Synthesis of a Photo-Crosslinked Stable Nonlinear Optical Polymer and Application to External Electro-Optic Measurement

DAMING ZHANG,[1] JINGZHI SUN,[2] JIACONG SHEN,[2] MAOBIN YI[1]

[1] State Key Laboratory on Integrated Optoelectronics, Jilin University Region, Changchun, 130023, China

[2] Key Laboratory for Supramolecular Structure and Spectroscopy, Jilin University, Changchun, 130023, China

Received 10 May 1999; accepted 26 December 1999

ABSTRACT: A photo-crosslinked side-chain second-order nonlinear optical polymer was synthesized with bis-phenol-A as the polymer backbone, *p*-nitroaniline as the chromophore and cinnamyl group as the photo-sensitizer. The characterization of the polymer was made by nuclear magnetic resonance, infrared, ultraviolet-vis, and dynamic mechanical analysis methods. An electro-optic film was obtained by spin coating of the polymer and corona poling then photo-crosslinking reaction. An external electro-optic measurement system was established based on the film and reflective light path configuration, and successfully applied to measure the electrical signals propagating on the under-test circuits. The poled and crosslinked film showed high glass transition temperature (160°C) and improved chromophore orientation stability. The measuring principle was analyzed by electro-optic tensor matrix and index ellipsoid methods. The results showed that the designed polymer film had the linear electro-optic effect, the voltage sensitivity of the system was measured to be 5 $mv/\sqrt{Hz}$ at the condition of 1 kHz input signal. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1506–1512, 2000

Key words: nonlinear optical polymer; thin film; photo-crosslinking; synthesis and application

INTRODUCTION

Recently, organic/polymer nonlinear optical (NLO) materials have attracted much attention for their desirable properties such as large NLO coefficient, high optical damage threshold, high responding speed, small dielectric capacity, low production cost, and good mechanical property.[1,2] Considerable effort has been spent to develop new NLO polymer materials for the applications in optical computation, telecommunication, electro-optic (EO) modulation, second harmonic generation, and high-speed signal processing.[3–5] Because second-order NLO polymers can be used as linear EO materials, they have potential application value in integrated circuits (ICs) measurement. One approach, or internal EO measurement, is based on the EO effect of the circuit's substrate; the electrical signals are converted to modulated optical probe beam by the substrate. But the practical application of this internal EO is limited because most of the commercial circuits are made of non-EO materials. The external EO measurement of ICs, as an alternative technique, can be used to the circuit's substrate without own EO effects. By measuring the modulated signals con-

---

Correspondence to: D. Zhang (ioskl@mail.jlu.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 69876014.

Contract grant sponsor: The Research Fund for the Doctoral Program of Higher Education; contract grant number: RFDP 97018311.

Journal of Applied Polymer Science, Vol. 77, 1506–1512 (2000)

veyed from the EO material overlaid on the under-test circuits, the internal dynamic properties of the circuits can be detected. One of the key components to build a practical system is the EO probe. Although inorganic EO materials had been proven to be an effective technique for making noninvasive and time-domain measurement of the internal dynamic properties of integrated circuit chip, the practical high spatial resolution application was obstructed because of their disadvantages such as large dielectric capacity and high product cost.[6–9] Therefore, many researchers turned their attention to the organic EO materials which have the desired long-term stability for the practical application. One of the promising strategies of improving the long-term stability is incorporating the EO chromophores into solid crosslinked three-dimensional molecular networks by suitable chemical modifications. For example, photo-crosslinking is a simple and effective method toward this strategy.[10] There is almost no restriction on the kinds of substrate on which the polymer films can be coated, so large surfaces can be processed at low cost. Based on this conception, in this article, we report the synthesis and characterization of the designed NLO polymer and establishment of an external EO system to measure electrical signals propagating on coplanar stripe (CPS) electrodes.

