

# Synthesis and Properties of Two Kinds of Nonlinear Optical Interpenetrating Polymer Networks

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## SYNOPSIS

Two kinds of interpenetrating polymer networks (IPNs) containing 4-(4'-nitrophenylazo)aniline chromophore groups were synthesized. A polyacrylate network was prepared by polymerization of Dispersed Red-19 (DR-19) diacrylate, whereas an epoxy resin network was formed by reaction of Bisphenol A-type epoxy resin E44 with 4(4'-nitrophenylazo)-3-amino aniline. A polyurethane network was synthesized by reaction between ( $\beta$ -hydroxyl propyl acrylate-DR-1 methacrylate) copolymer and phenol-capped isocyanate-terminated DR-19. IPNs based on polyacrylate/epoxy resin and IPNs based on polyurethane/epoxy resin were obtained by carrying out two corresponding kinds of reactions simultaneously. Both kinds of IPNs were characterized by gel content, IR spectra, and DSC. The first kind of IPNs exhibits two glass transition temperatures at 122 and 165°C, while the second kind of IPNs showed one broad glass transition temperature at 172°C. Thin and transparent poled films of both IPNs were prepared by spin-coating, followed by thermal curing and corona poling at 160°C for 1 h. The second-order nonlinear optical properties of the poled films were studied by a visible light absorbance measurement according to the one-dimensional rigid oriented gas model. The polyurethane/epoxy resin IPNs were more stable in dipole alignment than were the polyacrylate/epoxy resin IPNs at temperature higher than 120°C. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Recently, polymers with second-order nonlinear optical (NLO) properties have been of increased interest in frequency doubling and electro-optical modulation, since they possess good NLO properties, ultrafast optical response, high laser damage threshold, ease of processing, and, especially, unlimited architectural flexibility for optimizing optical nonlinearities, as compared to those of the inorganic NLO materials, such as lithium niobate, which are now used in devices. Second-order NLO polymers derive their NLO properties from the hyperpolarizability of chromophores in them. The chromophores with delocalized  $\pi$ -electron systems capable of exhibiting charge-transfer resonances can exhibit large molecular second-order hyperpolarizability.

When chromophores in a polymer are aligned in a noncentrosymmetric manner after poling, it presents NLO properties. The alignment of NLO chromophores in the poled polymer must be sufficiently stable at temperature up to 80°C, so as to be useful in practical integrated electrooptical devices. However, the major disadvantage of NLO polymers is the decay of their second-order nonlinearities, which is attributed to the relaxation of the NLO chromophores from the electric field-induced noncentrosymmetric alignment to a random configuration.

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 et al.<sup>1-3</sup> synthesized NLO IPNs based on epoxy resin/phenoxy-silicon polymer containing chromophore groups and reported that the poled IPN showed no change in its NLO activity

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after being heated at 110°C for 168 h but decreased apparently at 120°C. Recently, we<sup>4</sup> reported a kind of NLO IPNs based on polyacrylate/polyurethane containing 4-(4'-nitrophenylazo)aniline chromophores, which shows a good temporal stability of NLO properties at 120°C over 160 h.

This article deals with synthesis and corona-poling of IPNs based on polyurethane/epoxy resin and IPNs based on polyacrylate/epoxy resin, both containing 4-(4'-nitrophenylazo)aniline chromophore groups, as well as study of the temporal stability of the poled IPNs at different temperatures.

## EXPERIMENTAL

### Synthesis of Chromophores Compounds

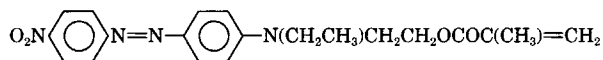
4-(*N*-Ethyl, *N*-2-hydroxyethyl)amino-4'-nitroazobenzene (DR-1) was synthesized as follows: To a 90 mL methanol/water (2/1 volume ratio) solution containing 5 g freshly prepared *N*-ethyl, *N*-(2-hydroxyethyl)aniline was added slowly an equal molar amount of 4-nitroaniline diazonium salt in an ice bath with vigorous stirring for 1 h, followed by neutralization with sodium acetate to pH 5–6. After stirring for 0.5 h, the precipitate was filtered and dried. The crude product was recrystallized from acetone and a 6.6 g purified product was obtained as a dark red powdered crystal with 70.5% yield; mp 162–163°C.

