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R. J. Jeng[a]; Y. M. Chen[b]; J. Kumar[b]; S. K. Tripathy[a]
[a] Departments of Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts [b] Departments of Physics, University of Massachusetts Lowell, Lowell, Massachusetts

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NOVEL CROSSLINKED GUEST–HOST SYSTEM WITH STABLE SECOND-ORDER NONLINEARITY

R. J. JENG (1), Y. M. CHEN (2), J. KUMAR (2), and S. K. TRIPATHY* (1)

Departments of Chemistry (1) and Physics (2)
University of Massachusetts Lowell
Lowell, Massachusetts 01854

ABSTRACT

An epoxy-based nonlinear optical (NLO) polymeric material incorporating 4-(4′-nitrophenylazo) phenylamine has been synthesized and subsequently functionalized with acryloyl groups. A glass transition temperature (T_g) of 108°C and a degradation temperature (air) of 251°C were recorded. After crosslinking at 160°C for 2 hours, the T_g of the polymer increased to 146°C. In order to increase the nonlinear optical chromophore concentration and the crosslinking density, the crosslinkable NLO dye, 2,4-acryloyloxy (4′-phenylazo nitrobenzene), was processed and poled in this epoxy-based NLO material matrix in a manner similar to a typical guest–host system, and thermally crosslinked under the above condition in the poled phase. The crosslinked guest–host material was found to be amorphous with a T_g of approximately 132°C. It also exhibits a second-order nonlinear optical coefficient d_{33} of 14.14 pm/V at a maximum doping level of 33% by weight of the NLO dye, and retains 93% of its original d_{33} value after being subjected to thermal treatment at 100°C for 168 hours. The behavior of the crosslinked polymer and the crosslinked guest–host polymer is discussed.

INTRODUCTION

Enhanced temporal stability of second-order NLO properties in a poled polymer system can be obtained when a certain degree of crosslinking is introduced [1–4]. In the crosslinked polymer, the NLO moieties are covalently bound into a rigid polymer network and are, therefore, much less likely to relax to random orientation. Such an approach was first reported by Eich et al. [2] in an epoxy system in which the NLO moieties are incorporated either in the multifunctional epoxy or amine components.

A new class of photo-crosslinked systems has been achieved by a variation on the guest–host approach [5–7]. The guest NLO molecules and host polymer contain functionalized groups through which crosslinking may be introduced. The system can be photo-crosslinked in the poled state to yield a material with stable optical nonlinearity. A guest–host system containing a crosslinkable NLO dye and a thermally-crosslinkable NLO epoxy-based polymer was chosen for the present investigation. Both the dye and polymer are functionalized with the same type of reactive groups. This approach is based on the intermolecular and intramolecular thermal-crosslinking reactions of a functionalized NLO dye and an epoxy prepolymer (Fig. 1). In this system, not only the NLO chromophore content is increased by adding the crosslinkable NLO dye, but the crosslinking density increases as well.

The second-order susceptibility is directly proportional to the concentration of the NLO moieties, and the temporal stability is related to the degree of crosslinking in the polymer matrix. Thus, large and stable NLO properties are expected from these crosslinked polymers. In this study we report our investigations on a new guest–host crosslinking system based on the epoxy of the diglycidyl ether of Bisphenol A and 4-(4′-nitrophenylazo) phenylamine (Disperse Orange 3) functionalized with acryloyl groups, and the crosslinkable NLO dye, 2,4-acryloyloxy (4′-phenylazo nitrobenzene). The acryloyl group was chosen as the reactive functional group. At a reasonably high temperature (>140°C), rapid reaction between the acryloyl groups is anticipated without the aid of catalyst or initiator. Upon heating the reactive epoxy polymer and functionalized NLO dye form a crosslinked network.

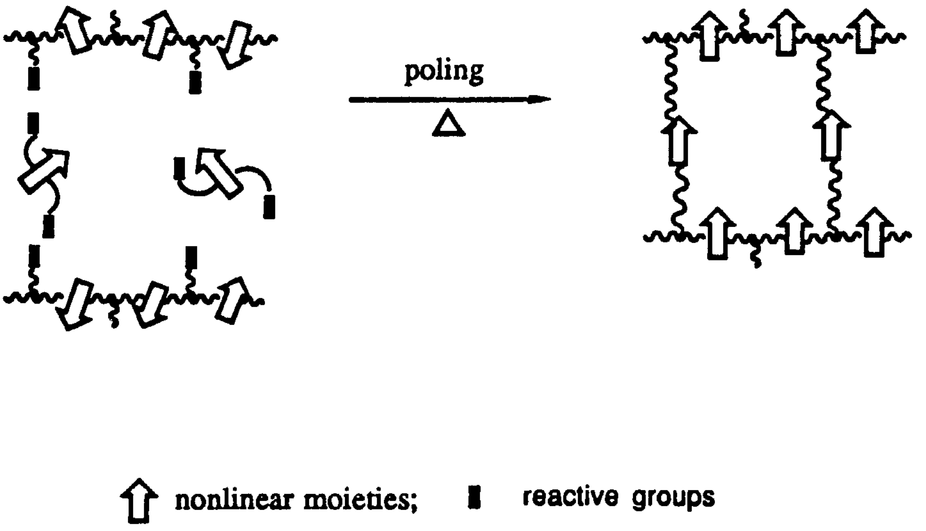

FIG. 1. Schematic for the preparation of stable second-order nonlinear optical polymers.

