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13. ABSTRACT (Maximum 200 Words)

A new guest-host system based on the azo dye disperse red 1 and phenyl siloxane polymer has been investigated. The second order susceptibility of the polymer cured at 220 °C was found to be stable at room temperature and decays to 60 % of its original value after being maintained at a temperature of 100 °C for nearly 30 hours. The linear and second-order nonlinear optical(NLO) properties of this material are measured and reported. Curing at higher temperature is expected to lead to greater stability of NLO properties.

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A New Guest-Host System: Towards Stable Second-order Optical Nonlinearity

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A new guest-host system based on the azo dye disperse red 1 and phenyl siloxane polymer has been investigated. The second order susceptibility of the polymer cured at 220 ^{o}C was found to be stable at room temperature and decayed to 60 % of its original value after being maintained at a temperature of 100 ^{0}C for nearly 30 hours. The linear and second-order nonlinear optical(NLO) properties of this material are measured and reported. Curing at higher temperature is expected to lead to greater stability of NLO properties.

1. Introduction

Second order nonlinear optical polymeric materials have recently been extensively investigated [1-6]. The interest in these materials is mainly due to their large electronic nonlinear susceptibility and the ease of processing them into good optical quality thin films. Dye incorporated second order materials have the potential for fast waveguide electro-optic modulation and frequency doubling applications provided the nonlinearity shows reasonable stability at ambient temperatures. Unfortunately a system of aligned (poled) dipoles is not in a state of thermodynamic equilibrium and at finite temperatures would inevitably relax to a random configuration in the absence of a poling field. However, the motion of the poled molecules within the host may be restricted, so that susceptibility shows no appreciable decay for extended length of time at room temperature. The usual approach is to incorporate the NLO chromophores in a polymer which has a high glass transition temperature (T_g). Thus at temperatures much lower than the glass transition temperature the motion of the poled molecules is considerably restricted. A somewhat different approach is to incorporate the NLO chromophores in a host which can be poled at lower temperatures and subsequently crosslinked to provide effectively a high T_g polymer with very restricted molecular motion. The polymers can be crosslinked by either thermal means [5, 7, 8] or by photochemical means by irradiation with violet or UV radiation [9, 10, 11, 12] .

In this paper we report our investigations on a guest-host system based on the azo dye disperse red 1 and phenyl siloxane polymer. Upon heating to high temperatures, the phenyl siloxane polymers lead to a crosslinked network. This process, with polycondensation (and subsequent vitrification) of molecular or polymeric precursors, is usually used to prepare glasses

and ceramics [13, 14]. Phenyl siloxane polymers have been processed at high temperatures (to 420 ^{o}C) to lead to optically clear low loss glasses. The guest-host samples can be poled and cured simultaneously. This ensures that the NLO dye will be locked in the three-dimensional network of the glass matrix in a noncentrosymmetric way with acceptably slow relaxation even at elevated temperatures. We report on the stability at room temperature and at 100 ^{0}C of the second order nonlinearity of the cured polymer films. The linear and second-order nonlinear optical properties of poled and cured DR 1/phenyl siloxane polymer were measured at 1.06 microns and are reported.

2. Materials and processing

The samples for which data are presented use Accuglass 204 (A204), a phenyl siloxane polymer in alcohol solvents available from Allied Signal. The formula for the compound provided by the manufacturer is as follows:

$$[(SiO)_a(C_6H_5)_b(OC_2H_5)_c(OH)_d]_n$$

$$a \geq 1;\ b, c, d \leq 0.5;\ n=5\text{-}100$$

The guest molecule disperse red 1 (DR1), 4-[ethyl(2-hydroxyethyl)amino]-4'-nitroazobenzene (Figure 1) is available from Aldrich Chemical and was recrystallized from benzene. 20 mg of DR1 in 0.14 g of 1, 4-Dioxane was added into 2 g of A204 solution. Films were prepared by spin-coating the dye/siloxane polymer solutions onto 1-mm-thick transparent microscope slides (Fisher

Premium), and then baked at 70 ^{0}C under vacuum for 12 hours to remove residual solvent trapped in samples. Typical thickness obtained was approximately 600 nm. Indices of refraction at three different wavelengths (532 nm, 633 nm and 1064 nm) was measured using an ellipsometer. The absorption characteristics of the NLO molecules in the polymeric film were recorded on a UV-Vis-NIR spectrophotometer. The absorption peak wavelength of the NLO chromophore and the other linear optical properties of the A204/DR1 sample are summarized in table 1.

