Reflection measurement technique of electro-optic coefficients in lithium niobate crystals and poled polymer films

Yoshito Shuto and Michiyuki Amano
NTT Opto-electronics Laboratories, Nippon Telegraph and Telephone Corporation, Tokai, Ibaraki 319-11, Japan

(Received 18 October 1994; accepted for publication 5 January 1995)

A simple reflection technique proposed by Teng and Man [Appl. Phys. Lett. 56, 1734 (1990)] as well as independently by Schildkraut [Appl. Opt. 29, 2839 (1990)] for measuring the electro-optic coefficients of poled polymer films is applied to measure the $r_{33}$ values of both z-cut lithium niobate crystal and diazo-dye-substituted polymer films. The measured $r_{33}$ value of the lithium niobate crystal is in excellent agreement with the known value, and the observed $r_{33}$ values of the poled polymer films agree well with those predicted from the second-harmonic-generation measurements. © 1995 American Institute of Physics.

I. INTRODUCTION

The electro-optic (or Pockels) effect is the simplest and one of the most important nonlinear optical effects. Laser applications often require a technique for modulating the amplitude, phase, frequency, or direction of a light beam at high speed. In order to modulate the light, it is necessary to rely on optical interactions with electrical fields via the electro-optic (EO) effect of matter. Various EO modulators made of inorganic ferroelectric crystals such as KH$_2$PO$_4$ (KDP) and LiNbO$_3$ (LN) have been experimentally demonstrated.

In recent years, organic polymeric systems (poled polymers) containing molecular units with large second-order nonlinear susceptibilities have emerged as a promising class of EO materials. The poled polymers may be grouped into two systems:

1. guest-host systems, where the nonlinear-optical organic molecules (guests) are dissolved in a polymer “host;”
2. substituted systems, where the organic molecular units are covalently bound to a polymer backbone.

The large second-order nonlinear susceptibilities of the organic molecules and molecular units arise principally from $\pi$-electron conjugated systems substituted by electron donor and acceptor groups. The most striking advantage of poled polymers results from their unique EO mechanism. Unlike inorganic ferroelectric crystals, where the EO response is dominated by acoustic- and optical-phonon contributions, the EO effect in poled polymers arises mainly from electronic excitations in individual nonlinear molecules and molecular units. As a result, the poled polymers exhibit relatively large EO coefficients of 10-40 pm/V$^4$ with little dispersion from dc to optical frequencies, and 18-40 GHz optical intensity modulators have been demonstrated using the poled polymers.

In the first part of this article we describe an experimental setup for linear EO measurements at wavelength $\lambda = 1.31$ $\mu$m, the principle of which is the comparative determination of the phase-modulation indices by a reflection technique. This technique was recently proposed by Teng and Man as well as independently by Schildkraut for measuring the EO coefficients $r_{33}$ of poled polymer films. The reflection technique has been used for measuring the EO coefficients of several poled polymer films. In this article we have also applied this technique. First, the basic equations are derived for the phase retardations of the parallel ($p$-polarized wave) and perpendicular ($s$-polarized wave) components of the optical field which are due to the EO effect. Next, this technique is applied to measure the $r_{33}$ values of both lithium niobate crystal and diazo-dye-substituted poled polymers.

Second-harmonic-generation (SHG) and EO effects are both described by a second-order susceptibility tensor $\chi^2(-\omega_2,\omega_1,\omega_2)$. In the SHG case, all frequencies lie in the optical range, and the main contribution is electronic. In the EO case, one of the frequencies $\omega_1$ or $\omega_2$ is below the low-frequency resonances. The EO tensor therefore differs from the SHG tensor because of the additional contributions arising from photoelastic and piezoelectric vibrations. Dispersion of the local-field factors also plays a role in the dispersion between the two tensors. A few comparative studies of EO and SHG effects have already been reported with organic crystals and organic polymeric films. In the last part of this article we present a comparison between the SHG and EO coefficients of the diazo-dye-substituted poled polymer films, which are analyzed at a microscopic level.

II. OPTICAL PROPERTIES OF LITHIUM NIOBATE AND POLED POLYMER FILMS

A. Basic equations of reflection in uniaxial crystals

Equations relating to reflection and transmission at the boundary between a vacuum (or isotropic medium) and a uniaxial medium oriented with the optical axis normal to the interface have already been derived by several authors. In the particular case shown in Fig. 1, the uniaxial crystal (or film) is characterized through the use of ordinary and extraordinary complex dielectric constants $\varepsilon_r = n_r^2$ and $\varepsilon_c = n_c^2$. The very thin (40-150 nm) transparent electrode is sand-
wiched between isotropic air (or glass) and anisotropic crystal (or film) layers, and is usually ignored because of its thinness.