EXPERIMENTAL

The Preparation and Synthesis

The epoxy was selected as the building block of polymer backbone for its low contract and expands coefficience and chemical stability. The *p*-nitroaniline (PNA), a typical NLO chromophore, was co-polymerized with bis-phenol-A epoxy. The ultraviolet (UV)-visible absorption maximum wavelength of PNA is at 378 nm, which leads to a relative broad range of light transparency. The cinnamyl group was chosen to be the candidate of photo-sensitizer for photo-crosslinking and was grafted onto the polymer side chain. The synthetic route toward the designed polymer is shown in Scheme 1.{SCH 1} The bis-A-epoxy was distilled in reduced pressure at 70°C to remove the residual water and benzene, then mixed homogeneously with PNA in a hermetically sealed chamber and heated to 130–140°C for 4 h, then to 170°C for 3 h. A light brown product of epoxy-*p*-nitroaniline (EPNA) was obtained. A solution of cinnamyl chloride and tetrahydrofuran (THF) was introduced from a dropping funnel into the flask containing 5 g of EPNA and 15 mL of THF. The reactants were stirred continuously for 24 h at the ambient temperature, the mixture product was precipitated by methanol and filtered, the dry filter cake was dissolved in THF and re-precipitated by methanol to purify the product. Finally, a brown-yellow product of EPNA-cinnamyl (EPNAC) was obtained.

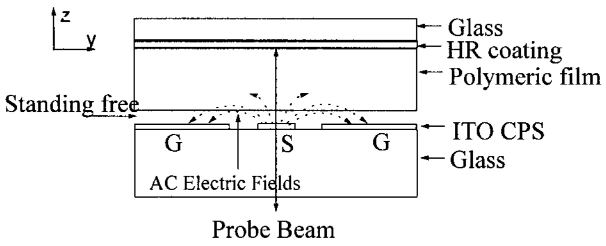


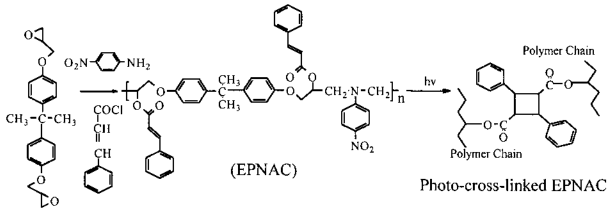
Figure 1 The configuration of EPNAC external EO probe.

Characterization of the Polymer

The thin films of EPNA and EPNAC were fabricated by spin coating of their THF solution on quartz and CaF_2 substrates, and the residual solvent was removed by vacuum evaporation for at least 12 h at 40°C. The derived thin films can be characterized on a Shimadazu UV-3100 UV-visible spectrometer and a BRUKER IFS 66V infrared (IR) spectroscopy. The ^{1}H-nuclear magnetic resonance (NMR) spectra were obtained on a UVI-400 spectroscopy in their dimethyl sulfoxide solution. The molecular weight of EPNA and EPNAC were determined on a Shimadazu LC-4A GPC with polystyrene as standard. The glass transition behavior was performed on a GPP-polymer material dynamic mechanical analysis (DMA) instrument with the vibration frequency of 0.1–10 Hz and a temperature rising rate of 2°C/min.

The Fabrication of EO Sensor

The illustration of the EPNAC external EO process is shown in Figure 1. A high-reflectivity coating was evaporated in high vacuum onto the glass slide. A 2–3 μm-thick layer of the EPNAC thin film was spin coated onto the high-reflectivity surface from a solution of EPNAC/THF. Overnight baking was done at 40°C under vacuum to remove residual solvent trapped in the film. The EPNAC film was corona poled at 90°C for approx-



Scheme 1 The synthesis of polymers EPNA, EPNAC, and photo-crosslinked system.

imately 30 min with 6 μA poling current. For providing a large uniform poled area, we selected a tungsten wire other than a tungsten pin as the poling positive electrode. Photo-crosslinking reaction was then performed through photosensitive cinnamyl groups by irradiating with a 40-W UV light for 45 min. Then the film was cooled down to the atmosphere temperature gradually with the poling voltage kept on. The poled film was free-standing on the under-test indium-tin oxide (ITO) CPS, thus an external EO sensor was fabricated.