We report on the stability at 100°C and at room temperature (25°C) of the second-order nonlinearity of the crosslinked polymer films. The linear and second-order nonlinear optical properties of poled and crosslinked polymer were measured at 1064 nm and are reported.

EXPERIMENTS

Materials

Chemical synthesis of functionalized epoxy polymer of diglycidyl ether of Bisphenol A and 4-(4′-nitrophenylazo) phenylamine with the reactive acryloyl groups (BPAZO) is described elsewhere [3]. A 38% functionalization of hydroxyl groups into acryloyl groups was achieved. The content of functionalization was measured by the acetyl chloride titration method [8]. The chemical structure of the polymeric product is illustrated in Fig. 2.

The crosslinkable NLO dye 2,4-acryloyloxy (4′-phenylazo nitrobenzene) (APAN) was synthesized by the functionalization of hydroxyl groups of 4-(4′-nitrophenylazo) resorcinol (commercially available) into acryloyl moieties [3] (Fig. 2).

BPAZO was dissolved in mixed propylene glycol methyl ether acetate and 1,4-dioxane (volume ratio 3:1) with a weight ratio of 1:10. The solution was spin-coated onto glass slides, quartz slides, and KBr plates and then baked at 50°C

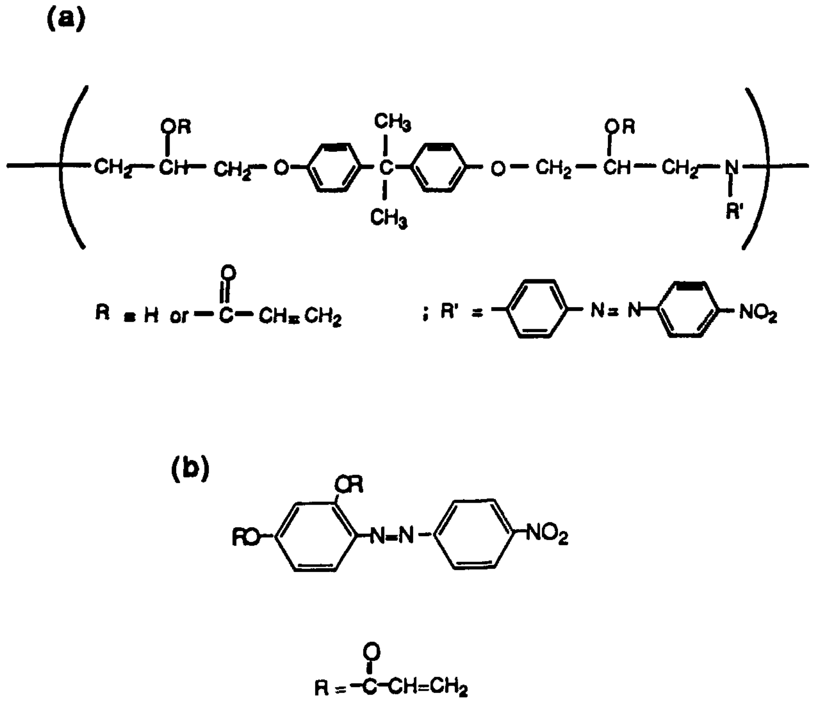

FIG. 2. The chemical structures of (a) BPAZO and (b) APAN.

under vacuum for 12 hours. Typical thickness obtained was approximately 0.60 μm. Indices of refraction at 532 nm and 1000 nm were measured using an ellipsometer. The samples of the crosslinked guest-host system BPAZO/APAN were prepared in the same manner as BPAZO. The weight ratio of BPAZO to APAN was 2:1. If the ratio is higher than 2:1, immiscibility is apparent in the thin films of this guest-host material.

Instruments

The glass transition temperatures, T_g, and the reaction behavior of the polymers were obtained from differential scanning calorimetry using a TA Instrument DSC2910 at a heating rate of 10 K/min. The isotrack technique of DSC was applied to obtain the optimum curing conditions. The thermal degradation temperatures (T_d) of the polymers were determined on a TA Instrument TGA2950 with a heating rate of 10 K/min under air. UV/Vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded on a Mattson FTIR.

