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Synthesis and properties of two crosslinked polymers with stable non-linear optical properties

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Two kinds of crosslinked polymers, containing 4-(4′-nitrophenylazo) aniline chromophore groups, were synthesized. Crosslinked polyacrylate was synthesized by polymerization of Dispersed Red-19 (DR-19) diacrylate, whereas crosslinked polyurethane was obtained by the reaction between (β-hydroxy propyl acrylate–DR-1 methacrylate) copolymer and phenol-capped isocyanate-terminated DR-19. The crosslinked polymers were characterized by infra-red spectra, gel content and differential scanning calorimetry. The crosslinked polyacrylate and the crosslinked polyurethane exhibit glass transition temperatures at 125 and 160°C, respectively. Thin, transparent, poled films of both crosslinked polymers 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 visible light absorbance measurement according to a one-dimensional, rigid oriented gas model. Long-term stability of the dipole alignment at 140°C was demonstrated for the crosslinked polyurethane.

(Keywords: crosslinked polymer; non-linear optical material; polyurethane; polyacrylate; chromophore)

INTRODUCTION

Recently, increased interest has been shown in the frequency doubling and electro-optical modulation of polymers exhibiting second-order non-linear optical (NLO) properties. Such polymers have been studied because of their good NLO properties, ultrafast optical response, high laser damage threshold, ease of processing and potentially unlimited architectural flexibility for optimizing optical non-linearities. Several second-order NLO polymers have been developed to exhibit large second-order NLO coefficients comparable to those of the inorganic NLO materials, such as lithium niobate, that are currently used in electro-optical devices. For a second-order NLO polymer to be useful in practical integrated electro-optical devices, it must contain chromophores aligned in a non-centrosymmetric manner by poling. Additionally, the alignment of NLO chromophores in the poled polymer must be sufficiently stable at temperatures of up to 80°C. For instance, an electro-optical modulator for telecommunication applications needs to be stable over the range from −70 to 70°C for many years. Similarly, an electro-optical modulator in a desktop computer may be exposed to temperatures as high as 80°C during use. However, the major disadvantage of NLO polymers is the decay of their second-order non-linearities. This decay is attributed to the relaxation of the NLO chromophores from the electric field induced non-centrosymmetric alignment to a random configuration.

To reduce the relaxation or decay of the dipole alignment, crosslinking of the polymer containing the chromophore groups has been used to retard the mobility of the polymer segments, thereby preventing the aligned NLO chromophores from relaxing to a random orientation. Tripathy *et al.*[1] synthesized a photocrosslinked poly(vinylcinnamate) with a photocrosslinkable dye, the poled film of which was stable at 160°C for several hours. Chen *et al.*[2] obtained new polymers containing disperse red dye as an NLO active chromophore in conjunction with photocrosslinkable groups. The NLO coefficient of the crosslinked polymer was stable for 1000 h after poling. Jeng *et al.*[3] 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[4] 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[5]. However, the NLO coefficient of the poled film decreased to about 80% of its initial value within 400 h at 100°C. Levenson *et al.*[6] 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.

This paper deals with the synthesis and poling of crosslinked polyurethane and crosslinked polyacrylate containing 4-(4′-nitrophenylazo) aniline chromophore

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groups, as well as the study of temporal stability of NLO properties at different temperatures.

EXPERIMENTAL

Synthesis of chromophore compounds

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

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

Synthesis of monomers

Methacrylate-terminated DR-1 was prepared as follows: To a mixture of 8.8 g DR-1, 35 mg *p*-hydroxyphenol, 100 ml dichloromethane and 4.3 ml triethylamine under a nitrogen atmosphere, 10 ml of a dichloroethane solution of 3.2 ml freshly prepared methacryloyl chloride was added dropwise with stirring at room temperature for 3 days. The reaction product was washed with saturated $NaHCO_3$ solution and saturated NaCl solution successively, each two times. 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 red powder with 89% yield (m.p. 91–92°C).

Acrylate-terminated DR-19 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 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 chromophore 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. 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 group could be detected by aniline. After cooling the mixture, the product was precipitated out with ethanol. Yield was 91.5%.

Synthesis of prepolymer

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

Preparation of poled polymer film

According to the composition of crosslinked polyacrylate desired, weighed amounts of DR-19 diacrylate and DR-1 methacrylate were dissolved in tetrahydrofuran (THF) to a concentration of 10%. This solution was filtered and the filtrate was spin-coated onto a clean glass slide at a rotation speed of 1500 rev min^{-1} for 30 s. The film coated on the glass slide was vacuum dried for 24 h to remove the residual solvent. Film thickness was measured by an ellipsometric technique to be $\sim 0.5\,\mu$m.