RESULTS AND DISCUSSION

Synthesis

The polymer EPNAC was prepared in a three-step reaction according to Scheme 1. The co-polymerization of PNA and bis-phenol-A epoxy is a two-stage reaction. The first stage is the reaction between the amino group on PNA and one epoxy side group to produce the monomer at 130–140°C, and at the higher temperature 160–170°C, the monomers polymerized to form EPNA. The precursor polymer EPNA showed a number average molecule weight of 6822. The grafting reaction could be prompted by pyridine, and the pyridine can be easily separated in the precipitation process. In the ^{1}H-NMR spectrum of EPNAC before UV exposure, the missing of the peak at 3.98 ppm, which was a strong peak in ^{1}H-NMR spectrum of EPNA, indicated that the grafting reaction was completed.

The IR spectrum of EPNAC is shown in Figure 2. The assignment of the characteristic vibrations are included in Table I. The amount (wt %) of PNA, cinnamyl groups contained in EPNAC, and the degree of photo-crosslinking of EPNAC can be quantitatively investigated by determining the areas of correspondent vibration peaks. The homogenous mixtures of bis-phenol-A epoxy and PNA in different ratios were coated on the CaF_2 plates and their IR spectra were determined. The working diagram of PNA amount (wt %) in the PNA/bis-phenol-A epoxy mixtures was obtained, as shown in Figure 3. Based on this diagram, the PNA amount in EPNA can be found by quantitatively calculating the ratio between the area of the 1510 cm^{-1}(—NO_2) peak and the area of internal standard peak at 1242 cm^{-1}(C—O aromatic acid). In our EPNA, the PNA amount is calculated to be 25.4%.

In the same way, we obtained the working diagram (Fig. 4) for the amount (wt %) of cinnamyl group in EPNA/cinnamic acid mixtures. First, we prepared a series of samples with different ratios of EPNA and cinnamic acid, and measured their Fourier transform infrared spectra in KBr pellets. From the diagram, the cinnamyl group amount in EPNAC was calculated to be 28.8% according to the ratio between the area of the 1714 cm^{-1} (—C=O carbonyl) peak and the area of internal standard peak at 1510 cm^{-1} (—NO_2) of their IR spectra.

The Poling Conditions

When the dipoles of the chromophores are isotropic in a polymer film, the EO property cannot be presented macroscopically. The EO property can be derived when the chromophores have good orientation and the dipoles are arranged orderly. We used the corona poling technique to pole the EPNAC film. The order parameter is a standard scale to measure the orientation of the chromophores; it can be described as:

$$\varphi = 1 - A_p/A_0 \tag{1}$$

where φ, A_p, and A_0 are order parameter of the film, absorption after and before poling, respec-

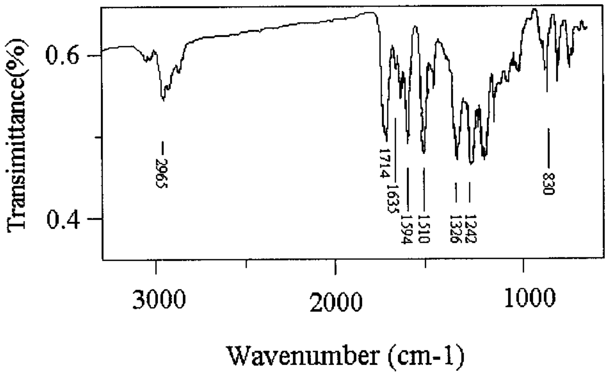


Figure 2 IR spectrum of polymer EPNAC (in KBr).

