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Nonlinear optical properties of epoxy/acryl semi-IPN

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Summary

Effects of IPN (Interpenetrating Polymer Network) structures on the nonlinear optical properties of the polymers were studied. The IPN's were prepared using simultaneous polymerization, spin coating and post curing. The second order nonlinear optical properties of polymer films were evaluated by Maker-fringe experiment using the facilities in IBM research center at Almaden. The noncentrosymmetric structure for second order optical nonlinearity was obtained by applying an electric field using corona poling. The d_{33} values of epoxy,semi-IPN(50/50) and acrylic resin were 12.2 pm/V, 4.2 pm/V and 0.9 pm/V respectively. Semi-IPN had good stability after initial decay.

Introduction

In recent years, interest in the nonlinear optical properties of organic and polymeric materials has been grown due to the potential application in the field of optical communication and optical information processing. Organic nonlinear optical chromophores with large second order hyperpolarizability can be dispersed into polymer matrices or covalently bound to amorphous polymer backbone, which suffer from relaxation of the electric field induced noncentrosymmetric alignment indispensable for second order nonlinear optical properties.(1,2,11,12,15,18) In order to reduce these relaxations , nonlinear optical chromophores were crosslinked as a main chain unit or side chain unit. In this paper, the effects of semi-IPN structure, the physically interpenetrated system of one linear and one crosslinked component, on the second order nonlinear optical properties were studied using second harmonic generation measurement , absorbance study and birefringence study.(4,7)

Experimental

Materials

As the linear polymer of the semi IPN, acrylic monomer was prepared from hydroxy ethyl methacrylate (HEMA) and 4 - nitrophenylene isocyanate (NPI), which has NLO chromophore, via typical urethane reaction at room temperature as illustrated in Fig.1. The acrylic monomer, p-nitro benzyl carbamic ethyl methacrylate (NCEM), was polymerized at 60°C with an initiator of AIBN via radical polymerization in dimethylformamide(DMF). As the crosslinked component, the diglycidyl ether of Bisphenol-A(BISA) was reacted with 4-nitro-1,2-phenylene diamine (NPDA), which has NLO chromophore, to give a prepolymer soluble in solvents like propylene glycol monomethyl ether acetate (PM-Acetate). The semi-IPN was

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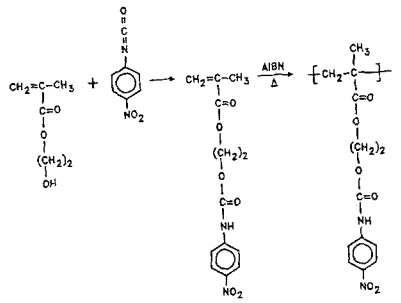
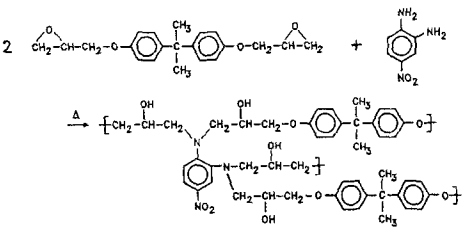
synthesized from the solution mixtures of BISA-NPDA prepolymer and NCEM by polymerizing simultaneously via different reaction mechanisms, which are step polymerization and radical polymerization.(6)



(a)



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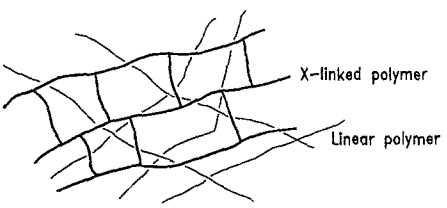

(c)

Fig.1. Chemical structures of (a) poly(p-nitrobenzyl carbamic ethyl methacrylate)(p-NCEM) starting from hydroxy ethyl methacrylate and 4-nitro phenylene isocyanate (NPI), (b) BISA-NPDA polymer starting from diglycidyl ether of Bisphenol-A (BISA) and 4-nitro phenylene diamine and (c) semi-IPN consisting of p-NCEM (linear polymer) and BISA-NPDA polymer (crosslinked polymer)

Sample preparation

Polymer films were prepared by spin coating oligomer solutions onto ITO coated quartz at 2000-4000 rpm in a clean room after filtering through 0.2μm Teflon filter to remove impurities. The solid content ranged from 15-40%. Solvents were removed by vacuum oven at 80°C for 1 day after the spin coating. Before spin coating, ITO coated quartz was cleaned in concentrated sulfuric acid, deionized water and isopropyl alcohol.

