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13. ABSTRACT *(Maximum 200 Words)*

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Photocrosslinkable Polymers with Stable Second
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by

X.F. Zhu, Y.M. Chen, L. Li, R.J. Jeng, B.K.
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PHOTOCROSSLINKABLE POLYMERS WITH STABLE
SECOND ORDER OPTICAL NONLINEARITY

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Linear and nonlinear optical properties of photocrosslinkable polymers are reported. These polymers exhibit relatively stable second order nonlinearity. Electro-optic and second harmonic generation coefficients are reported for these new materials.

1. Introduction

Nonlinear optical (NLO) polymeric materials have recently received considerable attention for waveguide electro-optic (EO) modulation and frequency conversion [1]. For poled polymers, it is important to maintain the alignment of the aligned NLO moieties [1,2] against thermal relaxation . We have recently utilized a photocrosslinking technique to obtain stable poled polymers, where crosslinking of the aligned molecules is performed by irradiating the sample with UV light during the late phase of poling [3,4]. These materials are processed similar to a doped polymer system except photocrosslinking groups are attached to the guest NLO molecules as well as the host polymer. These polymers can be directly patterned by shining UV light through a mask for making channel waveguides and other integrated optical devices [5]. Thus, they combine both ease of processing and stable nonlinear response.

Photocrosslinkable polymers with NLO groups in the main chain have been synthesized [6]. In this paper, we report on optical properties of these novel NLO polymers. These polymers have been designed with nitroaniline type NLO chromophores and are transparent in the mid-visible range. Stability of the second order nonlinearity has been investigated. A modified Michelson interferometer has been employed to measure the EO coefficients.

2. Materials and processing

Fig. 1 shows the structures of the new NLO polymers which have been numbered one through four. The details of the synthesis of these polymers are described in ref. [6]. Polymers 1 and 2 are functionalized with cinnamoyl group which is commonly used in traditional photoreactive polymer, polyvinyl-cinnamate. Polymers 3 and 4 contain a styrylacryloyl group as the photocrosslinking group and are sensitive to violet and near UV light. Samples were prepared by spin coating a solution of a polymer in propylene glycol methyl ether acetate (PGMEA). The films were placed in a vacuum oven at room temperature for 12 hours and at 40 °C for another 12 hours to remove residual solvent. Typical film thickness obtained was about 0.5 µm. Glass transition temperature T_g was measured by a differential scanning calorimeter in the uncrosslinked state. Refractive index n was measured by an ellipsometer. The absorption characteristics were measured and the absorption peak wavelengths of the NLO chromophores along with the other results are summarized in table 1. The refractive index of polymer 1 at 532 and 633 are different only in the decimal place. For polymers 3 and 4, absorption curve of the NLO chromophores was overlapped by that of the photoreactive chromophores.

INSERT fig. 1 and table 1

The samples were poled by corona discharge in either wire- or needle-to-plane configuration. The detailed poling set-up in wire-to-plane geometry has been reported earlier [7]. For needle-to-plane poling, a sharp tungsten needle at a high potential is positioned above the sample placed on a heated aluminium plate. This apparatus was used for *in situ* second harmonic generation (SHG)

measurements to study and control the poling and crosslinking process. It took about 15 min to heat the sample from room temperature to the poling temperature which was 5 °C lower than the glass transition temperature. Typical poling time was 5 min. The sample was cooled down to room temperature by blowing air for about 5 min.

Crosslinking was performed by UV irradiation with the poling field turned on. A mercury lamp producing an intensity of 2 mW/cm^2 on the sample surface with emission peak at 254 nm was employed for polymers 1 and 2. A lamp emitting primarily at 366 nm and providing 8.5 mW/cm^2 intensity was used for the other materials. The exposure time was 10 min and 1 min respectively for the two different types of materials.

3. EO measurements

The EO coefficient is an important parameter for the design of modulators and several measuring methods have been utilized [1,8-10]. We have used a simple Michelson interferometer with lock-in detection to measure the EO coefficient of thin films. For this configuration, sample preparation is simple and effects of air currents, vibrations, and temperature fluctuations are much smaller than those for a Mach-Zehnder interferometer.