4-(*N,N*-di-2-hydroxyethyl)amino-4'-nitroazobenzene (DR-19) was synthesized in the same way as that of DR-1 except that *N,N*-di(2-hydroxyethyl)aniline was used instead of *N*-ethyl,*N*-(2-hydroxyethyl)aniline.

2,4-Diamino-4'-nitroazobenzene (DANA) was prepared as follows: To 5.4 g *m*-aminoaniline were added 9 mL concentrated hydrochloric acid and 60 mL water to make its salt solution. *p*-Nitroaniline, 6.9 g, water, 18 mL, and NaNO<sub>2</sub>, 3.6 g, were mixed to form a paste, which was poured into a mixture of 12.8 g crushed ice and 12.8 mL concentrated hydrochloric acid. The reaction was carried out for 0.5 h in an ice bath. The diazonium salt solution was added slowly into the solution of *m*-aminoaniline salt during stirring and the mixture reacted for 1 h. After neutralizing with 50 mL ammonia water for 0.5 h, the product was filtered and washed with water until neutral. After drying, it was purified by recrystallization from benzene. Yield was 92.6% with an mp of 215–216°C.

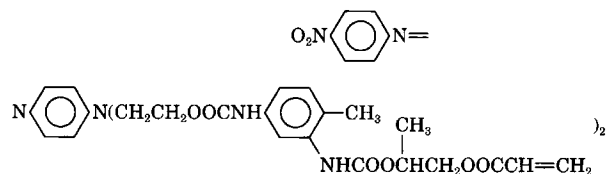
### Synthesis of Monomers

Methacrylate-terminated DR-1 is represented by



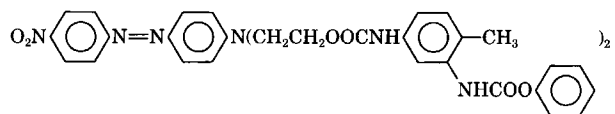
which was prepared as follows: To a mixture of 8.8 g DR-1, 35 mg *p*-hydroxyphenol, 100 mL dry dichloromethane, and 4.3 mL triethylamine was dropped into a 10 mL dichloroethane solution of 3.2 mL freshly prepared methacryloyl chloride under a nitrogen atmosphere with stirring at room temperature for 3 days. The reaction product was washed with a saturated NaHCO<sub>3</sub> solution and a saturated NaCl solution successively, each twice. After drying with anhydrous MgSO<sub>4</sub> and evaporating off the solvent, the crude product was recrystallized with acetone/petroleum ether (bp 60–90°C). The purified product was obtained as red powder with 89% yield; mp 91–92°C.

Acrylate-terminated DR-19 is given by



which was synthesized in the following way: Stoichiometric amounts of DR-19 and toluene diisocyanate (TDI) were reacted in dimethylformamide (DMF) at 75°C for 1 h and then at 90°C for 2 h. Then, an equivalent amount of 2-hydroxypropyl acrylate was added and the reaction was carried out at 60°C with stirring for 3 h, until no isocyanate group was detected with aniline. The product was precipitated out with methanol. Yield was 86.4%.

Phenol-capped isocyanate-terminated DR-19 is represented by



which was prepared by reaction of DR-19 with TDI, followed by capping with phenol as follows: Stoichiometric amounts of DR-19 and TDI were reacted in DMF at 75°C for 1 h and then at 90°C for 2 h. Then, a stoichiometric amount of phenol was added to cap the isocyanate group remaining. The capping reaction was carried out at 100°C for about 2 h, until no isocyanate group could be detected by aniline. After cooling, the product was precipitated with ethanol. Yield was 91.5%.

### Synthesis of Prepolymer

Polyhydroxyl polymers containing chromophores were prepared by polymerization of DR-1 methacrylate and 2-hydroxypropyl acrylate in a weight ratio of 1/1 at 65°C using 2 mol % azobisisobutyronitrile as the initiator and chlorobenzene as the solvent under nitrogen atmosphere at 60°C for 24 h. The crude product was precipitated out with methanol and purified twice using dichloromethane as the solvent and methanol as the precipitating agent. The purified product was vacuum-dried at 80°C for 24 h. Based on the working curve of the absorbance measurement, its chromophore content was estimated to be  $8.9 \times 10^{20}$  mol/g.