The reflection and refraction of light by a nonmagnetic transparent anisotropic medium have already been investigated by Landau and Lifshitz. In an anisotropic medium the wave vectors \( \mathbf{k} \) are given by

\[
\mathbf{k} = \left( \frac{2 \pi}{\lambda} \right) \mathbf{n},
\]

where \( \lambda \) is the optical wavelength and \( \mathbf{n} \) is the wave-normal vector. The magnitude \( n \) of the wave-normal vector in an anisotropic medium depends on its direction, whereas in an isotropic medium \( n \) depends only on the wavelength. The magnitude \( n \) is still called the refractive index, although it no longer bears the same simple relation to the law of refraction as in isotropic bodies.

The refractive indices of an anisotropic crystal (or film) for the optical field components parallel (\( \rho \)-polarized wave) and perpendicular (\( \sigma \)-polarized wave) to the plane of incidence are assumed to be \( n_{\rho} \) and \( n_{\sigma} \), respectively. In this condition, the phase shift of the \( \rho \) or \( \sigma \) wave component on reflection through a crystal (or film) of thickness \( d \) is expressed as follows (see the Appendix):

\[
\phi_\rho = 2d k_z = \left( 4 \pi d / \lambda \right) n_{\rho} \cos \alpha_\rho,
\]

where \( n_{\rho} \) is the \( \rho \) or \( \sigma \) wave component of the wave-normal vector (or refractive index) normal to the plane of the crystal (or film).

Mosteller and Wooten show that when the optical axis is normal to the surface, the ordinary wave in the uniaxial crystal is polarized normal to the plane of incidence (\( \sigma \) polarized) whereas the extraordinary wave is polarized parallel to the plane of incidence (\( \rho \) polarized). They have derived the relationship between the \( n_{\rho} \) values and the ordinary and extraordinary refractive indices \( n_o \) and \( n_e \). For an \( \sigma \)-polarized wave this is

\[
n_{\sigma}^2 = n_o \left( 1 - \sin^2 \theta / n_o^2 \right)^{1/2} \approx n_o \cos \alpha_\sigma,
\]

and for an \( \rho \)-polarized wave it is

\[
n_{\rho}^2 = n_o \left( 1 - \sin^2 \theta / n_o^2 \right)^{1/2} \approx n_o \cos \alpha_\rho,
\]

where \( \theta \) is the angle of incidence and \( \alpha_\sigma \) and \( \alpha_\rho \) are the refraction angles of \( \sigma \)- and \( \rho \)-polarized waves in a crystal (or film), respectively.

Next, we define the difference between the phase shifts of the \( \sigma \)- and \( \rho \)-polarized waves. By using Eqs. (2)–(4), the phase-shift difference \( \phi_{\sigma\rho} \) is expressed as follows:

\[
\phi_{\sigma\rho} = \left( 4 \pi d / \lambda \right) n_o \left( \cos \alpha_\sigma - \cos \alpha_\rho \right) = \left( 4 \pi d / \lambda \right) \left[ (n_o^2 - \sin^2 \theta)^{1/2} - (n_e / n_o)(n_e^2 - \sin^2 \theta)^{1/2} \right].
\]

**B. LN crystal**

LN is a uniaxial crystal belonging to the 3\( m \) class. The birefringence of a crystal can be expressed in terms of its index ellipsoid. The index ellipsoid has axes which are equal to the three crystal indices. In a uniaxial crystal of the 3\( m \) class such as LN, the equation for this ellipsoid can be written

\[
\frac{x^2 + y^2}{n_o^2} + \frac{z^2}{n_e^2} = 1,
\]

where \( n_o \) and \( n_e \) are the ordinary and the extraordinary refractive indices. The EO tensor for the LN crystal is given by

\[
\begin{pmatrix}
0 & -r_{22} & r_{13} \\
r_{22} & r_{33} & r_{13} \\
r_{51} & 0 & 0 \\
r_{51} & 0 & 0 \\
r_{22} & 0 & 0
\end{pmatrix}
\]

If an electric field is applied to the crystal, the index ellipsoid is deformed as

\[
\frac{1}{n_o^2} + \frac{1}{n_e^2} + \frac{z^2}{n_e^2} = 1,
\]

where \( E \) is the applied electric field in the direction of its subscript.

In Fig. 1 the uniaxial LN crystal is assumed to be cleaved normal to the optical axis (\( z \) cut). The laser beam is incident obliquely into the LN crystal (thickness \( d \)) at an angle \( \theta \), and then reflected back at the bottom of the crystal, as shown in Fig. 1. Here the \( z \) axis is the optical axis of the crystal and the incidence plane is the \( xz \) plane. In the following calculation the size of the beam is ignored.