INSERT   fig. 2

Fig. 2 schematically shows the experimental arrangement of the Michelson interferometric technique. In the sample arm, a laser beam propagates through an indium-tin-oxide (ITO) coated glass substrate, a thin NLO polymer film, and is then reflected back by a metal electrode. The intensity of an interference fringe is given by

$$I(\phi) = I_r + I_s + 2\sqrt{I_r I_s} \cos\phi \tag{1}$$

where I_r and I_s are the intensities of the beams in the reference and sample arms respectively, and ϕ is the phase difference between the two beams. The change in the intensity due to a small change in the phase difference is therefore given by

$$\Delta I = -2\sqrt{I_r I_s} \sin\phi \, \Delta\phi = -\frac{I_{max} - I_{min}}{2} \sin\phi \, \Delta\phi \tag{2}$$

where $I_{max} = I(0)$ and $I_{min} = I(\pi)$ are the maximum and minimum intensities. ϕ is biased at either $\pi/2$ or $-\pi/2$ where ΔI is linearly proportional to $\Delta\phi$. To set the bias, a translation stage was used to adjust the position of the slit detector so that the intensity is at $(I_{max} + I_{min})/2 = I(\pi/2) = I(-\pi/2)$. For a film with a thickness d and a linear EO coefficient r_{13} and a modulating voltage $V = V_m \cos\Omega t$,

$$\Delta\phi = \frac{2\pi}{\lambda} 2d\Delta n = -\frac{2\pi n^3 r_{13} V_m}{\lambda} \cos\Omega t \tag{3}$$

where λ is the wavelength of the light source. In our experiments, Ω was chosen to be in the kHz range. From these equations at the bias points $\phi = \pm\pi/2$,

$$\Delta I = \pm \frac{(I_{max} - I_{min}) \pi n^3 r_{13} \, V_m}{\lambda} \cos \Omega t \equiv I_{\Omega}^{\pm} \cos \Omega t \; . \qquad (4)$$

Thus at the bias points the modulated intensity changes have the same amplitude, but the opposite sign. The effect of reflection at various interfaces and other spurious outputs can be eliminated by subtracting the modulated outputs at the bias points. We therefore obtain the relation

$$r_{13} = \frac{1}{2\pi n^3} \frac{I_{\Omega}^{+} - I_{\Omega}^{-}}{I_{max} - I_{min}} \frac{\lambda}{V_m} \qquad (5)$$

which is same as that for a Mach-Zehnder interferometer, except for the factor of 2 due to the round trip of light in the sample. It is not required to measure the sample thickness to determine the linear EO coefficient.

The quadratic EO coefficient s_{13} can also be measured by the same configuration. In this case, s_{13} is given by

$$s_{13} = \frac{1}{\pi n^3} \frac{I_{2\Omega}^{+} - I_{2\Omega}^{-}}{I_{max} - I_{min}} \frac{\lambda d}{V_m^2} \qquad (6)$$

where $I_{2\Omega}^{+}$ and $I_{2\Omega}^{-}$ are the modulated intensity changes at the bias points at a frequency of 2Ω because the phase change depends on the square of the modulating field.

We measured the Pockels coefficient of several samples using this interferometric method. Measurements were also carried out using the birefringence method [8], and the results agreed within 10 %, if one assumes $r_{33}=3r_{13}$. Typical measured values of parameters defined in eq. (5) for polymer 2 are as follows: $\lambda = 0.633$ µm, $V_m= 4.3$ V, $I_{max}=36.5$ (relative unit for intensities), $I_{min}=2.7$, $I_{\Omega}^+= 49 \times 10^{-4}$, $I_{\Omega}^-= -59 \times 10^{-4}$. From these quantities, an r_{13} value of 1.6 pm/V was obtained. The measured EO coefficients of the new polymers are also summarized in table 1.

To prevent instability in the laser output, the interferometer was aligned so that no light was reflected back into the laser cavity. The main source of error in interferometric measurements is the instability of the modulated intensity because of random path length changes due to vibrations, air currents, and temperature fluctuations. The modified Michelson interferometer used in our experiments has fewer components and is much more compact than a Mach-Zehnder interferometer. Consequently, noise is considerably reduced. In principle, the setup can be made even more compact by directly depositing a mirror onto the beam splitter cube.

4. SHG measurements

Second order NLO properties of poled films have also been measured by SHG experiments. The light source was a Q-switched Nd-YAG laser of 10 ns pulse width with 15 mJ pulse energy at 1.064 µm. The detailed SHG

experimental arrangement and calculations of the second order NLO coefficient d_{33} have been described elsewhere [7,11,12]. The measured d values are also summarized in table 1.

Fig. 3 shows the time behavior of second harmonic (SH) intensity for one of the poled polymers (polymer 2). The crosslinked material is quite stable in its NLO properties compared with the uncrosslinked one.