The film was poled with a corona discharge in a wire-to-plane configuration. The details of the corona poling set-up was reported earlier [15]. After the sample was poled at 80 ^{0}C for 6 min, the temperature was elevated up to 220 ^{0}C to vitrify the sample. During this period (curing time) the poling field was kept on. The sample was maintained at 220 ^{o}C for 4 hours, and then cooled down to room temperature with the poling field left on. The curing temperature was chosen to be 220 ^{0}C because the thermal decomposition temperature of DR1 was determined to be approximately 254 ^{0}C by a thermogravimetric analyzer (Dupont TGA2950) at a heating rate of 10 ^{0}C/min in air.

3. Second harmonic and linear electro-optic measurements

The second order NLO properties of the poled A204/DR1 sample was measured by second harmonic generation (SHG) and electro-optical modulation techniques. The polarized Q-switched Nd:YAG laser with 10 ns pulse width and 20 Hz repetition rate was used as the light source. The typical energy per pulse of the laser was 15 mJ. The fundamental laser beam was blocked by

$CuSO_4$ solution and a 532 nm interference filter after passing through the sample. The second harmonic signal was detected by a photomultiplier tube, and averaged over 300 pulses in a boxcar integrator. The SH intensity of a Y-cut single crystal of quartz with known thickness and d_{11} value (d_{11}=0.364 pm/V) [16] was measured as a reference mounted at the same position as that of the sample. The detailed experimental set-up and calculations of the second-order NLO coefficient d_{33} have been previously discussed [17, 18]. The measurement of linear electro-optic coefficient, r_{33}, was performed utilizing the method described by Teng et al. [19] (Table 2). The details of the experimental arrangement and the calculation of r_{33} have been described earlier[19, 20].

4. Results and discussion

The curing behavior of A204 was studied by FTIR (Mattson Instruments) and differential scanning calorimetery (ramp 10 ^{0}C/min.). The dried A204 has an extremely broad glass transition zone from 60 ^{0}C to 130 ^{0}C due to the wide molecular weight distribution. After 4 hours of curing at 220 ^{0}C, the glass transition shifts to a much higher temperature region (110 ^{0}C to 252 ^{0}C).

After curing of A204 at 220 ^{0}C for 4 hours, an appreciable decrease of absorbance in IR spectra is observed due to the disappearance of hydroxyl groups around 3400 cm^{-1}, Si-ethoxyl bonds at 1136 cm^{-1}, hydroxyl and ethoxyl groups at 951 cm^{-1} [21, 22] (Fig. 2). Monosubstituted phenyl ring attachment to Si can be identified by the absorption peaks at 738 cm^{-1} and 698 cm^{-1} [21, 22]. The absorbances of these two peaks decrease slightly after curing. The absorption peak of Si-O-Si increases moderately after curing [21, 22]. From the IR spectrum, formation of a crosslinked network due to thermal condensation with the removal of the hydroxyl and ethoxyl

moieties is clearly indicated. The cured A204/DR1 sample was soaked in THF (good solvent for DR1) for 2 hours. The solvent did not extract any measurable concentration of dye from the cured sample. This implies that the NLO dye is firmly locked in the glass matrix.

The stability of second-order NLO properties of the poled/cured sample was monitored both at room temperature and at 100 ^{0}C by monitoring the SH signal with time. A 4.7% decay was observed after heating the sample to 100 ^{0}C for a 1 hour period. The rate of decay of the SH signal became smaller for longer heating times. The SH signal for poled/cured A204/DR1 sample was monitored over a period of 30 hours. The experimental results are plotted in Fig. 3. The second harmonic coefficient, $d_{33}(t)$, is quite stable at room temperature as seen in Fig. 3 and decays slowly at 100 ^{0}C. The stability could be further improved if an NLO dye with a higher degradation temperature is used as the guest, permitting curing at higher temperatures without the concomitant degradation of the NLO dye. Curing at higher temperatures can lead to more extensive crosslinking and smaller relaxation at 100 ^{0}C. The dye densities could be considerably enhanced by using siloxane polymers with covalently attached NLO dyes.