In this configuration (Fig. 1), the electric field is applied to the \( z \) direction of the lithium niobate. For the field in the \( z \) direction \( (E_x = E_y = 0) \), Eq. (8) is reduced to

\[
\frac{1}{n_o^2} + \frac{1}{n_e^2} + \frac{z^2}{n_e^2} = 1.
\]

Now we rewrite Eq. (9) as follows:

\[
\frac{x^2 + y^2}{(n_o + \delta n_o)^2} + \frac{z^2}{(n_e + \delta n_e)^2} = 1,
\]
where $\delta n_\alpha$ and $\delta n_\varepsilon$ are the electro-optically induced changes in the refractive indices $n_\alpha$ and $n_\varepsilon$, respectively. From a comparison of Eqs. (9) and (10) we have

$$\delta n_\varepsilon = -n_\varepsilon r_{33} E_z/2,$$

(11)

$$\delta n_\alpha = -n_\alpha r_{13} E_z/2.$$

(12)

Next, we consider the EO change in the phase-shift difference $\phi_{sp}$ under the electric field $E_z$. By using Eqs. (5), (11), (12), this change $\delta \phi_{sp}$ is given by

$$\delta \phi_{sp} = \frac{2 \pi}{\lambda} \frac{r_{13} n_\alpha}{r_{33} n_\varepsilon} \left( \frac{n_\alpha r_{33} \sin^2 \theta}{(n_\varepsilon^2 - \sin^2 \theta)^{1/2}} + \frac{n_\varepsilon^4}{(n_\varepsilon^2 - \sin^2 \theta)^{1/2}} \right).$$

(13)

C. Poled polymer film

Polymeric films poled normal to the surface (z direction) have $\alpha mm$ symmetry with the uniaxis in the z direction. They can detect a longitudinal $E_z$ field. The EO tensor for the poled polymer films is written as

$$r_{ij} = \begin{pmatrix} 0 & 0 & r_{13} \\ 0 & 0 & r_{13} \\ r_{13} & 0 & 0 \end{pmatrix}.$$

(14)

Birefringence induced by the applied $E_z$ field is described using the index ellipsoid as

$$\left( \frac{1}{n_\alpha^2} + r_{13} E_z \right) x^2 + \left( \frac{1}{n_\varepsilon^2} + r_{33} E_z \right) z^2 = 1.$$  

(15)

Equation (15) is exactly the same as Eq. (9) for the LN crystal; therefore, Eqs. (10)–(13) described above also hold for the poled polymer films.

We can, however, use the following approximation for the poled polymer films which cannot be applied to the LN crystal:

$$n_\alpha \approx n_\varepsilon \approx n.$$  

(16)

By using this approximation and, from symmetry considerations, $r_{33} = 3 r_{13}$, the phase change $\delta \phi_{sp}$ for the poled polymer film with thickness $d$ is given by

$$\delta \phi_{sp} = \frac{4 \pi}{3 \lambda} \frac{d r_{13} E_z}{n_\varepsilon^2 \sin^2 \theta} \left( \frac{n_\varepsilon^2}{(n_\varepsilon^2 - \sin^2 \theta)^{1/2}} \right).$$  

(17)

III. EO MEASURING TECHNIQUE

A. Sample preparation

One side of a 0.5-mm-thick z-cut LN plate was coated with a 1500-Å-thick indium tin oxide (ITO) layer, and the other was coated with 2000-Å-thick gold layer. ITO is a transparent conducting material. The ITO and gold layers were fabricated with the electron-cyclotron-resonance (ECR) sputtering method and the dc magnetron sputtering method. Each layer serves as one of two electrodes used for the modulating field in the EO measurement.

The molecular structure of the polymer material we investigated is shown in Fig. 2. This material is a random copolymer of methyl methacrylate and diazo-dye-substituted methacrylate, and is hereafter abbreviated as 3RDCVXY. A molar ratio of diazo-dye-substituted methacrylate to methyl methacrylate is 3:17. The synthesis procedure of 3RDCVXY was described in detail by Amano et al. The diazo dye contains a dicyanovinyl group as an electron acceptor and a diethylamino group as an electron donor. This dye contains three benzene rings connected with azo groups, which form a longer $\pi$-conjugated system than that of a conventional monoazo dye [Disperse Red 1 (DR1)] compound. As a result, the second-order molecular hyperpolarizability $\beta_{33}$ (2.8×10$^{-27}$ esu) and dipole moment $\mu$ (8.0 D) of the diazo dye are greater than those of DR1 dye.

