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A New Approach to Design of Cross-Linked Second-Order Nonlinear Optical Polymers

by

B.K. Mandal, J.Y. Lee, X.F. Zhu, Y.M. Chen,
E. Prakeenvincha, J. Kumar and S. Tripathy

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Thin Film Processing of NLO Materials. VII

A NEW APPROACH TO DESIGN OF CROSS-LINKED SECOND-ORDER NONLINEAR OPTICAL POLYMERS

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ABSTRACT

A new class of cross-linked second-order nonlinear optical (NLO) polymers has been developed by processing a NLO-dye and a polymer similar to conventional 'doped polymer' system. Intermolecular cross-linking was carried out by UV radiation subsequent to electric field induced poling of the composite. Cinnamate (C_6H_5-CH=CH-CO_2-) and styrylacrylate (C_6H_5-CH=CH-CH=CH-CO_2-) moieties are selected as the photoreactive chromophores which are attached to both the NLO molecules at two positions and randomly substituted to a vinyl polymer. The poled cross-linked polymers exhibit stable nonlinear activity over a long period of time as characterized by temporal response of second-harmonic generation signal and UV absorption characteristics.

INTRODUCTION

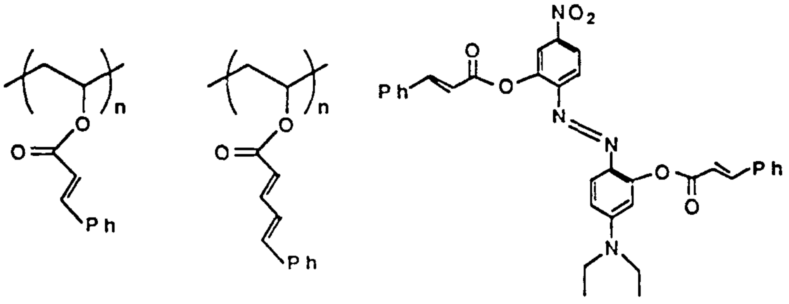
Second-order nonlinear optical (NLO) polymers exhibit excellent retention of nonlinear activity over time when a certain degree of cross-linking is introduced into the polymer. Cross-links between the polymer chains restrict the molecular motion of the segments and hence prevent the deorientation of the ordered NLO molecules. This approach was first reported by Eich et al [1] in an 'epoxy' system in which the NLO moieties are incorporated either in the multifunctional epoxy or amine components or in both. First, a low molecular weight prepolymer is made to impart adequate processability of the NLO components. Subsequently, long term poling and thermally induced cross-linking are performed simultaneously in order to obtain a three-dimensional NLO polymer. The problem of slow relaxation of electric field induced aligned NLO moieties, which is an inherent property of NLO-dye doped polymers [2-4] and NLO-dye functionalized side chain polymers [5-7], is eliminated. A high degree of loading of NLO molecules is also possible without the problem of phase segregation. In addition, the cross-linked system is expected to possess enhanced thermal stability due to its net-work structure.

Recently, we have reported an alternative approach to obtain a cross-linked second order NLO polymers [8]. The principle is based on the *2+2* photodimerization reactions between the photoreactive carbon-carbon double bonds which are substituted in both the NLO-dye and the polymer. In this paper, we describe some of the physical characteristics of the photocross-linkable systems derived from a cinnamate functionalized NLO-dye and the photoreactive polymers, polyvinylcinnamate (PVCN) and polyvinylstyrylacrylate (PVSA).

EXPERIMENTAL

Materials

The structures of the NLO-dye and the polymers used in the present work are shown in Fig. 1. The synthesis of azo dye, 3-cinnamoyloxy-4-[4-(N,N-diethylamino)-2-cinnamoyloxy phenylazo] nitrobenzene (CNNB-R), has been reported elsewhere [8]. Commercially available PVCN (Polysciences) was used as received. The synthesis of PVSA was performed according to the procedure described by Tanaka et al [9].