INSERT   fig. 3

Acknowledgements

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Figure captions

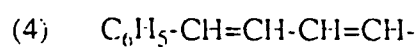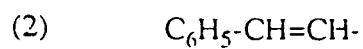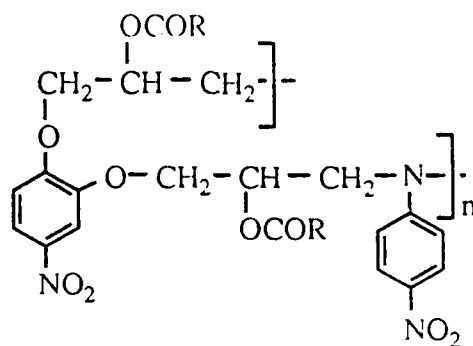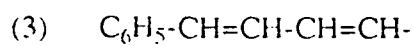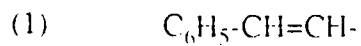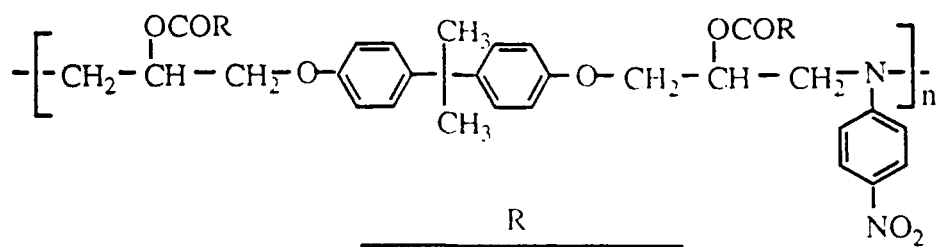Fig. 1. Structures of the new photocrosslinkable NLO polymers.
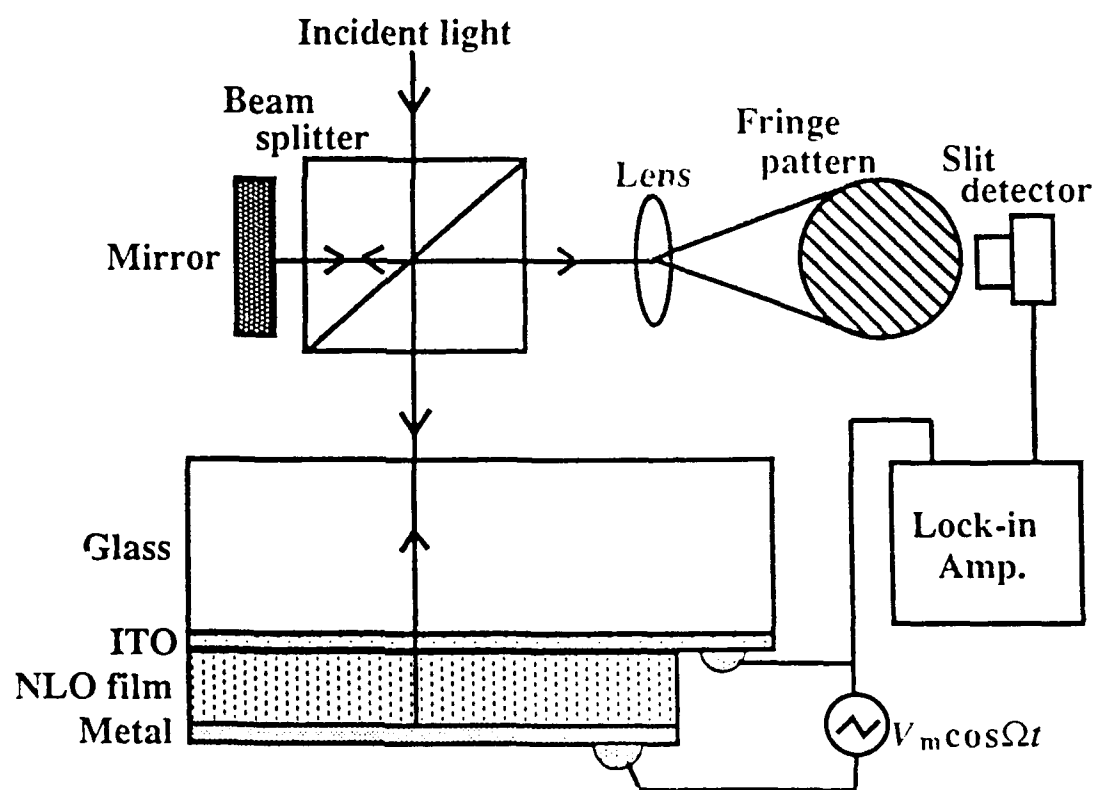
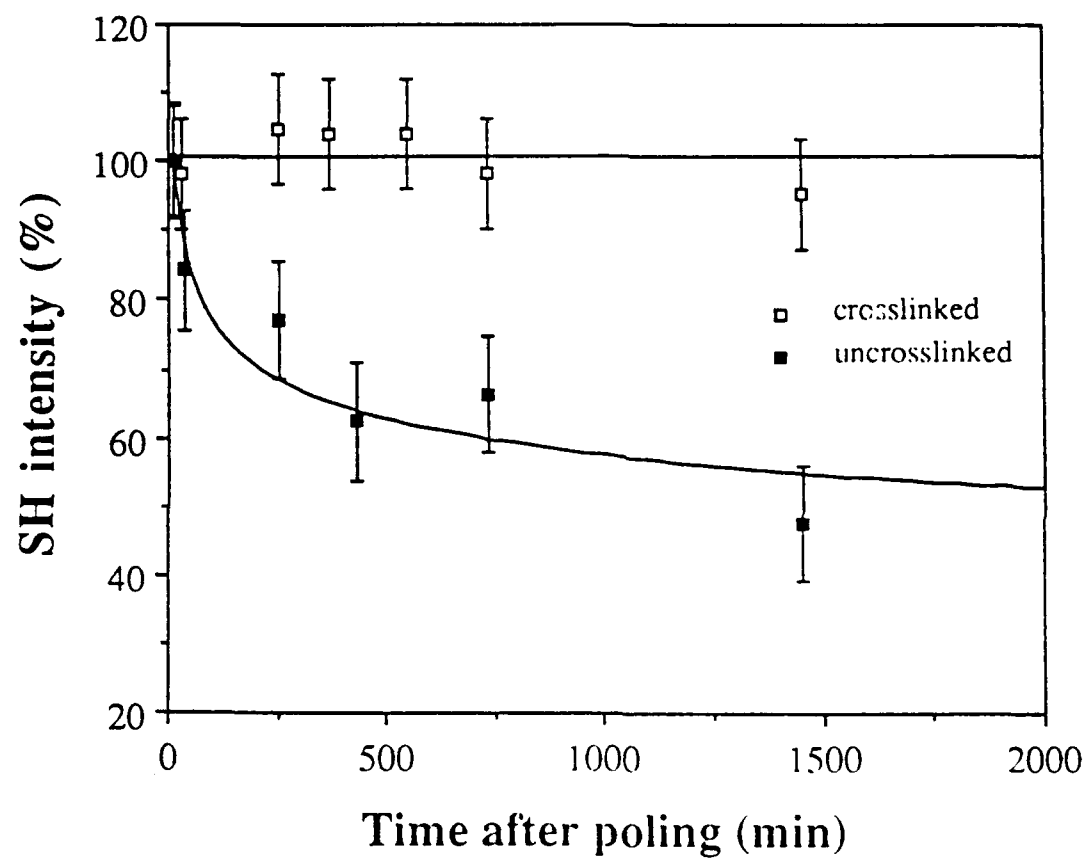Fig. 2. Experimental setup of the lock-in Michelson interferometer for EO measurements.