Poling

Poling was performed with insitu corona poling / second harmonic generation measurement facility as is shown schematically in Fig.2. Corona wire with grid was positoned above a grounded transparent electrode onto which the polymer film was coated. Temperature was controlled by a hot plate of the assembly. The voltage of corona wire was DC 5000 - 6000 V and that of the grid was DC 100 - 800 V. The corona discharge is a partial breakdown of air which is usually initiated by a discharge in an inhomogeneous electric field. The onset of corona discharge occurred at the voltage which depends usually on the supplying voltage and distance between polymer film and grid. Poling was done for 1 hr at 20°C above the T_g of the linear polymers. For crosslinking system, poling was done simultaneously with curing reactions. Electric field was maintained during cooling for both cases after poling. Poling should be done very carefully watching SHG signal at optimum temperature since the polymer became somwhat conductive at high temperature that corona discharge could not be

deposited on polymer surface but flow through the grounded apparatus resulting in poor poling.(9,16)

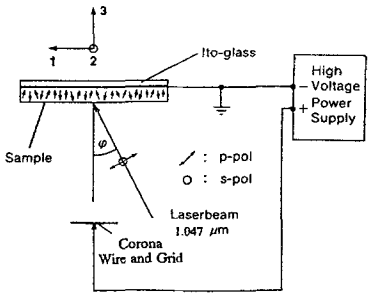

Fig.2. Schematics of in situ corona poling/SHG experiment

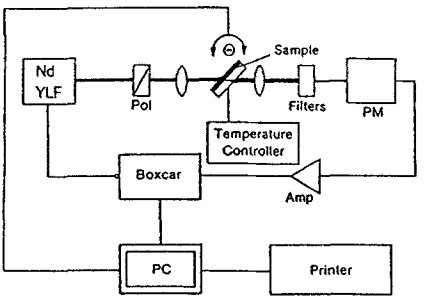

Fig.3. Schematics of SHG measurement setup

Measurement

The second harmonic coefficients of the polymer films, d_{33} and d_{31}, were obtained from Maker-fringe measurements for incident light of 1.047 μm using quartz reference(for which $d_{11} = 0.5$ pm/V) as illustrated in Fig.3. The sample was mounted on a temperature controlled goniometer stage. The polarized and Q-switched fundamental beam was focused onto the sample and then blocked by high pass filter. The second harmonic signal was detected by photomultiplyer tube and amplified. The averaged signal from a box integrator was stored as a function of angle of incidence in an IBM PS/2. Maker fringe data were fitted to the appropriate theoretical formula to obtain the NLO coefficients, d_{33} and d_{31}. The relaxation experiment was done with the same apparatus. Optical absorption was measured with an IBM 9430 UV-VIS spectrophotometer. A metricon PC 2000 prism coupler was used to measure the refractive indices for s- and p-polarized light (i.e., transverse electric TE and transverse magnetic TM modes of the travelling light). The refractive indices were measured at the wavelengths of 543.5 nm, 594.1 nm, 632.8 nm and 1064.2 nm. The sample thickness was also derived from these experiments. It was confirmed by an Alpha Step 200 (Tencor Instruments) stylus profiler with a resolution of ± 0.005 μm. The refractive indices at ω and 2ω for calculation of NLO coefficients were obtained by the Sellmeier fit. The glass transition temperature was measured by differential scanning calorimetry (DSC) with 10°C/min heating rate.

Results and discussion

The linear polymer p-NCEM had T_g of approximately 60°C. The T_g's of the crosslinked polymers such as BISA-NPDA and semi-IPN(50/50) varied with their curing histories. The T_g's approached the curing temperature as the curing reaction proceeded. The T_g's of BISA-NPDA and semi-IPN(50/50) samples used for SHG measurements were 106°C and 90°C respectively. Semi-IPN(50/50) had a single T_g and didn't show any phase separation.