Epoxy resin E44 was purchased from Baling Petrochemical Co. The epoxy value was determined by the acetone-HCl method to be 0.422.

### Preparation of Poled IPN Film

For preparation of polyacrylate/epoxy resin (PA/EP) IPNs, a weighed amount of DR-19 diacrylate, E44, and DANA according to the composition of the IPN and the epoxy/NH<sub>2</sub> molar ratio were dissolved in tetrahydrofuran to make up a 10% concentration. After filtration, the filtrate was spin-coated onto a clean glass slide with a rotation speed of 1500 rpm for 30 s. The film coated on the glass slide was vacuum-dried for 24 h to remove the residual solvent. The thickness of the film was measured by the ellipsometric technique.

In the case of the preparation of the polyurethane/epoxy resin (PU/EP) IPN phenol-capped DR-19, the polyhydroxyl prepolymer, E44, and DANA were weighed according to the composition of the IPN and the molar ratios of NCO/OH and epoxy/NH<sub>2</sub> and dissolved in tetrahydrofuran to make up a 10% concentration. Then, the procedure was carried out in the same way as in the case of PA/EP IPN.

Alignment of the chromophores and crosslinking of the film were carried out in a corona poling apparatus with a heating rate of 2°C/min. The apparatus consisted of a tungsten needle as the positive electrode and a copper disc as the negative electrode with a distance of 1.5 cm between the electrodes. The optimum conditions for poling and crosslinking are as follows: As the temperature was increased 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 cooled naturally to 100°C and then quickly to room temperature by cooling with a water jacket. Finally, the

corona field was put off. The whole poling procedure needed 3 h. Another sample with the same composition and the same visible light absorption (difference of peak absorption < 2%) spin-coated on another glass slide was crosslinked by heating in the same way but without corona poling and was used as a reference.

### Characterization of the Poled Film

The visible light spectra of the IPNs were taken by a UV-240 spectrophotometer. The IR spectra of the IPNs were recorded on an IR-435 spectrophotometer using KBr crystal spin-coated with a polymerization mixture and cured at 160°C. DSC curves were obtained with a CDR-1 differential scanning calorimeter with a heating rate of 10°C/min. The thickness and refractive indices of the poled films were estimated by a TP-77 ellipsometric polarizing spectroscopy using a wavelength of 632.8 nm. The gel content of polyurethane, polyacrylate, epoxy resin, or IPNs was determined by immersing a weighed film in tetrahydrofuran for 24 h, followed by filtering, drying, and weighing the insoluble gel.

### Temporal Stability of the Second-order NLO Properties of the IPNs

The relaxation behavior of the second-order NLO properties of the IPNs was studied by monitoring the decay of the order parameter as a function of time at different temperatures. The order parameter ( $\phi$ ) 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 and Characterization of PU/EP IPNs

Though the crosslinked product obtained from the reaction of E-44 and DANA cannot form a uniform cured film owing to serious contraction, the IPNs prepared from E-44, DANA, phenol-capped NCO terminated DR-19, and the polyhydroxyl prepolymer appear as uniform films with good optical quality. The purpose of using phenol-capped NCO-terminated chromophores in the formation of the PU network is to avoid the reaction between NCO-terminated chromophores and moisture. The phenol-capped chromophores began to decap at about 120°C and then reacted with the polyhydroxyl prepolymer

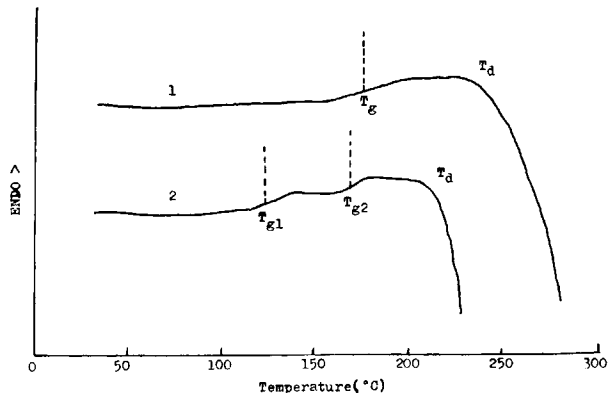
to form PU networks. Table I shows that the gel content of PU reached about 67% at 140°C for 30 min, whereas that of EP reached about 48%. This implies that the formation rates of the two networks show only a little difference, especially at 160°C. During formation of IPNs at 160°C, the gel content reached about 94 and 99% for 30 and 60 min, respectively. This indicates that the two kinds of networks formed simultaneously.