PVCN PVSA CNNB-R

Fig. 1. Structures of the photoreactive polymers (PVCN and PVSA) and the NLO-dye (CNNB-R).

Processing

Homogeneous solutions of the polymer and the dye were prepared either in toluene/dichlorobenzene (1:3; v/v) mixture (for PVCN) or in DMF (for PVSA) using an ultrasonic mixer at 25 to 35°C. The solution was then filtered through 0.5 µm teflon filter to remove undissolved particles and spun over substrates such as glass, quartz and indium-tin-oxide (ITO) coated glass at 2000 to 4000 rpm depending on the desired film thickness. The samples were then baked in a vacuum oven at 60°C for at least 12 h prior to physical measurements.

All films in the present investigation were poled by corona poling technique using wire-to-plane geometry [4]. The poling temperature was chosen close to 70°C, about 10 to 15°C below the glass transition temperature (T_g) of the composite. Mercury lamps with the spectral peak at 254 nm and 366 nm were used as the source of UV radiation in order to cross-link the PVCN and PVSA matrices respectively. The intensity of incident radiation on the film surface was approximately 2 mW/cm^2 at wavelength 254 nm and 13 mW/cm^2 at wavelength 366 nm. The exposure time for desired cross-linking was established from the UV-Vis spectra of the doped polymer films.

For the measurement of electro-optic coefficient the poled and cross-linked film over ITO coated substrate was further spin coated with a thin film of polyvinylalcohol (PVA) prior to the deposition of gold electrode (about 46 nm) by thermal evaporation. The coating of PVA was found useful in order to avoid shorts which may occur due to the pinholes generated during the corona poling process.

Instrumentation

Absorption characteristics of the polymer films coated over quartz or glass plates were investigated with a Perkin Elmer Lambda-9 UV-VIS spectrophotometer. The index of refraction was determined either by using an Ellipsometer (Rudoph Research) or by waveguiding experiment [10]. Calorimetry studies were performed with a DuPont 2000 differential scanning calorimeter (DSC). A Nd:YAG laser (Quantel) was used as the fundamental light source (1.063 µm) for second-harmonic generation (SHG) experiment. Electro-optic measurements were carried out using a He-Ne laser at wavelength 0.633 µm.

RESULTS AND DISCUSSION

Linear and nonlinear optical properties of PVCN films doped with CNNB-R are reported in our earlier communication [11]. Stable NLO activity was observed in the case of the photo-crosslinked polymer.

DSC studies have been performed to investigate the photocross-linking behavior of the dye-doped PVCN. The T_g of the undoped PVCN is observed close to 88°C. Doping of 10% CNNB-R by weight decreases the T_g to 84°C due to the plasticizing effect. However, no significant change in T_g of the doped polymer films was observed with the increase of radiation dosage (at 254 nm). The polymer, PVCN, has a high molecular weight to begin with (M_w ~ 170,000) and further increase in molecular weight due to cross-linking does not effect the T_g (Fig. 2a). On the other hand, as the polymer gets increasingly cross-linked the segmental motion is hindered leading to a complete loss of T_g at high level of cross-linking. In such a situation the degree of photocross-linking reaction can be best studied by calculating the changes in specific heat capacities at T_g, $(\Delta C_p)_{T_g}$, going from the glassy to the rubbery phases [12]. Fig. 2b shows the $(\Delta C_p)_{T_g}$ decreases with the increase of radiation dosage upto zero where the matrix forms an intractable net-work.