A poled polymer film,containing noncentrosymmetric structure, is uniaxial and can be represented by $C_{v}\infty$ symmetry. Based on the spatial symmetry consideration and

poling field parallel to the axis labelled 3 in Fig.2 , the second harmonic polarization can be written

$$P^{NL} = d \cdot\cdot EE = \begin{bmatrix} 2d_{31}E_1E_3 \\ 2d_{31}E_2E_3 \\ d_{31}E_1^2 + d_{31}E_2^2 + d_{33}E_3^2 \end{bmatrix} \quad (1)$$

where d_{33} and d_{31} denote the second order nonlinear coefficients and E = (E_1,E_2,E_3) the optical field at the fundamental beam. In general, the second harmonic power by the nonlinear polarization in eq'n(1) for the radiation incident on polymer films from the glass side was already derived by Kurtz and Jephagnon, and others (3,5,17).

$$P^{2\omega} = (512\pi/A)t_g^4 t_\omega^4 T_2^\omega d^2 p^2 P_\omega^2 \left[1/(n_\omega^2 - n_{2\omega}^2)^2\right] \sin^2\Phi(\theta) \quad (2)$$

$$\Phi(\theta) = (\pi l/2) \times 4 | n_\omega \cos\theta_\omega - n_{2\omega} \cos\theta_{2\omega} | / \lambda \quad (3)$$

where $P^{2\omega}$ is the transmitted second harmonic power, P^ω is the incident fundamental power, A is the laser beam area, dp is the product of appropriate second harmonic coefficients with angular factors resulting from projection of the nonlinear polarization components onto the direction of $E_{2\omega}$ in the film, t_ω and $T_{2\omega}$ are Fresnel like transmission factors, t_g is the Fresnel transmission factor of the fundamental light through the glass substrate, and the n is the refractive index at the indicated frequency, Φ is an angular factor resulting from inteference between free and bound waves, θ_ω and $\theta_{2\omega}$ are the internal angles of incidence, l is the sample thickness, λ is the wave length of fundamental beam.

d_{33} and d_{31} value can be determined by p-polarization and s-polarization measurements. The details of the procedure of this were reported well previously.(8,9,10)

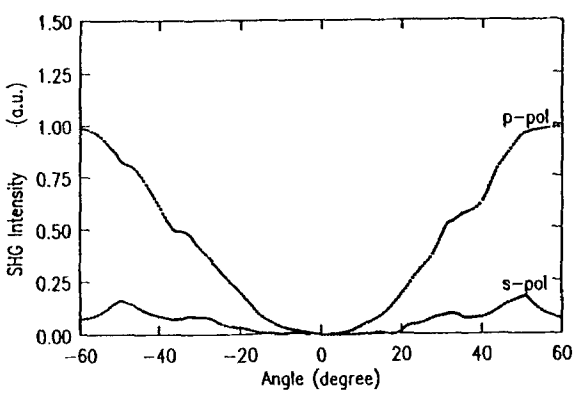

Fig.4. Plot of Maker-fringe data as a function of incidence angle for a poled and cured semi-IPN film (thickness 1.6μm)

As is shown in Fig.4., a symmetric increase of the second harmonic signal with an increase of the incident angle were observed. That behavior was almost same for BISA-NPDA polymer, semi-IPN(50/50), and p-NCEM because the sample thicknesses were much less than the coherence length. The second harmonic coefficient and Maker-fringe data of BISA-NPDA was already reported by IBM researchers in 1989. The second harmonic coefficients, d_{33},of BISA-NPDA, semi-IPN, and p-NCEM were 12.2 pm/V, 4.2 pm/V, and 0.9 pm/V respectively. The value of d_{33} for semi-IPN(50/50) was lower than the average value of BISA-NPDA and p-NCEM. Usually linear correlations exist between NLO

coefficients and NLO chromophore's density.(12) In terms of chromophore's density, semi-IPN(50/50) has average density of BISA-NPDA and p-NCEM. Even though semi-IPN had single T_g and had a good transparency, we could not say it was perfectly homogeneous mixture. So some domain might scatter the second harmonic signal. Actually we tried to make the polymer blend of BISA-NPDA and p-NCEM and the full IPN of them. But they showed phase separation and became opaque and the transmittance was very low.