However, the isocyanate group may also react with the amino groups of DANA. Hence, there may occur some links between the two IPNs. Nevertheless, the IR spectra of the cured and uncured IPN films showed that at the molar ratio of epoxy/NH<sub>2</sub> = 1 during the synthesis of IPN the absorption peak at 1308 cm<sup>-1</sup> for the amino group and the peak at 910 cm<sup>-1</sup> for the epoxy group completely disappeared and no absorption peaks for the hydroxyl or NCO group appeared after curing and poling at 160°C for 1 h. Both the results of the IR spectra and the gel content indicate that a simultaneous PU/EP IPN was formed mainly through two different mechanisms upon heating at 160°C. The IPN film exhibited good transparency and its DSC curve (Fig. 1) shows that one broad glass transition temperature ( $T_g$ ) exists at about 172°C. The single broad  $T_g$  of the IPN suggests the comparatively less heterogeneity of the IPN, which may be attributed to the enhanced compatibility caused by the two polymer networks, containing the same chromophores, interpenetrating each other, and also to a little linkage between the two networks due to some probable reaction between amino and NCO groups.

Visible light absorption spectra of the reference film did not change after thermal crosslinking and poling, and IR spectra of the IPN film show no change of absorption peaks at 1338 cm<sup>-1</sup> for the nitro group and at 1600 cm<sup>-1</sup> for the phenyl group after heating and poling. These facts demonstrate that no evident de-

**Table I** Gel Content of Three Crosslinked Polymers and Two Kinds of IPNs Cured at Different Conditions

Polymer	Gel Content (%)		
	140°C, 30 min	160°C, 30 min	160°C, 60 min
Polyurethane	67.5	96.0	99.4
Epoxy resin	48.1	91.3	96.2
Polyacrylate	0	86.1	96.7
IPN (PU/EP = 50/50)	70.5	93.9	98.7
IPN (PA/EP = 50/50)	20.0	89.9	98.6



**Figure 1** DSC curves of the IPNs: (1) PU/EP = 50/50 (wt ratio); (2) PA/EP = 50/50 (weight ratio).

composition or volatilization of the IPN film occurred during heating at 160°C or with corona poling.

### Formation and Characterization of the PA/EP IPNs

Table I also shows that the gel content of the epoxy resin reached about 48% at 140°C for 30 min, whereas almost no gel of polyacrylate formed at the same conditions. However, at 160°C PA, EP and their IPNs possess a gel content over 85% for 30 min and over 96% for 60 min. The data of the gel content imply that formation of the epoxy resin is easier and faster than that of polyacrylate. It is probable that the heat of EP formation might promote the formation of the PA network, resulting in formation of simultaneous IPN. The presence of the EP network which formed first may prevent macrophase separation of the IPN. The IR spectra of the PA/EP IPN films showed that no absorption peaks for epoxy, amino groups, or double bonds appeared. Both the IR spectra and gel content demonstrated that the EP network and the PA network were formed simultaneously through two different mechanisms upon heating. Though the IPN film is still transparent, its DSC curve (Fig. 1) shows that two  $T_g$ 's exist at 122 and 165°C, which indicates that more microphase separation occurred in the PA/EP IPN than in the PU/EP IPN.