The poling technique used was corona poling in the wire to plane arrangement [9, 10]. Thin films of the polymers were poled and cured simultaneously. The poling was started at a temperature 10°C below the T_g of the polymer and then increased by 10 K/min. The crosslinking reaction proceeds reasonably fast only at temperatures above 140°C (this will be discussed in the Thermal Analysis Section). When the poling temperature reached 140°C, the temperature was advanced at a rate of 1°C/min. The corona field was carefully controlled in order to avoid electrical breakdown due to the high conductivity of epoxy-type materials. The strength of the electric field used for poling was approximately 5.0 MV/cm [11]. Thin films of the polymer were heated to a temperature at which the crosslinking is fast (approximately 160°C) with the electric field on. After a time sufficient to bring the T_g close to the curing temperature (2 hours), the sample was cooled to room temperature with the electric field on.

The second-order nonlinear optical coefficient (d_{33}) of the poled thin film was measured by second harmonic generation (SHG) from 1064 nm laser radiation. The relaxation behavior of the second-order nonlinear optical properties was studied by the decay of the second-order nonlinear optical coefficient (d_{33}) as a function of time at both room temperature (25°C) and at 100°C after poling and curing. These measurements were made with a Q-switched Nd-YAG laser (Quantel 660A). The p-polarized incident beam was separated by a beam splitter. One of the beams was passed through the sample, and the other was passed through a y-cut quartz reference. Both transmitted fundamental waves were blocked using $CuSO_4$ solution. Two narrow band interference filters centered around 532 mm were used to allow the second harmonic (SH) beam to pass. The SH signals were detected by two photomultiplier tubes, one for the quartz reference and the other for the sample. The signals were amplified and averaged in a boxcar integrator (Stanford Research SR-250). Figure 3 shows the experimental setup for the SHG measurement.

RESULTS AND DISCUSSION

Thermal Analysis

TGA scans at 10 K/min of BPAZO, APAN, and BPAZO/APAN (weight ratio 2:1) are shown in Fig. 4. The degradation temperatures, as taken from the

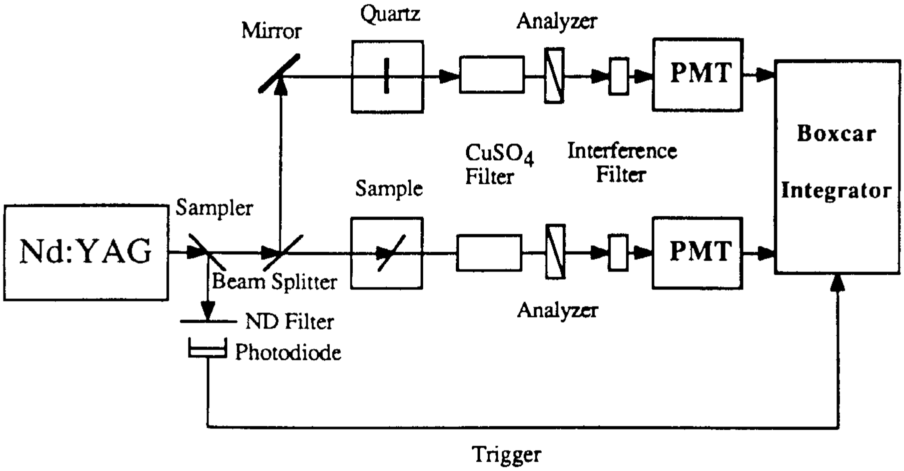

FIG. 3. Experimental setup for SHG measurement.