Polyurethane film was prepared by dissolving weighed amounts of polyhydroxyl prepolymer and phenol-capped DR-19 at a molar ratio of 1/1 in THF to give a concentration of 10%. Spin-coating and drying of polyurethane thin films were carried out as in the same manner as described for polyacrylate films.

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 UV-240 spectrophotometer. Infra-red (i.r.) spectra were recorded on an 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 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), using a wavelength of 632.8 nm. Gel content of the polyurethane or polyacrylate was determined by immersing a weighed film in THF for 24 h, followed by filtering, drying and weighing the insoluble gel.

The relaxation behaviour of the second-order NLO properties of the polymers was studied by monitoring the

Table 1 Gel content of polyurethanes and polyacrylates cured under different conditions

Crosslinked polymer	Gel content (%)		
	140°C, 30 min	160°C, 30 min	160°C, 60 min
Polyurethane	67.5	96.0	99.4
Polyacrylate[a]	0	86.1	96.7

[a] DR-19 diacrylate/DR-1 methacrylate (wt ratio) = 100/0

Table 2 Comparison of gel content and reactant loss during synthesis of polyacrylates at different reactant ratios

DR-19 diacrylate / DR-1 methacrylate (weight ratio)	Reactant loss (%)	Gel content (%)
100/0	1.4	96.7
80/20	3.8	95.9
60/40	7.6	63.9
45/55	9.1	0

decay of the order parameter as a function of time at different temperatures.

RESULTS AND DISCUSSION

Formation of crosslinked polymers

The purpose of using phenol-capped isocyanate-terminated chromophores is to avoid the reaction between isocyanate-terminated DR-19 and moisture. The phenol-capped chromophore began to decap at about 120°C and then react with the polyhydroxyl copolymer to form a polyurethane network. *Table 1* shows that the gel content of the polyurethane reached ~ 65% after 30 min at 140°C, whereas almost no gel formation was observed for the polyacrylate under the same conditions. However, after 30 min at 160°C, polyurethane network formation was almost complete while ~ 86% of the polyacrylate network was formed; crosslinking of the latter was almost complete 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, and that no absorption peak attributable to double bonds appeared for the polyacrylate formed under the same conditions.

In order to raise the concentration of chromophores in the crosslinked polyacrylate, we attempted to copolymerize DR-19 diacrylate with DR-1 methacrylate. The results showed that copolymerization at weight ratio of 80/20 DR-19 diacrylate/DR-1 methacrylate produced a crosslinked polyacrylate with a chromophore group content of 1.08×10^{21} molecules cm^{-3}, as compared with 8.39×10^{20} molecules cm^{-3} for the DR-19 diacrylate homopolymer. However, as shown in *Table 2*, with increasing content of DR-1 methacrylate used in the copolymerization, the reactivity of the monomer mixture seems to decrease and loss of monomer during the thermal crosslinking step increases, resulting in decreasing gel content. This may be due to the fact that DR-1 methacrylate contains fewer double bonds and is more sterically hindered than DR-19 diacrylate, which contains a urethane segment. As the weight of DR-1 methacrylate exceeds that of DR-19 diacrylate, no gel content is found in the reaction product obtained at 160°C for 1 h, as noted in *Table 2*.

Chromophore content of the crosslinked polyurethane did not increase with increase of the NCO/OH molar ratio used in polymerization.

Properties of poled crosslinked polymer films

The surface of the poled polymer films appeared very even and smooth, and no change was evident after immersion in dimethylformamide or tetrahydrofuran. 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 at 1338 cm^{-1} for the nitro group and at 1600 cm^{-1} for the phenyl group 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 3* indicates some properties of the poled crosslinked polyurethane and polyacrylate. Both the density and the refractive index of the polyacrylate are higher than those of the polyurethane. D.s.c. curves showed that the glass transition temperatures (T_g) for the crosslinked polyurethane and polyacrylate are 160 and 125°C, respectively. The decomposition temperatures (T_d) of the two crosslinked polymers are almost the same.

In order to obtain a large second-order NLO effect, it is necessary to increase the density of chromophores on one side of the polymer and to select a chromophore with a large β value and a large dipole moment μ. The β and μ values of the 4-(4′-nitrophenylazo)aniline chromophore used in this work are 125×10^{-30} esu (at 1.064 μm) and 8.7 D, respectively. The densities of chromophores (N) of the crosslinked polyurethane and polyacrylate were found through absorbance measurements to be 9.42×10^{20} and 8.39×10^{20} molecules cm^{-3}, respectively.