One of the problems encountered in the poling process of guest host systems at high temperatures is the sublimation of the dye at elevated temperatures. As long as the polymer is not vitrified there is considerable loss of NLO chromophores at high temperatures. After the process of vitrification the dye molecule loss is much less. Fig. 4 shows the absorption data (curve a) of the dye/polymer film before the crosslinking and poling process. During the initial heating of the film to raise its temperature to 220 ^{0}C for the curing process a substantial amount of the dye sublimes away and deposits on surrounding surfaces. The poled and crosslinked film shows a much smaller absorbance due to sublimation as well as orientation of the dye molecules (curve b).

It is important to note that the dye absorption spectrum shape is similar to the spectrum obtained before the curing cycle. This confirms that the azo dye left in the cured film has not degraded during the curing cycle. A guest host system was recently reported with a polyimide host [23]. However the UV-Visible spectrum showed a drastic difference before and after the curing cycle suggesting extensive dye degradation during the curing process. Curve c in Fig. 4 shows the absorption spectrum after heating the poled and cured sample for additional 138 hours at 100 ^{0}C. The increase in absorption of the sample is due to the slow but inevitable randomization of the polar orientation of the dye at 100 ^{0}C. The problem of the NLO dye loss in the curing cycle can be minimized by using siloxanes with covalently attached NLO chromophores [24].

The cured A204/DR1 sample has an absorption peak at wavelength 496 nm. The second harmonic coefficients were calculated by taking into consideration the absorption present at the doubled frequency and these values are obtained resonantly enhanced. The values of d_{33} and d_{31} obtained were 1.54 pm/V and 0.47 pm/V respectively. The ratio of d_{33} and d_{31} was about 3.3. The error in the measured values are mainly due to the errors in the values of refractive indices and thicknesses measured experimentally and uncertainties of a single crystal quartz reference. We estimated an error of 20% in values of d_{33} and d_{31} reported.

In conclusion, we have shown that a guest -host system based on crosslinked phenyl siloxane polymer and DR1 has excellent room temperature stability and a slow decay at 100 ^{0}C in a period of 30 hours. The stability of second order susceptibility achieved in this work is limited by the NLO chromophore degradation temperature. Higher cure temperatures can result in further vitrification of the material and increased stability at 100 ^{0}C. Siloxane polymers functionalized with NLO chromophores capable of withstanding higher cure temperatures may lead to thin films

with large and stable second order nonlinearity.

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Figure captions

Fig. 1. The chemical structure of disperse red 1.

Fig. 2. Infrared spectra of Accuglass 204, from bottom to top: pristine, cured.

Fig. 3. Time behavior of second harmonic coefficient of Accuglass 204 with DR1.

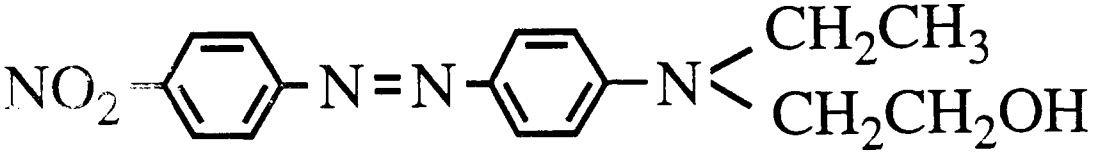
Fig. 4. UV-Vis absorption spectra of A204/DR1, from top to bottom: (a) pristine; (c) poled/cured samples, thermal treatment at 100 ^{0}C for 128 hrs; (b) right after poling/curing.