Table I Assignment of the vibrations in the IR spectrum of EPNAC

Vibrations	Vibrations
1714 cm^{-1}—$\nu_{C=O}$ Carbonyl	830 cm^{-1}—$\nu_{C—H}$ Substituted benzene
1635 cm^{-1}—$\nu_{Ph—C=C}$	1041 cm^{-1}—$\nu_{C—O}$ Fatty acid
1594 cm^{-1}—$\nu_{C=C}$ Aromatic	1242 cm^{-1}—$\nu_{C—O}$ Aromatic acid
1510 cm^{-1}—$\nu_{—NO2}$	2965 cm^{-1}—$\nu_{C—H}$ Alkyl

tively. The UV-vis absorption spectra of EPNAC before and after poling are shown in Figure 5. According to eq. (1) and Figure 5, the order parameter of the chromophores is approximately 0.26. The absorption maximum at 373.5 nm presented approximately 4.5 nm blue shift; this was ascribed to the hydrogen aggregate formation induced by poling process.

The poling temperature is an important factor influencing the order parameter. In the poling process, the arrangement of chromophores turns into an ordered state from chaos. The rising of poling temperature over the glass transition temperature (T_g) would emancipate the movement of the polymer chains and favor to the orientation of the chromophores. But high temperature may cause the deformation of polymer films and the degradation of the conjugated system. To balance these two opposite effects and consider that the T_g of EPNAC is approximately 85°C, we selected a temperature of 90°C as the poling temperature.

Another factor is the poling time. As a kinetic process, the chromophore orientation directly relates to the poling time. The order parameter increased with the prolonging of poling time at the fixed temperature and applied electrical field. Figure 6 demonstrates the relationship between the order parameter and the poling time under the condition of 90°C and 6 μA poling current; the φ value tended to be stable after poling about 30 min.

The Photo-Crosslinking and the Orientation Stability

The orientation stability is the key factor for the practical application of the EO materials. The order parameter of the chromophore dipoles could not persist for a very long time even if they were poled at high temperature and frozen in the polymer matrix, because the relaxation and transition are the intrinsic property of polymer materials. One way to overcome this notorious problem is to introduce the NLO chromophores into high T_g polymer materials.[11] The other way is to "lock" the orientation of chromophores by interpenetrating networks.[12] We used the second strategy by grafting cinnamyl groups to the EPNA polymer chains, then initiating the crosslinking reaction with UV light exposure. After the poling and

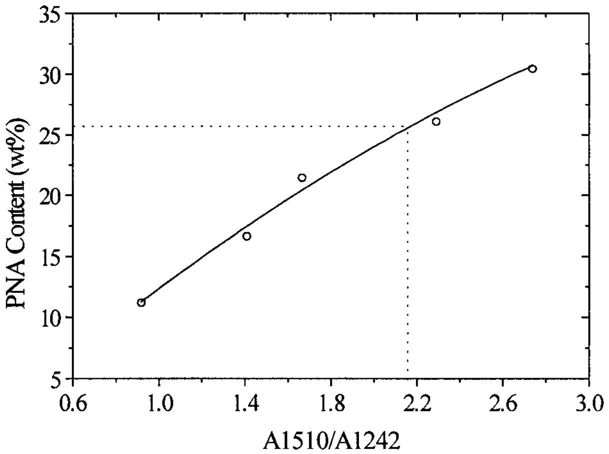


Figure 3 The working diagram of PNA amount (wt %) in the mixtures of PNA and bis-phenol-A epoxy.