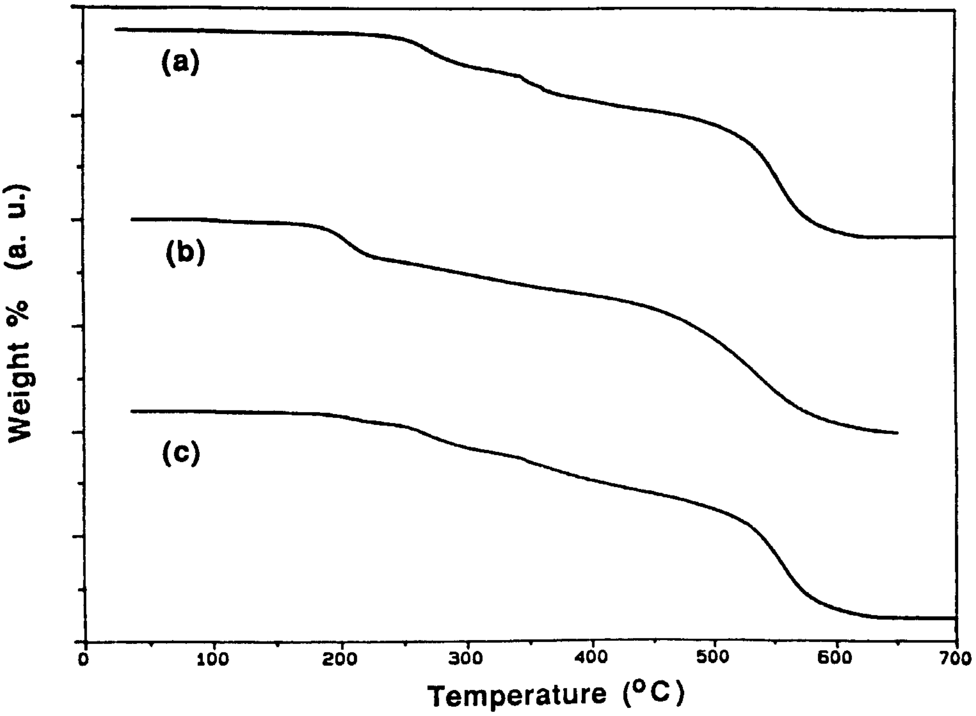

FIG. 4. Thermal degradation behavior of (a) BPAZO, (b) APAN, an (c) BPAZO/APAN.

onset point of the step transition are 251, 187, and 197°C, respectively. The curing temperature was kept below 180°C to avoid degradation.

A DSC scan at 10 K/min of BPAZO is shown at the top of figure 5. The exothermic reaction (curing) starts at approximately 140°C. The DSC isotrack technique permits good control of constant temperature of the sample, and is used to optimize the curing conditions. High curing temperatures are necessary for high T_g systems because of low reaction rates after vitrification. However, curing and thermal degradation often compete at such high temperatures [12]. These two factors were taken into consideration in our search for the optimum curing conditions. When the sample of BPAZO was heated at 160°C for 2 hours, its T_g advanced from 108 to 146°C (bottom of Fig. 5). On heating for another 2 hours at 160°C, the T_g of BPAZO remained unchanged. Similarly, after the sample of BPAZO was heated at 170°C for 2 hours, its T_g advanced from 108 to 148°C. On the other hand, upon heating the pristine polymer for 3 hours at 150°C, its T_g advanced from 108°C to only 136°C. Based on the above information, the optimum curing condition chosen for BPAZO and BPAZO/APAN is isothermal heating of the sample at 160°C for 2 hours (unless otherwise stated, this curing condition was used throughout the study).

DSC scans at 10 K/min of a mixed sample, BPAZO/APAN (weight ratio 2: 1), before and after curing are shown in Figs. 6 and 7, respectively. The curve for the pristine sample shows that the melting point of APAN is 140°C. On curing, the melting peak disappears and a T_g appears at about 132°C. This suggests that the crosslinkable NLO dyes have reacted after curing.

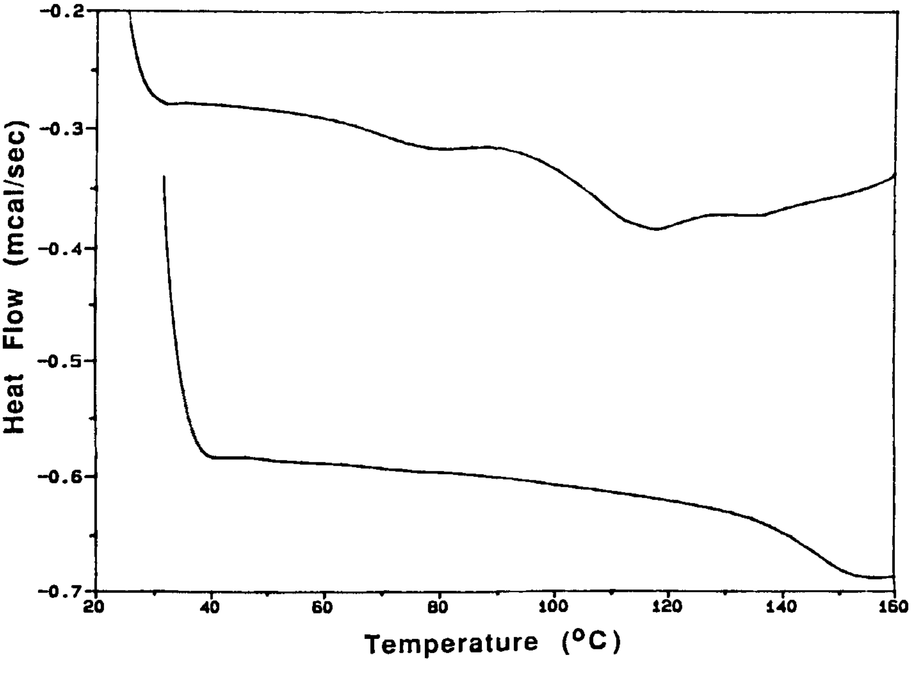

FIG. 5. DSC thermograms of BPAZO.