Fig. 3. Time behavior of SH intensity for a polymer 2 sample.

Table 1

Properties of the new polymers.

Polymer	1	2	3	4
T_g (°C)	83.4	78.2	84.6	88.0
Absorption				
peak λ (nm)	385	373		
n at λ (nm)				
532	1.64	1.70	1.66	1.71
633	1.64	1.68	1.63	1.66
1064	1.56	1.62	1.61	1.63
d_{33} (pm/V)	3.2	7.0	5.0	8.8
r_{33} (pm/V)	2.4	4.8	2.9	5.0

$$-\left[-CH_2-\underset{\underset{OCOR}{|}}{CH}-CH_2-O-\underzero\right]... $$

Structure (top):

−[−CH₂−CH(OCOR)−CH₂−O−C₆H₄−C(CH₃)₂−C₆H₄−O−CH₂−CH(OCOR)−CH₂−N(−C₆H₄−NO₂)−]ₙ

	R
(1)	C_6H_5-CH=CH-
(3)	C_6H_5-CH=CH-CH=CH-

Structure (bottom):

−[−(OCOR)CH₂−CH−CH₂−)− ; O−C₆H₃(NO₂)−O−CH₂−CH(OCOR)−CH₂−N(−C₆H₄−NO₂)−]ₙ

	R
(2)	C_6H_5-CH=CH-
(4)	C_6H_5-CH=CH-CH=CH-

Incident light

Beam
splitter

Mirror

Fringe
pattern

Lens

Slit
detector

Lock-in
Amp.

Glass

ITO
NLO film
Metal

$V_m \cos \Omega t$

crosslinked
uncrosslinked