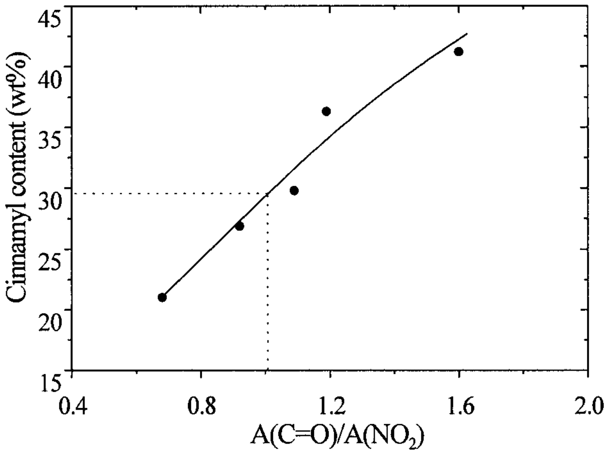


Figure 4 The working diagram of cinnamyl amount (wt %) in the EPNA/cinnamic acid mixtures.

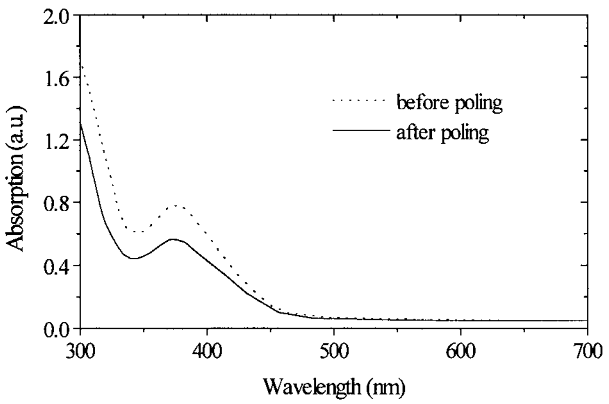


Figure 5 The absorption spectra of EPNAC film before and after poling.

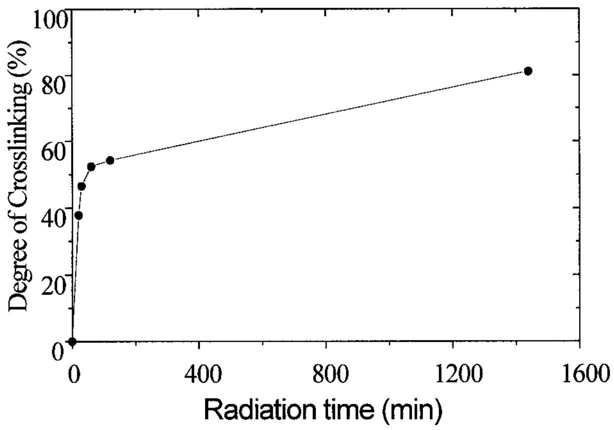


Figure 7 The relationship between the crosslinking degree of EPNAC and radiation time.

crosslinking at elevated temperature, the chromophores were subsequently oriented into noncentrosymmetrical organization and locked by the formation of networks below the T_g of the polymer.

We did not make the comparison of the NMR spectra before and after photo-crosslinking because the UV-cured sample is insoluble in any convenient D-substituted solvents. We also measured the cyclobutane structure in the final product after UV exposure indirectly by Fourier transform infrared spectra. In the IR spectrum of the EPNAC sample, the absorption band at 1635 cm^{-1} is corresponded to the C=C stretching vibration in the cinnamyl group. With the increasing of the crosslinking degree, the area of 1635 cm^{-1} peak decreased. Therefore, we can calculate the crosslinking degree by monitoring the changing of this characteristic vibration. We obtained the working diagram with the 1714 cm^{-1} vibration band selected as internal standard. The relationship between crosslinking degree and the time of exposure to 40-W UV light source is shown in Figure 7. It is obvious that the crosslinking did not complete even after a considerable length of time, because it was difficult for the cinnamyl groups to meet each other and take suitable configuration for photo-coupling reaction in the polymer matrix. At 90°C, for 45 min, the crosslinking degree was only 54%.