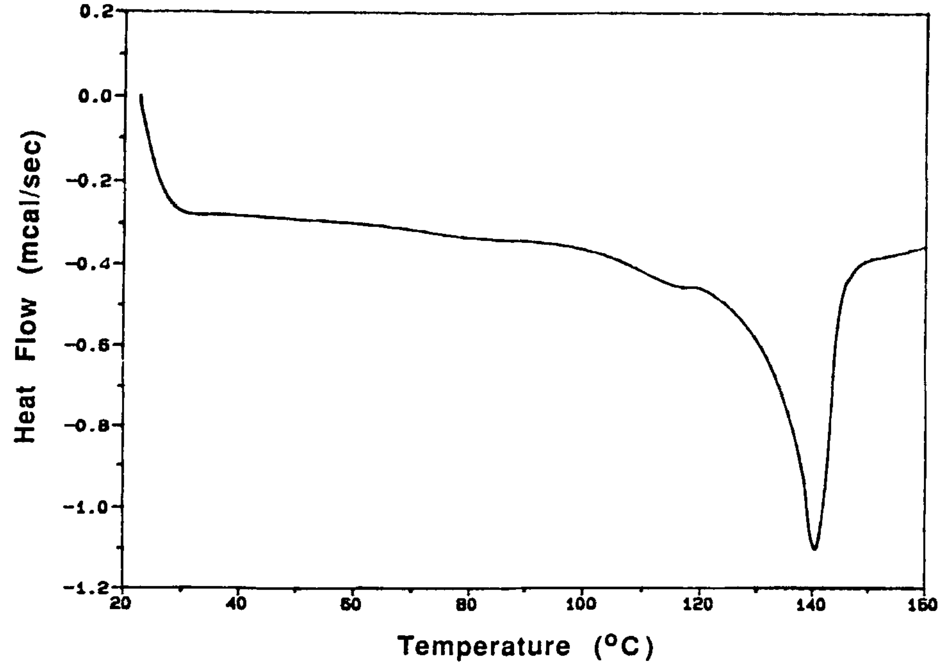

FIG. 6. DSC thermogram of pristine BPAZO/APAN.

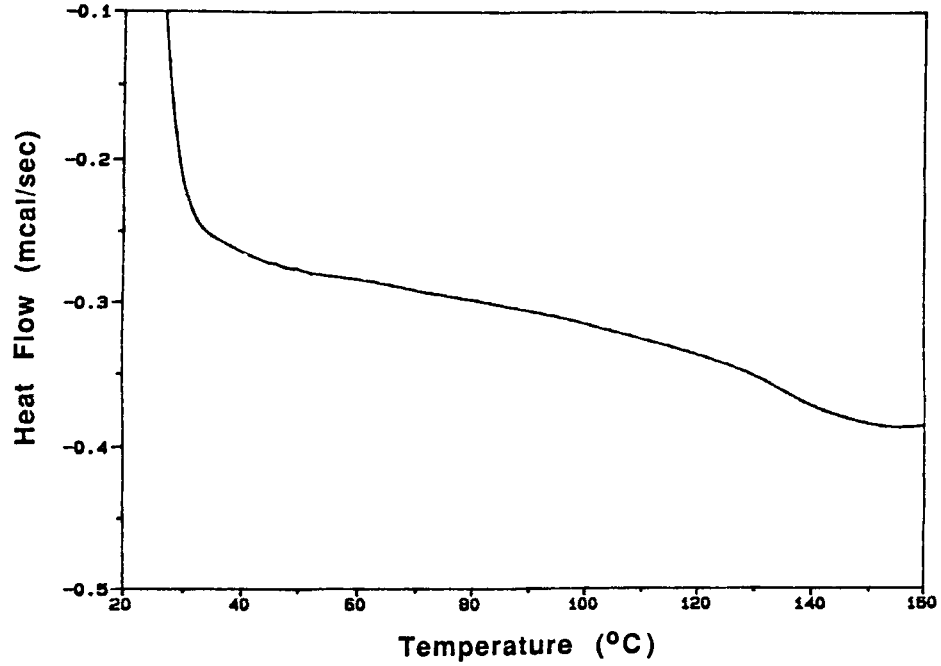

FIG. 7. DSC thermogram of cured BPAZO/APAN.

The ΔC_p (T_g) are 0.353 and 0.200 $J \cdot g^{-1} \cdot K^{-1}$ for the cured BPAZO and BPAZO/APAN, respectively. In comparison to the cured BPAZO, the decrease in ΔC_p (T_g) of the cured BPAZO/APAN indicates a net decrease in both chain mobility and vibrational contributions to C_p. This is considered to be a consequence of the formation of additional crosslinks [13, 14].