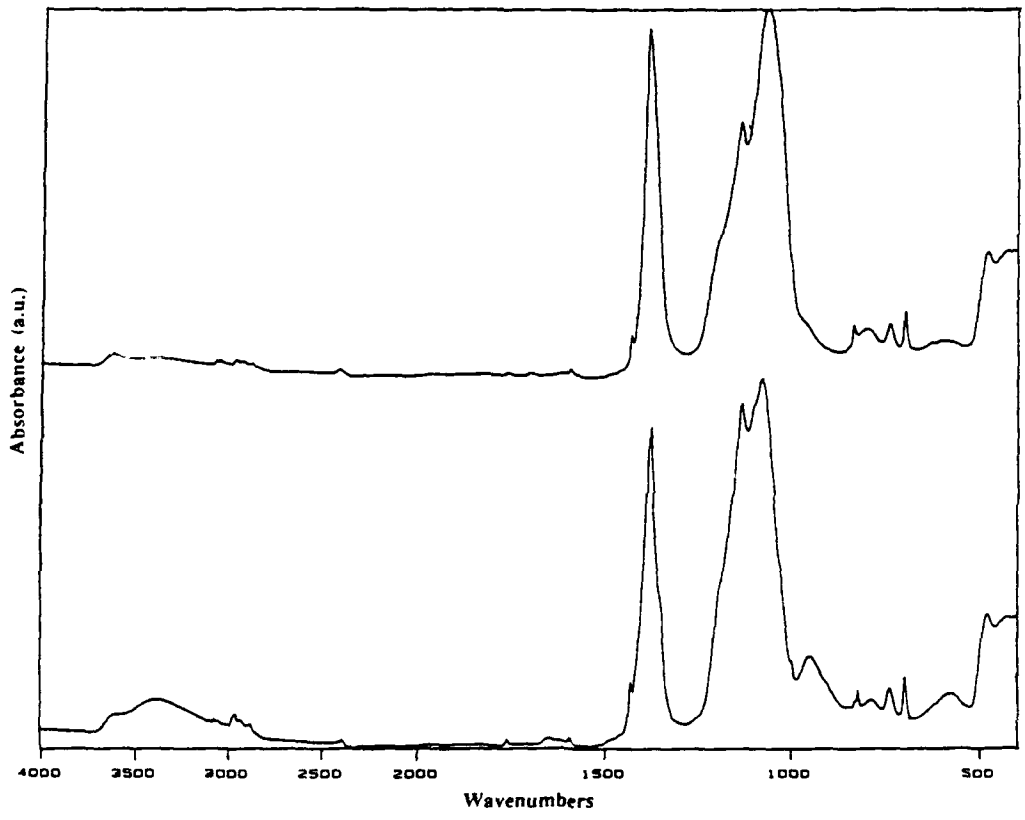
Table 1. Linear optical properties of Accuglass 204 with DR1.

Absorption peak wavelength (nm)	Thickness (nm)	n at wavelength (nm) 532	633	1064
496	600	1.577	1.555	1.488

Table 2. Second-order NLO properties of Accuglass 204 with DR1.

d_{33} (pm/V) at 1064 nm	d_{31} (pm/V) at 1064 nm	r_{33} (pm/V) at 633 nm
1.54	0.47	0.71