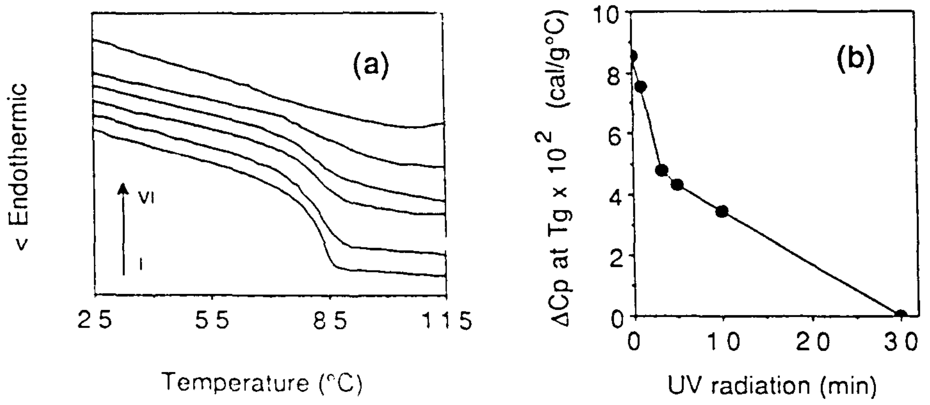


Fig. 2. (a) DSC curves of PVCN films doped with 10% CNNB-R. Cross-linking was performed by UV radiation at wavelength 254 nm; I = 0, II = 1, III = 3, IV = 5, V = 10, VI = 30 min respectively. (b) Decrease of specific heat capacity at T_g of PVCN film doped with 10% CNNB-R with UV radiation at wavelength 254 nm.

The electro-optic coefficient, r_{33}, of the poled PVCN film doped with 10% CNNB-R by weight was measured by the method described by Teng and Man [13]. A schematic of the experimental arrangement is shown in Fig. 3. The phase retardation between the p and s waves modulated at about 5 kHz causes modulation of the measured intensity amplitude I_m. A Soleil-Babinet compensator was used to bias the DC intensity at the half-maximum intensity I_c. r_{33} was obtained from the following equation:

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c} \frac{\left(n^2 - \sin^2\theta\right)^{3/2}}{\left(n^2 - 2\sin^2\theta\right) n^2 \sin^2\theta}$$

where λ is the wavelength, V_m is the modulating voltage, and n is the refractive index of the doped polymer. The value of r_{33} was obtained as 9 pm/V using He-Ne incident light at wavelength 0.633 μm. Very small amount of absorption of the doped polymer film at 0.633 μm was ignored in this calculation. These calculations also assumed r_{33} to be equal to three times r_{13}.

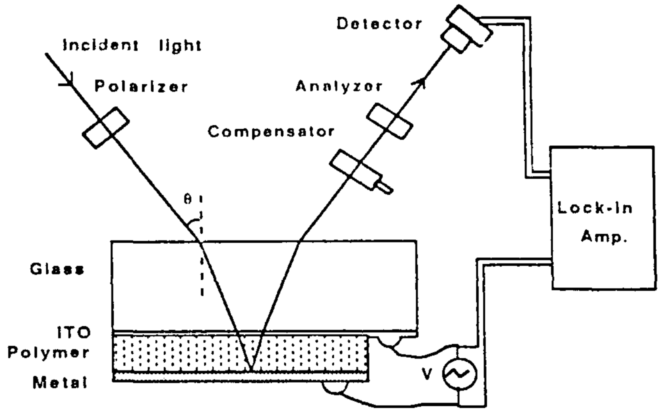


Fig. 3. Experimental set-up for the measurement of electro-optic coefficient, r_{33}.

PVSA, a known photoreactive polymer [14], has also been used in the present work. The λ_{max} of PVSA appears at a longer wavelength due to the presence of an additional double bond in the structure (Fig. 1). Typically, PVCN and PVSA films are effectively cross-linked at 254 and 366 nm respectively, although their absorption maxima occur at 270 and 300 nm respectively. In general, the photoreactivity of both the matrices is decreased when doped with the dye molecules. Figs. 4a and 4b describe the photoreactivity of doped and undoped polymer films in terms of the decrease in the absorption at the maximum characterizing the absorption by the photoreactive chromophores.