The macroscopic second-order NLO polarizability can be calculated according to a one-dimensional, rigid oriented gas model[7] as follows:

$$\chi^2 = N\beta f^{2\omega}(f^{\omega})^2 \langle\cos^3\theta\rangle \qquad (1)$$

where N is the density of chromophore molecules and f the local field factor. The superscripts 2ω and ω refer to second harmonic and fundamental radian frequencies,

Table 3 Some properties of the poled crosslinked polymers

Crosslinked polymer	Density at 20°C (g cm^{-3})	Refractive index at 632.8 nm	T_g (°C)	T_d (°C)	N (molecules cm^{-3})
Polyurethane	1.2961	1.637	160	295	9.42×10^{20}
Polyacrylate	1.3067	1.703	125	295	8.39×10^{20}

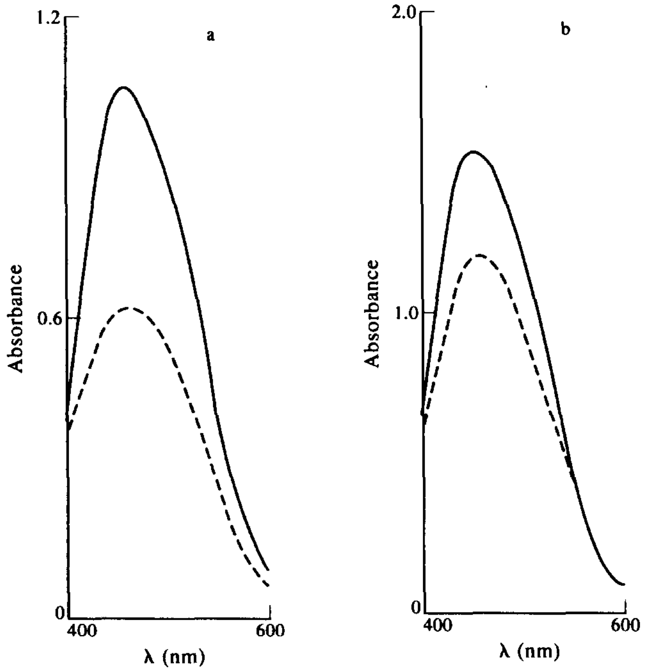

Figure 1 Absorption spectra of poled (- - -) and unpoled (——) crosslinked polymer films: (a) polyurethane; (b) polyacrylate.

respectively. Usually $f^{\omega} = (n_{\omega}^2 + 2)/3$, where n_{ω} is the refractive index of the poled film at light frequency ω. $\langle\cos^3\theta\rangle$ is the average alignment factor, which can be estimated according to its approximate relationship with the order parameter (ϕ): $\langle\cos^{-3}\theta\rangle \doteq (0.6\phi)^{1/2}$. 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 (A_1) to the poling direction: $\phi = 1 - A_1/A_0$.

Figure 1 presents the visible light absorbance spectra of the crosslinked polymer films before and after corona poling. 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 the peak absorbance of the incident light perpendicular to the film. The order parameter of the poled polyurethane film can reach about 0.4 and the second-order NLO coefficient χ^2 was calculated to be approximately 2.2×10^{-7} esu (at 1.064 μm) according to equation (1). The exact value of χ^2 should be determined with second harmonic generation in our future work. For the poled polyacrylate film the order parameter and χ^2 are about 0.23 and 1.7×10^{-7} esu, respectively.

Relaxation of chromophore alignment in poled polymer films

Both polyacrylate and polyurethane poled crosslinked films exhibited excellent temporal stability at room temperature. No change of order parameter (ϕ) was observed over 2 months.

Figure 2 indicates the temporal behaviour of the order parameter ratio $\phi(t)/\phi(0)$ for the poled crosslinked polyacrylate film at different temperatures. It can be seen that this film maintained 90% NLO activity for 320 h at 100°C after an initial rapid lowering of activity. Even at 120°C, which is slightly lower than the T_g of the crosslinked polyacrylate (125°C), the film still exhibited about 80% NLO activity for 160 h. This is attributed to the presence of a high degree of crosslinking, which retards the relaxation of aligned chromophore groups. No difference was observed between the behaviours of NLO properties for crosslinked polyacrylates with DR-19 diacrylate/DR-1 methacrylate weight ratios of 100/0 and 80/20.