However, such crosslinking degree led to a higher stability of the chromophore orientation. Figure 8 presents the orientation declination in the poled polymer thin film investigated with polarized UV-visible spectroscope. It is evident that the orientation stability for the crosslinked system is much better than that of the uncrosslinked

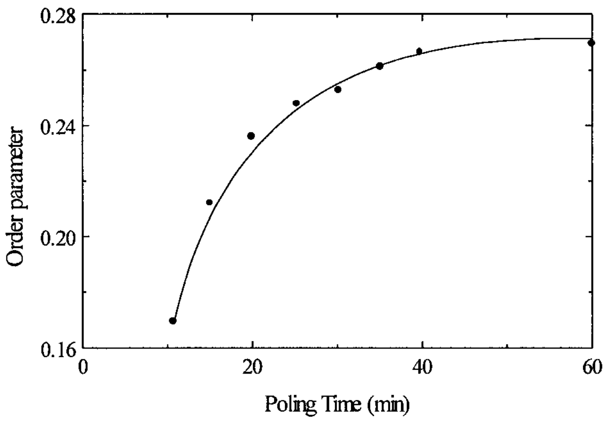


Figure 6 The relationship between the order parameter and the poling time.

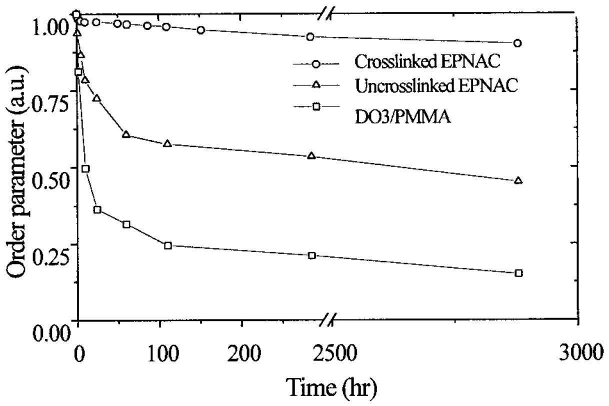


Figure 8 The orientation declination of the crosslinked EPNAC, uncrosslinked EPNAC, and the DO3/polymethylmethacrylate doping system.

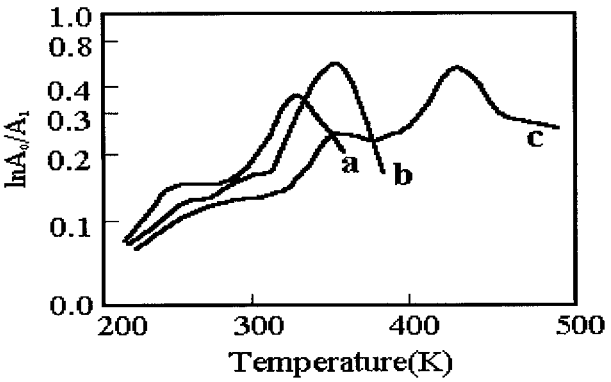


Figure 9 The dynamic mechanical properties of the polymer of (a) EPNA, (b) EPNAC, and (c) photo-crosslinked EPNAC, respectively.

system. The crosslinked system lost 10% of its chromophore orientation after 4 months. As a comparison, the uncrosslinked polymer systems lost 50%, a doping system—20 % wt doped a dye of disperse orange 3(DO3) in polymethylmethacrylate—lost nearly 80% its chromophore orientation after the same time span.

The glass transition behavior of crosslinked and uncrosslinked systems was studied with dynamic mechanical analysis. In Figure 9 we can see the T_g of the crosslinked system was deferred to a much higher temperature (approximately 160°C) than the uncrosslinked system (approximately 85°C). This postponed T_g transition was ascribed to the hindrance of the polymer chain movement caused by photo-crosslinking. This elevation of T_g was benefit to the stability of chromophore orientation.