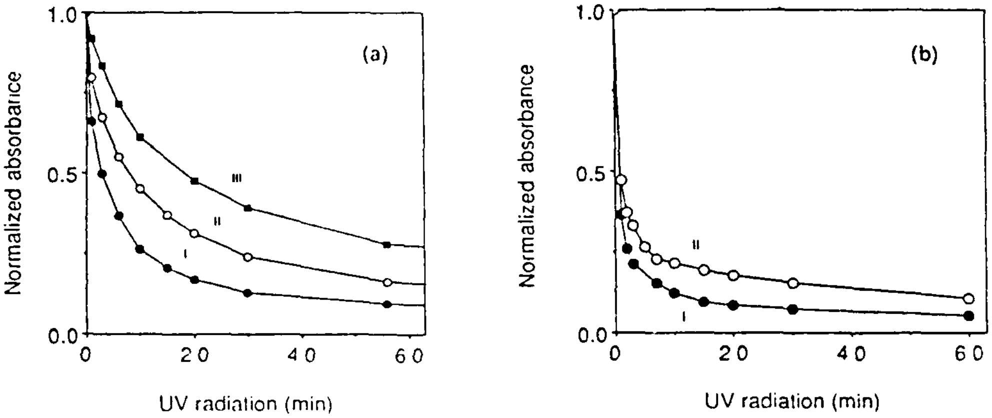
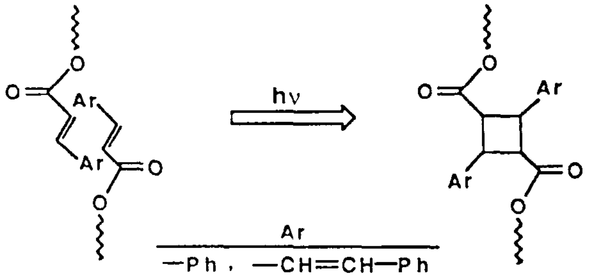


Fig. 4. Photoreactivity of the unpoled PVCN and PVSA films with the radiation dosage. (a) Absorption measured at 270 nm; I, PVCN; II, PVCN + CNNB-R (10%); III, PVCN + CNNB-R (20%). (b) Absorption measured at 300 nm; I, PVSA; II, PVSA + CNNB-R (10%).

The decrease in absorption with exposure time indicates the loss of the α,β-unsaturated double bonds which are converted into a saturated four membered ring as a result of intermolecular cross-linking.



The temporal stability of the orientational order of the NLO dyes can be monitored by UV absorption characteristics of the film with time. When a doped polymer film is subjected to poling the dipolar NLO molecules are ordered along the poling field. This causes a decrease in the absorption of the film for incident radiation polarized in the plane of the film. The second order properties are directly proportional to the orientational order of the NLO molecules in the matrix.

The stability of the poled cross-linked dye-doped PVSA system compared to a poled uncross-linked system is presented in Figs. 5a and 5b. The absorption spectrum of an unpoled uncross-linked PVSA-dye-doped film is shown in trace A of Fig. 5a, characterizing the absorption by the NLO dye. Subsequent to poling as shown in trace I there is substantial reduction in the absorption indicative of the alignment of the dye molecules. The absorption spectrum of the poled uncross-linked system continues to change with time slowly shifting towards the spectrum of the unpoled film (traces II to V). In Fig. 5b trace A again refers to an unpoled uncross-linked film and trace I is the absorption spectrum of a poled and cross-linked film. There is, however, little or no shift in the poled cross-linked spectrum as a function of time (traces II to V). The order induced upon poling has been vitrified by the extensive cross-linking in the system.