IR Study of the Chemical Reactions

Upon heating, the BPAZO undergoes reactions that can be analyzed by IR spectroscopy. As shown in Fig. 8, after 2 hours of heating at 160°C, the carbonyl absorption peak at 1722 cm^{-1} shifts to 1730 cm^{-1} and becomes slightly broader. This indicates that a certain extent of crosslinking has occurred. In addition, an absorption peak emerges at 1680 cm^{-1} after curing. This suggests that intermolecular hydrogen bonding exists in the cured sample. The hydrogen bonding weakens the C=O bond, resulting in absorption at lower frequency [15]. The absorption peaks of the major functional groups such as nitro (1338 cm^{-1}), phenyl (1601 cm^{-1}), and ether (1242 cm^{-1}) have decreased only slightly in intensity after curing [the methyl absorption peak (2964 cm^{-1}) as the reference]. It is, therefore, concluded that little thermal degradation has occurred during curing.

For the BPAZO/APAN, as shown in Fig. 9, after 2 hours of isothermal heating at 160°C, the carbonyl absorption peak at 1730 cm^{-1} not only shifts to

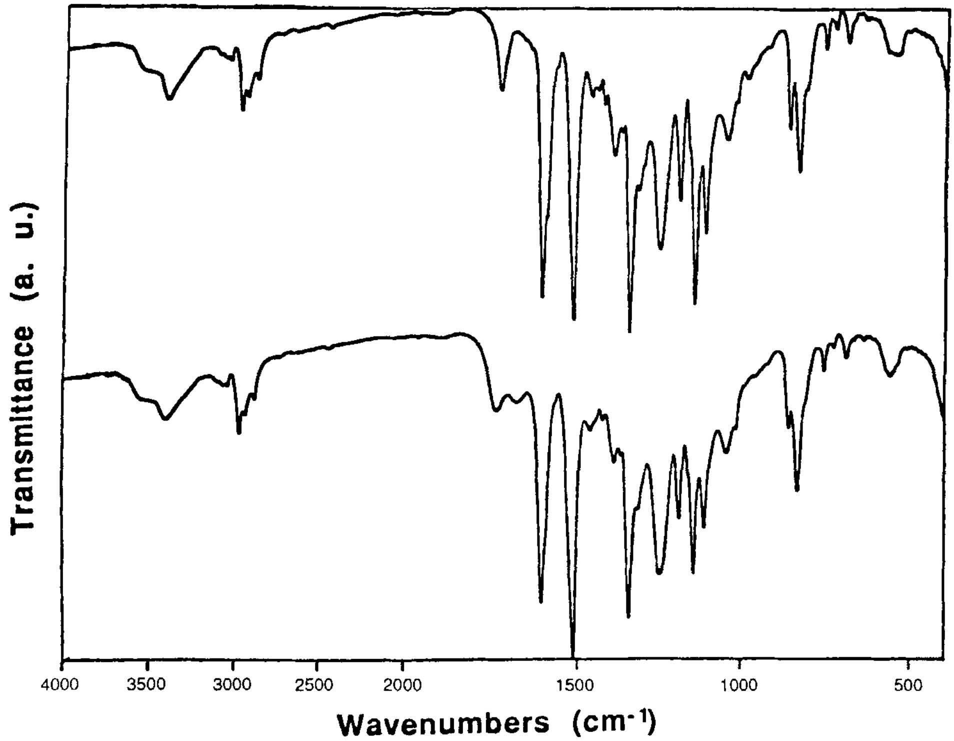

FIG. 8. Infrared spectra of BPAZO. Top: pristine. Bottom: cured.