### Properties of the Poled IPN Films

Table II indicates some properties of the two kinds of poled IPNs. The decomposition temperature ( $T_d$ ) of PU/EP IPN is higher than that of PA/EP IPN, while the refractive index of the former is lower. To obtain a large second-order NLO effect, it is necessary to increase the density of chromophores on

**Table II** Some Properties of the PU/EP IPN and PA/EP IPN

IPN	Density at 20°C (g/cm <sup>3</sup> )	<i>n</i> (at 632.8 nm)	<i>T<sub>g</sub></i> (°C)	<i>T<sub>d</sub></i> (°C)	<i>N</i> (Molecules/cm <sup>3</sup> )
PU/EP = 50/50	1.27	1.6306	172	230	$7.80 \times 10^{20}$
PA/EP = 50/50	1.28	1.6748	122, 165	210	$7.28 \times 10^{20}$

one side and to select a chromophore with a large  $\beta$  value and with a large dipole moment  $\mu$ . In this work,  $\beta$  and  $\mu$  values of the 4-(4'-nitrophenylazo)aniline chromophore is  $125 \times 10^{-30}$  esu (at 1.064  $\mu\text{m}$ ) and 8.7 D, respectively. The density of the chromophores (*N*) of the PU/EP IPN and of the PA/EP IPN was found through absorbance measurement to be  $7.80 \times 10^{20}$  and  $7.28 \times 10^{20}$  molecules/cm<sup>3</sup>, respectively.

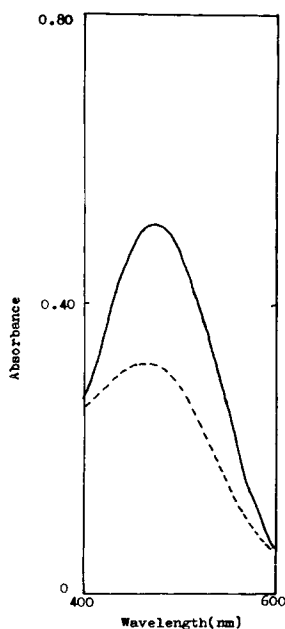
The macroscopic second-order NLO polarizability can be calculated according to a one-dimensional rigid oriented gas model<sup>5</sup> as follows:

$$\chi^2 = N\beta F \langle \cos^3 \theta \rangle$$

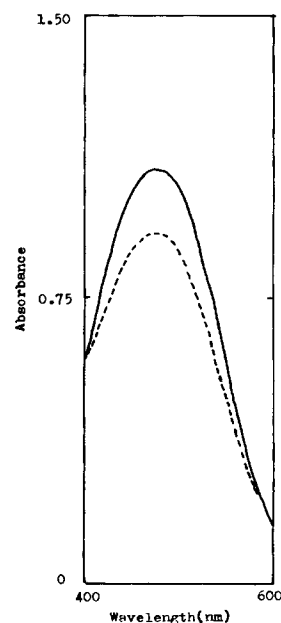
where *N* is the density of the chromophore molecules, and *F*, the local field factor.  $\langle \cos^3 \theta \rangle$  is the average alignment factor which can be estimated according to the approximate relationship between  $\langle \cos^3 \theta \rangle$  and the order parameter ( $\phi$ ):  $\langle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

Figures 2 and 3 illustrate the visible light absorbance spectra of the PU/EP and PA/EP IPN films before and after corona poling, respectively. During corona poling under a high-voltage field and heating the chromophore groups of IPN aligned along the field direction, resulting in decrease of the peak absorbance of the incident light perpendicular to the film. The order parameter of the poled PU/EP IPN film can reach about 0.38 and the second-order NLO coefficient  $\chi^2$  was approximately calculated to be about  $1.7 \times 10^{-7}$  esu, according to the one-dimensional rigid oriented gas model. The exact value of  $\chi^2$  will be determined with second harmonic generation in our future work.

It must be mentioned that the PA/EP IPN film in Figure 3 was obtained first by heat pretreatment at 140°C for  $\frac{1}{2}$  h and then poling at 160°C for 1 h. The PA/EP IPN film showed white spots without heat pretreatment at 140°C. Thus, the order parameter of the poled film cannot reach a higher value, since some crosslinkage occurred during pretreatment. The order parameter was only 0.17 according



