
Epoxy-based polymer	1.24	1.674	178	225	19.0
IPN[b]	1.41	1.788	142, 170	245	15.9

[a] BT-1-MA/2-hydroxypropyl acrylate = 1/1 (wt. ratio)
[b] Polyurethane/epoxy-based polymer = 1/1 (wt. ratio)

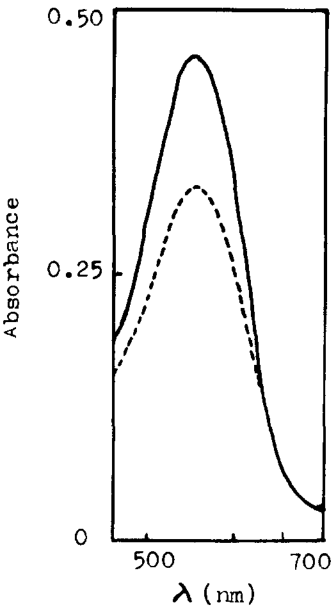


Figure 1 Absorption spectra of the crosslinked polyurethane film: (———) unpoled; (- - -) poled

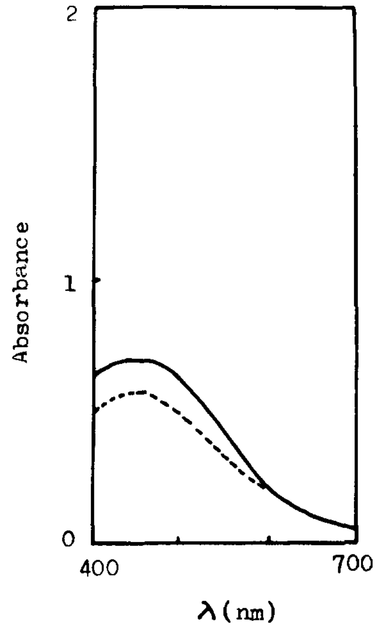


Figure 2 Absorption spectra of the crosslinked epoxy-based polymer film: (———) unpoled; (- - -) poled

order parameter $\phi(t)/\phi(o)$ for the films of three kinds of polymers at 120°C. It can be seen that both crosslinked polymers films maintained more than 95% NLO activity for 240 h at 120°C. This is attributed to the presence of a high degree of crosslinking which retards the relaxation of aligned chromophore groups. However, the poled epoxy-based polymer shows slightly better stability than the poled crosslinked polyurethane film with respect to the NLO properties. This difference may be due to the higher T_g of the epoxy-based polymer.

The temporal stability of the NLO properties of the IPN is better than that of both crosslinked polymers at 120°C. The ratio of $\phi(t)/\phi(o)$ remains at about 99% for 240 h at 120°C. This slow relaxation at higher temperature can be explained by the interpenetrating networks and the permanent entanglement between two networks which inhibit the motion of the aligned chromophores on one side and decrease the free volume within the polymeric material on the other side.

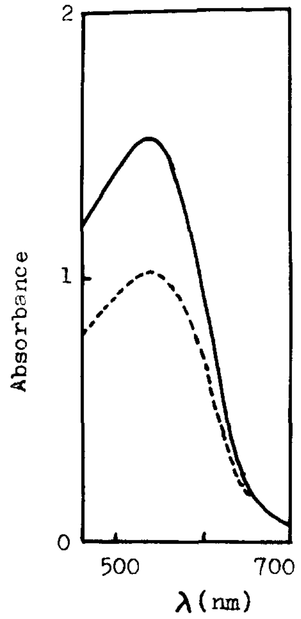


Figure 3 Absorption spectra of the IPN film: (———) unpoled; (- - -) poled

Table 3 Order parameter and χ^2 for the different poled films

Poled polymer	ϕ	$\langle\cos^3\theta\rangle$	F	$\chi^2 \times 10^7$ (e.s.u.)
Polyurethane	0.23	0.37	4.93	1.10
Epoxy-based polymer	0.19	0.34	4.10	1.59
IPN	0.32	0.44	5.20	2.18

Table 4 Temporal behavior of the order parameter ratio $\phi(t)/\phi(o)$ of the three films at 120°C

Poled film	$\phi(t)/\phi(o)$			
	24 h	48 h	96 h	240 h
Polyurethane	0.97	0.97	0.96	0.95
Epoxy-based polymer	0.98	0.98	0.98	0.97
IPN	0.99	0.99	0.99	0.99

CONCLUSION

Polymers with stable non-linear optical properties can be obtained by crosslinking special types of polyurethane and epoxy-based polymer containing azobenzothiazole chromophore groups. The crosslinked polyurethane and epoxy-based polymer possess a gel content of 99 and 96%, and a chromophore density of 9.99×10^{20} and 1.90×10^{21} molecules/cm^3, respectively. Simultaneous IPN based on the polyurethane and the epoxy-based polymer containing the same chromophore groups can be synthesized with a gel content of 99%, and a chromophore density of 1.59×10^{21} molecules/cm^3. The poled crosslinked polymers and IPN all showed good stability of NLO activity at 120°C. However the poled IPN exhibited better stability of NLO activity than the poled crosslinked polymers.

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