EO Measurement and Analysis

The longitudinal interaction geometry was chosen as a test case in our EO measurement system, and simple reflectance configuration was constructed to measure the electric field signal on the ITO CPS using similar Thackara's experimental technique.[13] The under-test signals were delivered into the ITO CPS by the coplanar probes. A new 1.3 μm InGaAsP/InP buried crescent diode laser was used as the probe beam source.[14] Since the poled film can be classified as $C\infty_V$ group, the relevant EO coefficients are γ_{13}, γ_{23}, and γ_{33}, with the relation $\gamma_{13} = \gamma_{23}$ ($\gamma_{23} = \gamma_{42} = \gamma_{51} = \gamma_{13}$) and from symmetry considerations, $\gamma_{33} \cong 3\gamma_{31}$. Where γ is the EO tensor and 3 and 1 represent directions, respectively, perpendicular and parallel to the film, thus EO tensor has the following form (contracted notation):

$$\gamma = \begin{bmatrix} 0 & 0 & \gamma_{13} \\ 0 & 0 & \gamma_{13} \\ 0 & 0 & \gamma_{33} \\ 0 & \gamma_{13} & 0 \\ \gamma_{13} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{2}$$

For the longitude EO measurement, when the CPS electrodes are used to apply the modulation voltage across the thin film sample, the field strength is approximated uniform through the film (thickness $\cong$3 μm) along the electrode. Considering that the width of CPS is greater than the wavelength, it is approximated along the E_Z direction as detecting the center of the CPS; in other words, in the presence of modulation electrical field E_Z, according to the polymer tensor, the index ellipsoid becomes[15]:

$$\left(\frac{1}{n_0^2} + \gamma_{13}E_Z\right)x^2 + \left(\frac{1}{n_0^2} + \gamma_{13}E_Z\right)y^2 + \left(\frac{1}{n_e^2} + \gamma_{33}E_Z\right)z^2 = 1 \tag{3}$$

where n_0 and n_e is the ordinary and extraordinary refraction index of the polymer, the new main axes refractive index after taking into account γE << ($1/n^2$) are obtained:

$$n'_x = n_0 - \frac{1}{2}n_0^3\gamma_{13}E_Z,\ n'_y = n_0 - \frac{1}{2}n_0^3\gamma_{13}E_Z,\quad n'_z = n_e - \frac{1}{2}n_e^3\gamma_{33}E_Z \tag{4}$$

Because $n'_x = n'_y$, it has no birefringence effect, so in the direction of E_Z, it has no phase retarda-

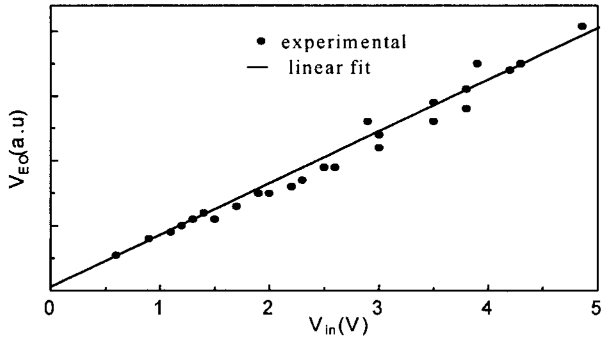


Figure 10 The EO output as a function of the input voltage.

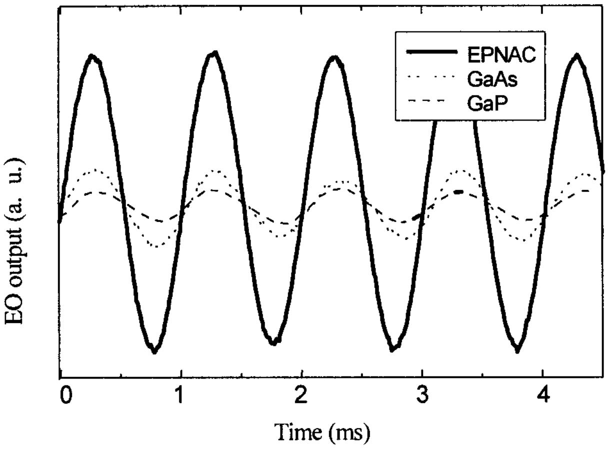


Figure 11 The 1-kHz sinusoid waveform measured with poled and crosslinked EPNAC, GaAs and GaP crystal probe, respectively.