**Figure 2** Absorption spectra of the PU/EP IPN film: (—) unpoled; (---) poled.



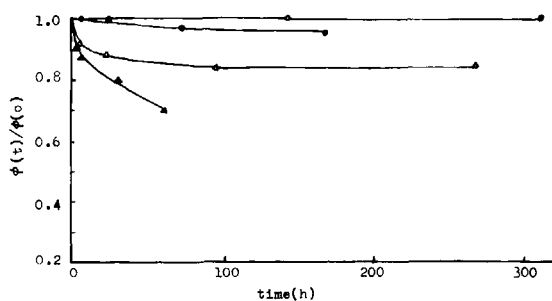
**Figure 3** Absorption spectra of the PA/EP IPN film: (—) unpoled; (---) poled.

to the absorbance measurement and  $\chi^2$  was estimated approximately to be  $1.2 \times 10^{-7}$  esu.

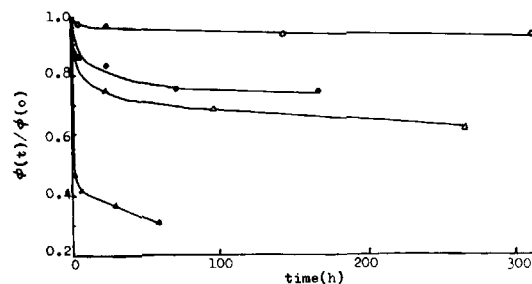
### Relaxation of Chromophore Alignment in the Poled IPN Films

The order parameter was used to describe the chromophore alignment which correlates to the NLO properties of the IPN. Figure 4 indicates the temporal behavior of the order parameter  $\phi(t)/\phi(o)$  for the poled PU/EP IPN films at different temperatures. It can be seen that the poled IPN film shows good stability at 120°C and the ratio of  $\phi(t)/\phi(o)$  remains at about 96% for 167 h. This slow relaxation at high temperature can be explained by the IPNs 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. However, at 140°C, relaxation seems to occur quickly at the initial stage, then very slowly after 100 h, and the ratio remained at 85% even after 268 h. The initial instability at 140°C may be due to the lower decomposition temperature of the epoxy network containing DANA chromophores. The visible light absorbance of the reference sample without poling decreased about 5% at 140°C within 100 h. At 165°C, which is near to the  $T_g$  of the PU/EP IPN, the aligned chromophores relaxed quite quickly and  $\phi(t)/\phi(o)$  decreased to 71% within 60 h and the visible light absorbance of the reference sample decreased about 30% at 165°C within 60 h.

Figure 5 shows the temporal behavior of the order parameter  $\phi(t)/\phi(o)$  for the poled PA/EP IPN films at different temperatures. It can be noted that the temporal stability of the NLO properties of the PA/EP IPN is poorer than that of PU/EP IPN. The poled PA/EP IPN film kept 93% of the order parameter at 100°C within 315 h and maintained only



**Figure 4** Temporal behavior of the order parameter of the poled PU/EP IPN film at different temperatures: (○) 100°C; (●) 120°C; (△) 140°C; (▲) 165°C.



**Figure 5** Temporal behavior of the order parameter of the poled PA/EP IPN film at different temperatures: (○) 100°C; (●) 120°C; (△) 140°C; (▲) 165°C.

74% at 120°C within 167 h. This is probably due to the lower  $T_g$  of the PA network (122°C).

### CONCLUSION

Simultaneous IPNs based on polyurethane and epoxy resin containing 4-(4'-nitrophenylazo)aniline chromophore groups showed stable second-order NLO properties at 120°C and can be synthesized with a chromophore density of  $7.80 \times 10^{20}$  molecules/cm<sup>3</sup> and gel content over 98%. The poled PU/EP IPN film is transparent and exhibits only one  $T_g$  at 172°C. Its  $\chi^2$  was calculated approximately to be  $1.7 \times 10^{-7}$  esu. Simultaneous IPNs based on polyacrylate and epoxy resin containing 4-(4'-nitrophenylazo)aniline chromophore groups can be synthesized with a chromophore density of  $7.28 \times 10^{20}$  molecules/cm<sup>3</sup> and gel content over 98%. The poled PA/EP IPN film shows two  $T_g$ 's and its  $\chi^2$  was estimated to be  $1.2 \times 10^{-7}$  esu. The temporal behavior of the NLO properties of the PA/EP IPN film is poorer than that of the PU/EP IPN film.

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