Additionally these coefficients strongly depended on the poling conditions, especially corona grid's voltage and temperature, and sample thickness. At high temperature for heating samples above T_g, current could flow through the film resulting in the decrease of SHG signal or serious sample damage as illustrated in Fig.5. On the other hand , if the temperature is too low, the mobility was poor for molecular rearrangement. For these reasons, it was necessary to pole the film very carefully checking SHG signal and the current through the film, not exceeding 0.2 μA.

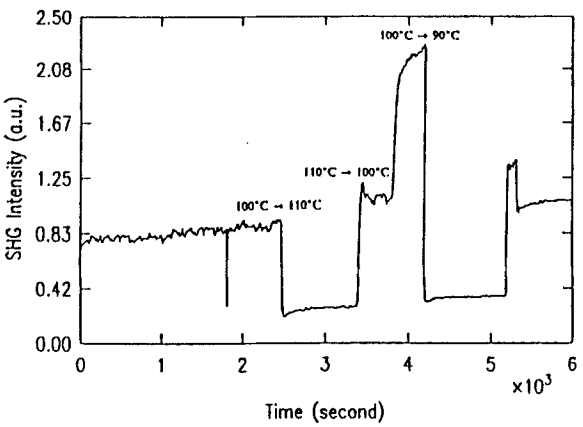

Fig. 5. SHG intensity behavior upon changing poling temperature of semi-IPN

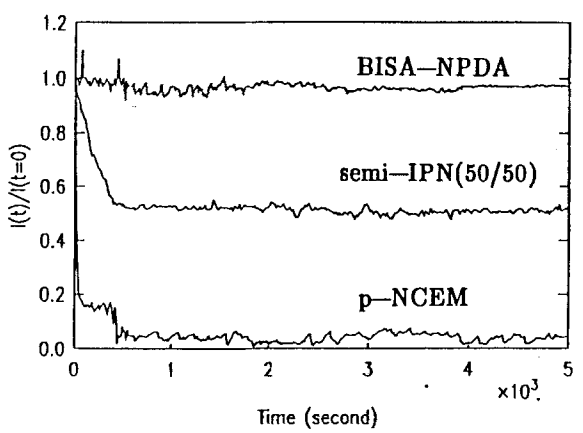

Fig. 6. SHG intensity ratio of t=t and t=0 after poling vs. time

Relaxation study was done with the SHG measurement setup. Fig.6. shows the relaxation at 50°C of BISA-NPDA, semi-IPN(50/50), p-NCEM. BISA-NPDA sample showed well known high stability of crosslinked system. Semi-IPN and p-NCEM showed fast relaxation at the beginning of electric field elemination. The d_{33} value of semi-IPN(50/50) was kept constant after 20 days at 60°C. After initial decay, semi-IPN showed good stability. Usual relaxation decays are exponential decay. This unusual steep decay seems to be the decrease of surface potentials. For p-NCEM, it was difficult to judge its stability because of the inherent low value of SHG intensity.(13)

Refractive indices were determined from measurements of the coupling angles for TE and TM modes in slab wave guide configuration. There were definite anisotropy between TE and TM polarizations in the unpoled samples after spin coating, as illustrated in Fig.7. It was dependent on the

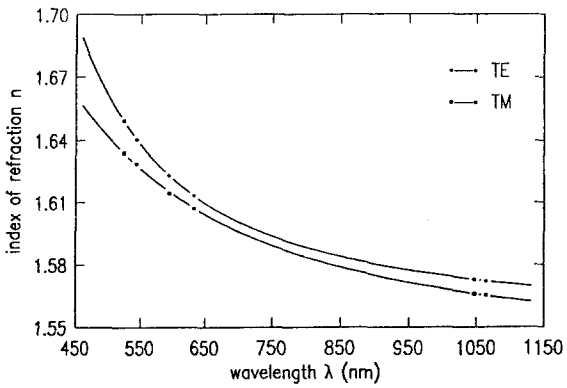

Fig. 7. Refractive index of semi-IPN(50/50) after spincoating vs. wavelength

orientation of the polymer backbone with spin coating. But no significant birefringence was observed after poling. As curing reaction proceeds, the polymer backbone seemed to lose its mobility for reversing of the anisotropy due to spin coating. Other linear polymers with high optical nonlinearity were reported to have definite birefingence after poling. (9,10) The values of the refractive indices were used subsequently in the analysis of the Maker-fringe fitting.