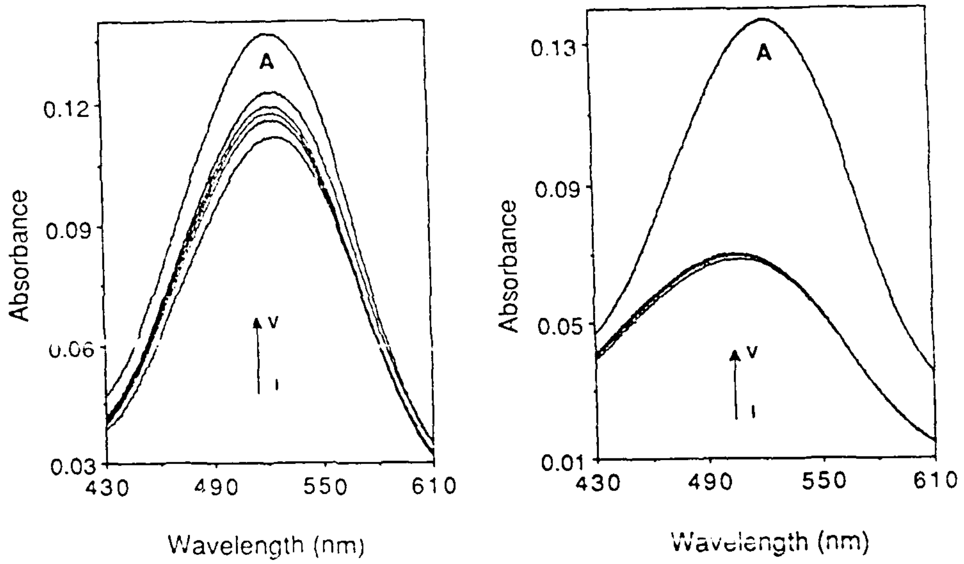


Fig. 5. Temporal stability of PVSA films doped with 10% CNNB-R with respect to the change in absorption of the NLO dye. Traces A in both (a) and (b) represent the absorption characteristics of unpoled and uncross-linked films. (a) Poled and uncross-linked films; I, 0 h; II, 1 h; III, 3 h; IV, 7 h; V, 22 h. (b) Poled and cross-linked films; I, 0 h; II, 1 h; III, 3 h; IV, 7 h; V, 22 h.

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REFERENCES

1 M. Eich, B. Reck, D. Y. Yoon, C. G. Willson and G. C. Bjorklund, **J. Appl. Phys. 66(7)** (1989) 3241.

2 K. D. Singer, J. E. Sohn and S. J. Lalama, **Appl. Phys. Lett. 49** (1986) 248.

3 J. R. Hill, P. L. Dunn, G. J. Davies, S. N. Oliver, P. Pantelis and J. D. Rush, **Electronics Lett. 23** (1987) 700.

4 M. A. Mortazavi, A. Knoesen, S. T. Kowel, B. G. Higgins and A. Dienes, **J. Opt. Soc. Am. B6(4)** (1989) 733.

5 C. Ye, T. J. Marks, J. Yang and G. W. Wong, **Macromolecules 20** (1987) 2322.

6 K. D. Singer, M. G. Kuzyk, W. R. Holland, J. E. Sohn, S. J. Lalama, R. B. Comizzoli, H. E. Katz and M. L. Schilling, **Appl. Phys. Lett. 53** (1988) 1800.

7 M. Eich, A. Sen, H. Looser, G. C. Bjorklund, J. D. Swalen, R. Tweig and D. Y. Yoon, **J. Appl. Phys. 66(6)** (1989) 2559.

8 B. K. Mandal, J. Kumar, J. C. Huang and S. K. Tripathy, **Makromol. Chem. Rapid. Commun.** *submitted.*

9 H. Tanaka, M. Tsuda and H. Nakanishi, **J. Polym. Sci. 10(A-1)** (1972) 1729.

10 J. D. Swalen, R. Santo, M. Tacke, and M. Fischer, **IBM J. Res. Dev. 21** (1977) 168.

11 B. K. Mandal, Y. M. Chen, J. Y. Lee, J. Kumar and S. Tripathy, **Appl. Phys. Lett.,** submitted.

12 S. Z. D. Cheng, M. Y. Cao and B. Wunderlich, **Macromolecules, 19** (1986) 1868.

13 C. C. Teng and H. T. Man, **Appl. Phys. Lett. 56(18)** (1990) 1734.

14 A. Reiser, **Photoreactive Polymers**, Wiley, New York, 1989, Ch. 2, p. 27.