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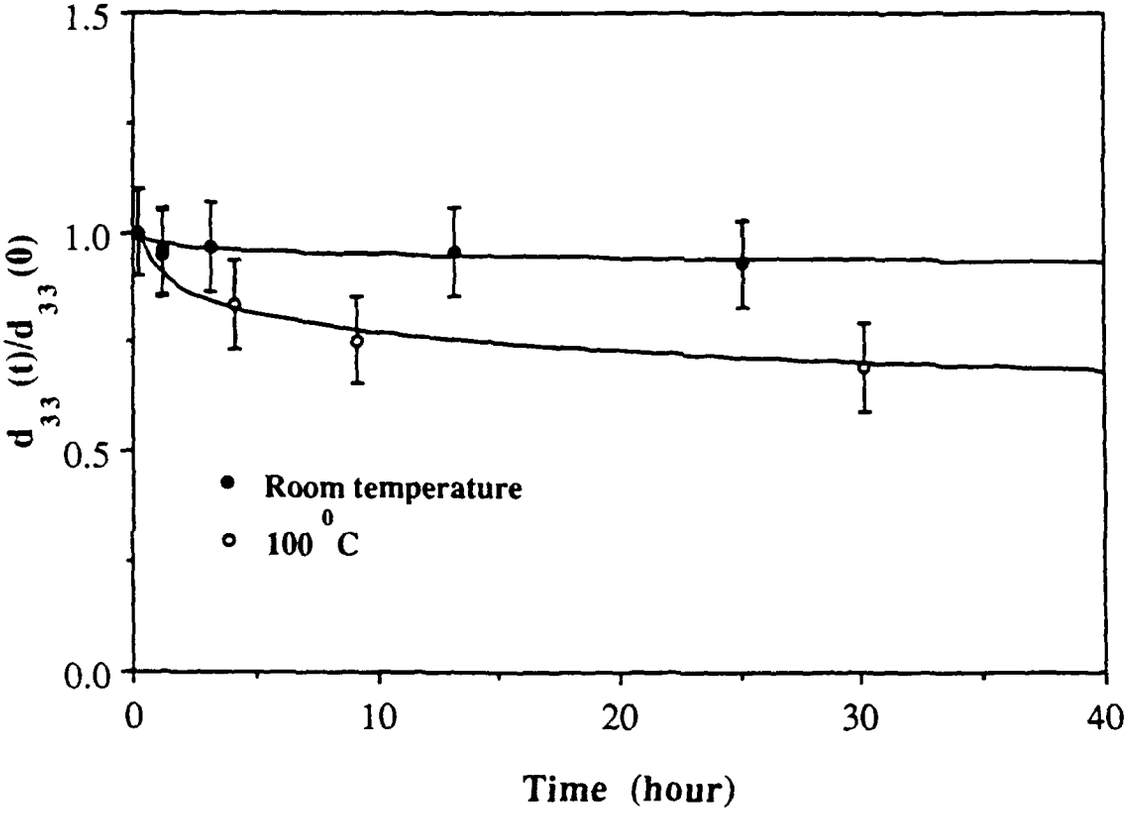
Wavenumbers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Room temperature
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20
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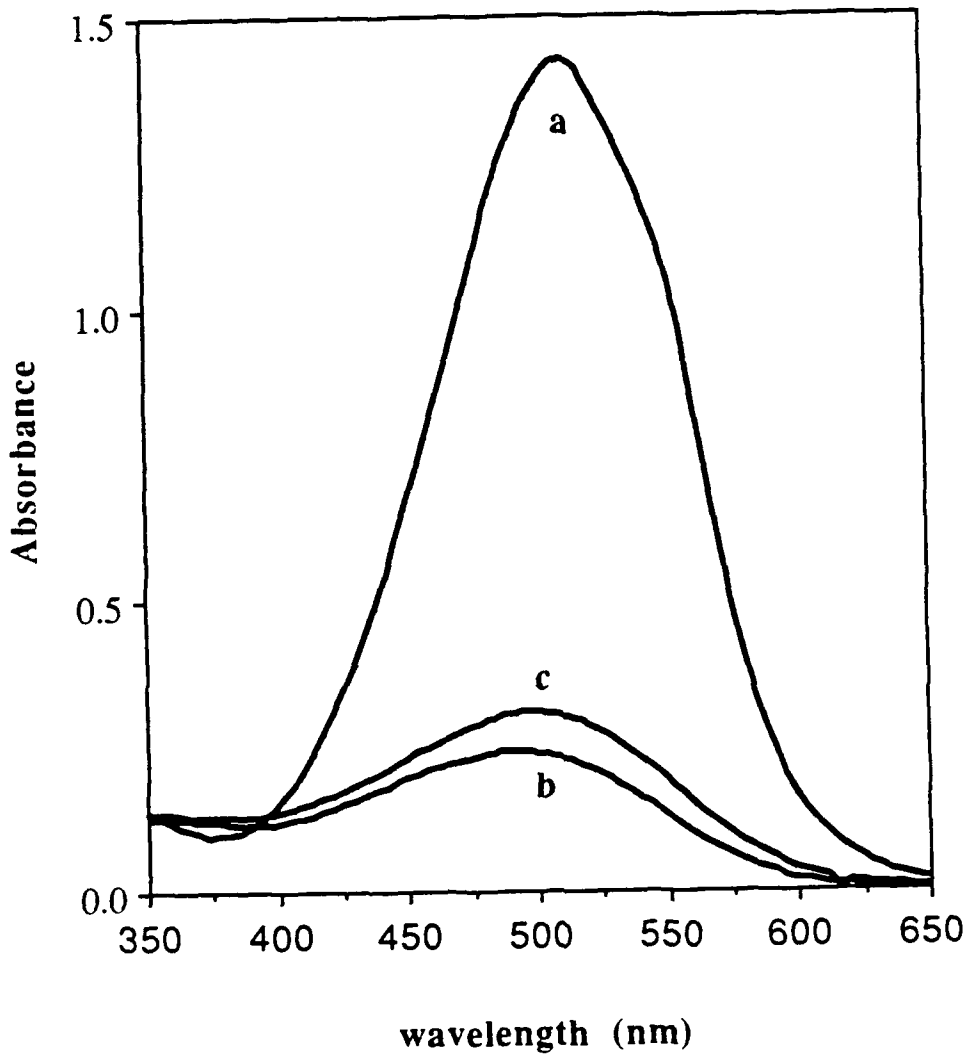
40
Time (hour)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Absorbance
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