tion between the ordinary and extraordinary wave, thus only phase modulation of the probe beam is produced; we adopted Thackara's technique to convert phase modulation to amplitude modulation.[13]

The system described above has been applied to measure the EO characteristic of the poled film and the propagation waveforms within the ITO CPS. The modulated signal was displayed on a digitizing oscilloscope via a preamplifier. Figure 10 showed the EO output as a function of input voltage. In Figure 10, the circles and solid line represented the measured values and the linear fit data respectively. The result showed good linear relationship between the output and the input voltage within 5 V; it indicated that the poled EPNAC film had linear EO effect. The electric signals propagating on the center electrode of the ITO CPS was measured by EPNAC film, GaAs and GaP crystal respectively. The waveforms are shown in Figure 11. The frequency of the input sine signal was a 1 kHz, and peak-to-peak amplitude was 3 V. The waveforms measured with EPNAC probe were sinusoid and had no significant saturation. The amplitude of the output signal with EPNAC probe was as much as three times of that with GaAs probe and four times of that with GaP probe. The voltage sensitivity of the system was measured in such a condition that the signal-to-noise ratio was 1. After taking account of the preamplifier bandwidth, the obtained voltage sensitivity in this system was 5 $mv/\sqrt{Hz}$ at the condition of 1 kHz input signals.

CONCLUSION

A photo-crosslinked stable EO polymer was synthesized. The crosslinked polymer material had high T_g and high orientation stability because the oriented chromophores were bound with the interpenetrating polymer networks. These properties, together with the wide-range of light transparency and low dielectric capacity, bestowed the possibility for the application in higher spatial resolution EO system and measuring the dynamic properties of the practical ICs.

The authors thank Prof. W. Sun and Prof. W. J. Tian for their helpful suggestions.

REFERENCES

1. Ulrich, D. R. Mol Cryst Liq Cryst 1988, 160, 1.
2. Tomme, E. V.; Van, P. P.; Baets, R. G. IEEE J Quantum Electron 1991, 27, 778.
3. Chen, D.; Fetterman, H. R.; Wang, W. Appl Phys Lett 1997, 70, 3335.
4. Cheng, T. R.; Huang, C. H.; Gan, L. B. J Mater Chem 1998, 8, 931.
5. Kenney, J. T.; Lam, J. C. Polym Prepr 1998, 73, 1012.
6. Nagatsuma, T. IEICE Trans Electron 1993, E76-C(1), 55.
7. Yi, M. B.; Sun, W.; Tian, X. J.; Jia, G.; Gao, D. S. Int J High Speed Electron Syst 1996, **7**, 463.
8. Weingarten, K. J.; Rodwell, M. J. W.; Bloom, D. M. IEEE J Quantum Electron 1988, 24, 198.
9. Dykaar, D. R.; Kopf, R. R.; Laskowski, E. J.; Zydzik, G. J. Appl Phys Lett 1993, 62, 1733.
10. Mandal, B. K.; Chen, Y. M.; Lee, J. Y. Appl Phys Lett 1991, 58, 2459.
11. Wu, J. W.; Valley, J. F.; Ermer, S. Appl Phys Lett 1991, 58, 225.
12. White, K. M.; Francis, C. V.; Isackson, A. J. Macromolecules 1994, 27, 3619.
13. Thackara, J. I.; Bloom, D. M.; Auld, B. A. Appl Phys Lett 1991, 59, 1159.
14. Zhang, B. J.; Yi, M. B.; Song, J. F. Electron Lett 1998, 34, 88.
15. Yariv, A. Optical Waves in Crystals Propagation and Control of Laser Radiation; John Wiley & Sons: New York, 1984; p. 179.