Figure 3 shows that the poled crosslinked polyurethane film had excellent thermal stability of NLO properties at temperatures as high as 140°C, except for a small initial rapid decrease. This result can be explained by the high degree of crosslinking and the high T_g (160°C) of the polyurethane. However, the NLO activity of the crosslinked polyurethane decreased seriously at 165°C; only 75% NLO activity was maintained for 60 h. At 165°C not only is relaxation of the aligned chromophore groups easier, but also the chromophore groups begin to decompose. It was observed from the visible light absorption spectra of the reference sample that the absorbance of the chromophore decreased to 84% of the original after 60 h at 165°C, whereas no change of the absorbance occurred at 140°C for a long time.

Both kinds of poled crosslinked polymer exhibit a rapid relaxation of aligned chromophore groups at the initial stage at higher temperature, as shown in *Figures 2* and *3*. This is because rapid cooling was used during the

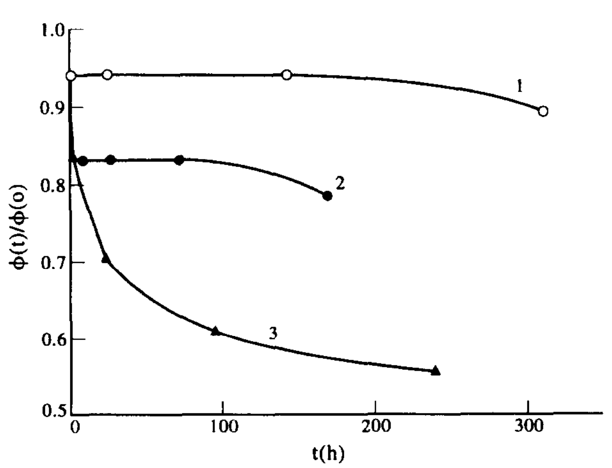

Figure 2 Temporal behaviour of the order parameter ratio $\phi(t)/\phi(0)$ of the poled polyacrylate films at different elevated temperatures: (1) 100°C; (2) 120°C; (3) 140°C

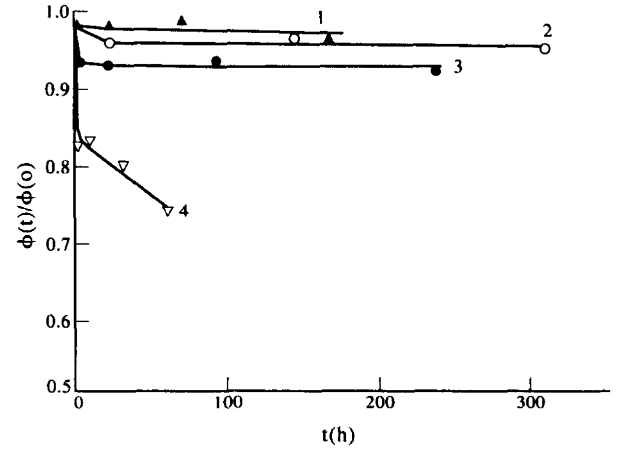

Figure 3 Temporal behaviour of the order parameter ratio $\phi(t)/\phi(0)$ of the poled polyurethane films at different elevated temperatures: (1) 120°C for the film cooled naturally under corona field for 12 h; (2) 100°C; (3) 140°C; (4) 165°C

latter stage of poling, resulting in a non-equilibrium state of the poled polymer film and some voids in the neighbourhood of the aligned chromophore groups, which are likely to relax when the film is subsequently heated. If the film, after poling and curing at 160°C for 1 h, is cooled naturally to room temperature while maintaining the corona field for 12 h, so as to allow the poled film reach a state of equilibrium, the NLO stability of the film thus obtained is enhanced at the intial stage, as shown in *Figure 3*. The poled crosslinked polyurethane film treated in such a way can maintain 98% NLO activity at 120°C for 160 h and 93% NLO activity at 140°C for 240 h, without an initial rapid decrease of activity.

CONCLUSIONS

Polymers with stable non-linear optical properties can be obtained by crosslinking special types of polyurethane and polyacrylate containing 4-(4′-nitrophenylazo) aniline chromophore groups. The crosslinked polyacrylate was synthesized by polymerization of DR-19 diacrylate, whereas the crosslinked polyurethane was obtained by the reaction between (β-hydroxypropyl acrylate–DR-1 methacrylate) copolymer and phenol-capped isocyanate-terminated DR-19. The poled crosslinked polyacrylate showed a long-term stability of NLO activity at 100°C, whereas the poled crosslinked polyurethane, cooled naturally to room temperature under a corona field for 12 h, can maintain 98% NLO activity at 120°C for 160 h and 93% NLO activity at 140°C for 240 h

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