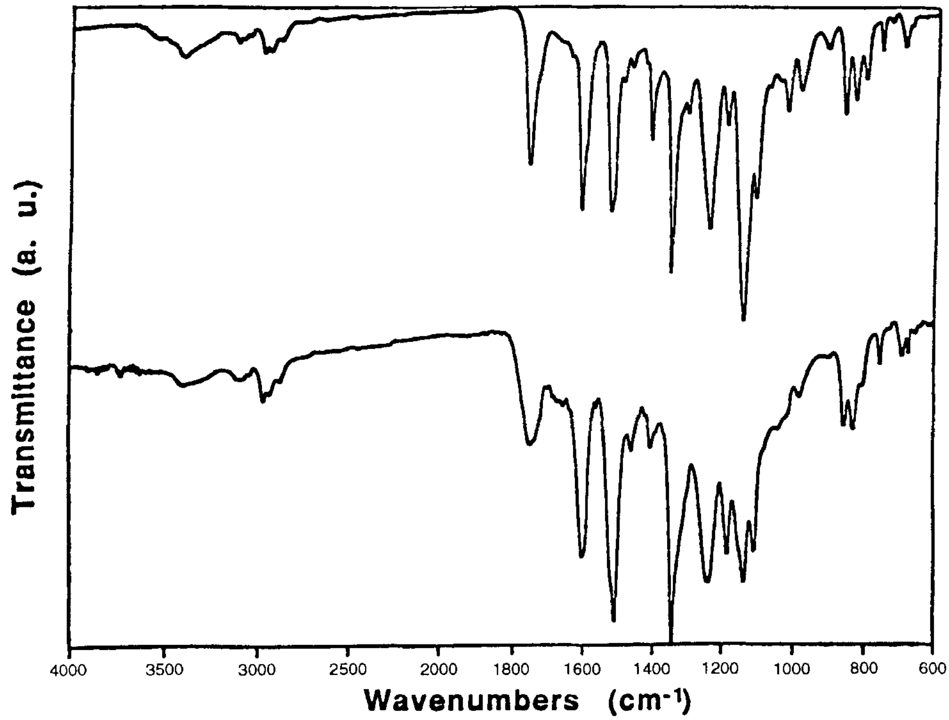

FIG. 9. Infrared spectra of BPAZO/APAN. Top: pristine. Bottom: cured.

1747 cm^{-1} but also becomes much broader. This suggests that a significant portion of the conjugated carbonyl groups are now nonconjugated. It was also observed that the absorption peaks of the major functional groups of the cured sample, such as nitro (1340 cm^{-1}), phenyl (1599 cm^{-1}), and ether (1238 cm^{-1}), all decrease to some extent in intensity [the methyl absorption peak (2964 cm^{-1}) as the reference]. This suggests that a certain amount of functionalized NLO dye either sublimed away or degraded during the curing process at 160°C.

Linear and Nonlinear Optical Properties

The second-order NLO properties of BPAZO and BPAZO/APAN have been characterized by second harmonic generation. The d_{33} values obtained for the 1064 nm fundamental wavelength are listed in Table 1 along with some linear optical properties. The poled and cured films have d_{33} values of 8.86 and 14.14 pm/V for BPAZO and BPAZO/APAN, respectively. The poled and crosslinked guest-host system BPAZO/APAN has a higher d_{33} value because it has a higher NLO chromophore density than BPAZO.

The temporal stability at 100°C of second-order nonlinearity after poling and crosslinking of BPAZO and BPAZO/APAN has been investigated (Fig. 10). The result clearly indicates that the poled and cured guest-host system BPAZO/APAN shows much better stability. Over 168 hours at 100°C, a reduction of 7% in d_{33} was observed for the poled and cured BPAZO/APAN. Most of this loss was in the first

TABLE 1. Optical Properties of Cured BPAZO and BPAZO/APAN

	BPAZO	BPAZO/APAN
Thickness (μm)	0.6	0.6
Refractive indices, λ (μm):		
0.532	1.762	1.712
1.000	1.664	1.592
d_{33} (pm/V) at 1.06 μm	8.86	14.14
d_{31} (pm/V) at 1.06 μm	2.42	3.98

few hours of heating. On the other hand, a reduction of 35% in d_{33} was observed for the poled/cured BPAZO under the same thermal treatment. As mentioned earlier, the T_g of BPAZO/APAN is 13°C lower than BPAZO. However, the crosslinking density of BPAZO/APAN is much higher than BPAZO because many more reactive sites (acryloyl groups) are available in the crosslinked guest-host system. This is confirmed by the comparison of ΔC_p (T_g) in the previous Thermal Analysis Section. More crosslinks between the polymer chains restrict the molecular motion of the segments and hence prevent the randomization of the ordered NLO molecules. In addition, the nonlinear optical coefficients (d_{33}) of the poled/cured BPAZO and BPAZO/APAN remained unchanged under ambient condition for at least 168 hours, the time to which these measurements were carried out.

UV-Vis Absorption Characteristics of Poled Films

To investigate the absorption behavior as a function of time, the absorption spectrum was taken regularly over a 168-hour period under thermal treatment at

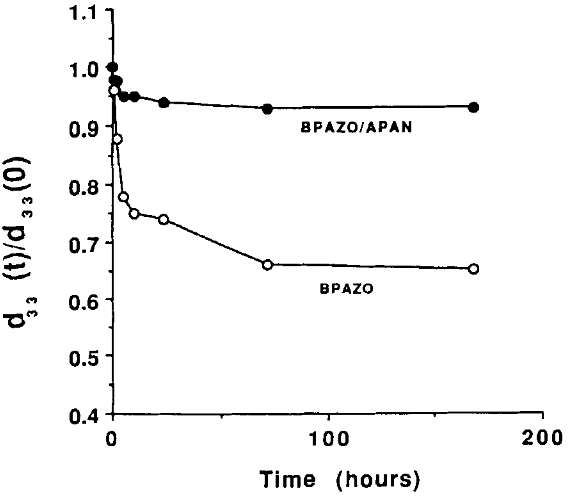

FIG. 10. Time behavior of second-order nonlinear optical coefficient of poled/cured BPAZO and BPAZO/APAN. The samples were subjected to thermal treatment at 100°C.