Optical absorbances of unpoled BISA-NPDA polymer, semi-IPN(50/50), p-NCEM and poled BISA-NPDA polymer, semi-IPN(50/50), and p-NCEM were plotted in Fig.8 . Semi-IPN(50/50) showed almost average absorbance of BISA-NPDA and p-NCEM polymers. Semi-IPN(50/50) and BISA-NPDA polymer showed definite macroscopic spectral change upon poling. p-NCEM didn't show the difference after poling.(14)

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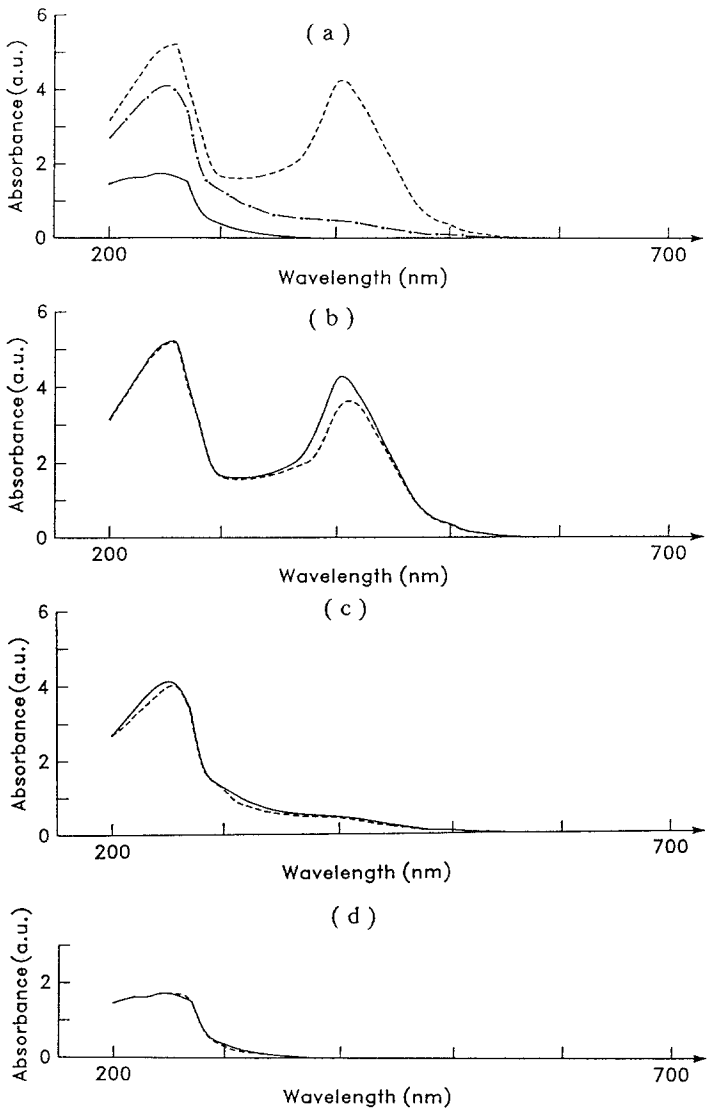

Fig.8. Absorption spectra of BISA-NPDA polymer, semi-IPN(50/50) and p-NCEM polymer as a function of the wave length of light
(a) BISA-NPDA polymer cured at 120°C (dashed line), semi-IPN(50/50) cured at 120°C (dash-dotted line), and p-NCEM (line). All are unpoled.
(b) unpoled BISA-NPDA polymer cured at 120°C (line) and poled/cured BISA-NPDA polymer (dashed line)
(c) unpoled semi-IPN(50/50) cured at 120°C (line) and poled/cured semi-IPN (dashed)
(d) unpoled p-NCEM (line) and poled p-NCEM (dashed)

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