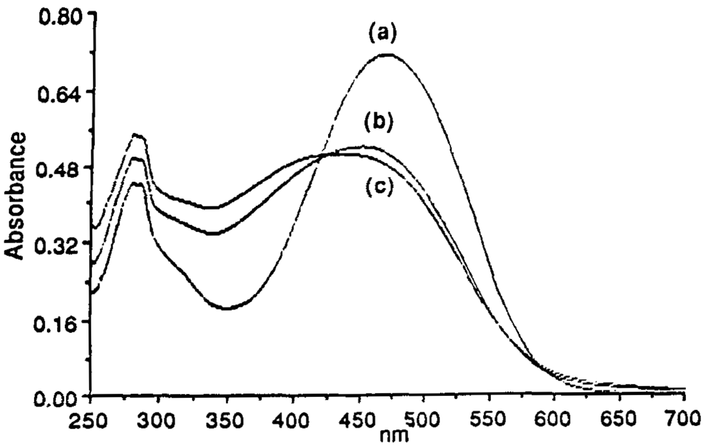

FIG. 11. UV-Vis absorption spectra of BPAZO: (a) pristine, (b) right after poling/curing, (c) poled/cured samples subjected to thermal treatment at 100°C for 168 h.

100°C for poled/cured BPAZO. An absorption peak at λ_{max} = 463 nm existed before poling/curing. After poling/curing, λ_{max} shifts to 447 nm with a decrease of absorbance. During the next 168 hours λ_{max} shifted further toward shorter wavelengths with a slight decrease in absorbance (Fig. 11). In addition, an isobestic point is shown at 430 nm in Fig. 11. This implies that the polymer and perhaps the chromophore possibly undergo a certain extent of conformation change during the thermal treatment at 100°C.

For BPAZO/APAN there are two absorption peaks, λ_{max} = 352 and 464 nm, corresponding to APAN and Disperse Orange 3 dye chromophores, respectively, in the spectrum of the pristine sample (Fig. 12). The absorption spectrum was also taken regularly over a 168-hour period under thermal treatment at 100°C. Immedi-

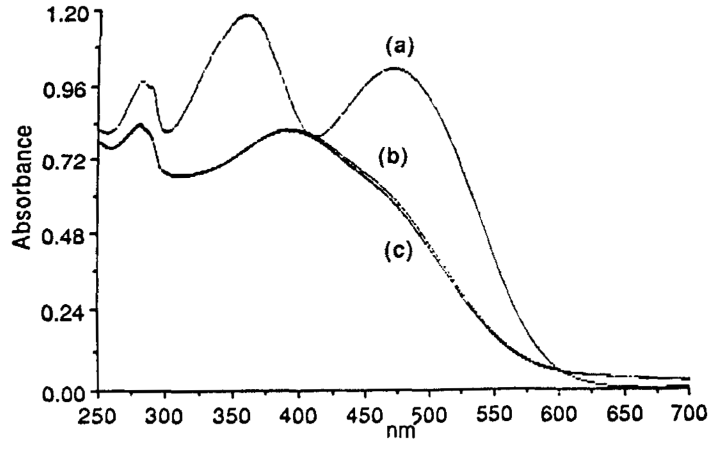

FIG. 12. UV-Vis absorption spectra of BPAZO/APAN: (a) pristine, (b) right after poling/curing, (c) poled/cured samples subjected to thermal treatment at 100°C for 168 h.

ately after poling/curing, a decrease in absorbance was observed. In addition, the two chromophores responded to the poling/curing process differently. Similar to the BPAZO case, the absorption peak of the Disperse Orange 3 chromophore shifted toward shorter wavelengths (the shoulder around 450 nm in spectrum b after poling/curing. On the other hand, the absorption peak of the APAN dye chromophore shifted toward longer wavelengths, $\lambda_{max} = 388$ nm, immediately after poling/curing. During the next 168 hours the absorption spectrum remained almost unchanged. This result suggests that the dye/polymer system did not degrade or sublime throughout the whole period of thermal treatment.

CONCLUSION

Linear epoxy polymer containing Disperse Orange 3 dye and crosslinkable groups, and crosslinkable NLO dye molecules have been synthesized. The uncrosslinked guest-host system has a very high NLO chromophore concentration and good solubility in common organic solvents. The curing time for this system is relatively short (i.e., 2 hours) compared to a typical thermally crosslinked epoxy [2] (approximately 16 hours). Highly stable second-order nonlinearity at 100°C has been achieved through this crosslinked guest-host polymer. The d_{33} of BPAZO/APAN retains 93% of its original value even after the poled/cured sample is subjected to thermal treatment at 100°C for over 168 hours. It is concluded that the temporal stability of the NLO properties was significantly improved by increasing the crosslinking density of the polymer. This type of material was obtained through doping a crosslinkable NLO dye into a crosslinkable polymer matrix.

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