A 5-μm-thick 3RDCVXY polymer film was spin coated onto a glass substrate that had been precoated with an approximately 250-Å-thick ITO layer. A gold layer approximately 1000 Å thick was then formed on top of the polymer layer by thermal evaporation. The ITO and gold layers were used as both poling and modulation electrodes. The poling was performed at 140 °C, which is above the glass-rubber transition temperature ($T_g$: 100–120 °C) of the 3RDCVXY film. As a dielectric breakdown occurred at the high electric field of 120–150 MV/m, relatively low electric fields (14, 21, 28, and 35 MV/m) were utilized for the poling. On the other hand, these poling electric fields were high enough to compress the 3RDCVXY film due to the electrostatic stress (0.3–2.0×10$^5$ dyn/cm$^2$) at 140 °C, although most of the electrostatic compressive force can be relaxed by the thermal-expansive force. Unfortunately, as the extension modulus above the glass-rubber transition temperature could not be measured, we cannot estimate an exact thickness of the 3RDCVXY film at 140 °C. Therefore, we assume in this article that the film thickness at 140 °C is the same as that (5 μm) determined at room temperature.

B. Measurement principle

Our measuring system is shown in Fig. 3. A laser beam at $\lambda = 1.31$ μm is incident on the back of the glass substrate.
at an angle $\theta$. It propagates through the substrate, the ITO electrode, and the LN crystal or polymer film, and is then reflected back out into the air by the bottom gold electrode (see Fig. 1). The polarization of the input beam is set at 45° to the plane of incidence so that the parallel ($p$-wave) and perpendicular ($s$-wave) components of the optical field are equal in amplitude. The reflected beam propagates through a Babinet–Soleil (BS) compensator, a half-wave plate and an analyzer (polarized beam splitter). Two detectors are employed to measure the intensities of the beams transmitted and rejected at the analyzer. These signals are then processed by a differential amplifier and a lock-in amplifier. The differential system provides a means for making the detection system less susceptible to laser fluctuations while doubling the voltage sensitivity. The modulated sample is optically biased (via the BS compensator) at its quarter-wave point in order to achieve a linear response as well as maximum voltage sensitivity.

In this crossed-polarizer configuration, the relationship between the phase difference $\phi_{sp}$ and the output laser intensity $I_o$ at the detector can be described by

$$I_o = 2I_c \sin^2(\phi_{sp}/2).$$

where $I_c$ is half the maximum intensity.

When a modulation voltage $V - V_m \sin \omega_mt$ is applied across the electrodes, the phase change $\delta \phi_{sp}$ is induced by the change in refractive indices of the ordinary and extraordinary waves due to the EO effect. As a result, the following equations can be derived for the uniaxial crystals:

$$\delta \phi_{sp} = \Gamma_m \sin \omega_m t,$$

Figure 4 shows a plot of the output beam intensity $I_o$ as a function of the phase difference between the $s$ and $p$ waves as described by Eq. (18). When this intensity is biased at half-intensity $I_c$, at point A, the curve is in its most linear region, and for small modulations the ratio between the modulated beam intensity $I_m$ and the half-intensity $I_c$ can be approximated by

$$I_m/I_c \approx \delta \phi_{sp}.$$

Therefore, by using Eqs. (19)–(21) and $\zeta = r_{13}/r_{33}$, the $r_{33}$ value of the uniaxial LN crystal is expressed as follows:

$$r_{33} = \left( \frac{\lambda}{2\pi} \right) \frac{I_m}{I_c V_m} \left[ \frac{n_o n_e \sin^2 \theta}{(n_e^2 - \sin^2 \theta)^{1/2}} + \zeta \left( \frac{n_e^4}{n_o^2} \right) \left( n_e^2 - \sin^2 \theta \right)^{1/2} \right]^{-1}.$$

For the poled polymer films the above equation is simplified as follows:

$$r_{33} = \frac{3\lambda}{4\pi n_e^2} \frac{I_m}{I_c V_m} \frac{(n^2 - \sin^2 \theta)^{1/2}}{\sin^2 \theta}.$$

C. Measurement results

In the EO measurement of the $z$-cut LN plate, a modulating voltage was applied across the ITO-Au electrodes at 1 kHz, and the incident angle $\theta$ of 1.31 $\mu$m laser light was set at 60°. Under this condition the half-intensity $I_c$ was determined as 80 mV. The relationship between the modulation-voltage amplitude $V_m$ and the measured modulated-beam intensity $I_m$ is shown in Fig. 5. The $I_m$ value is directly proportional to the $V_m$ value, and from the slope of this
The EO measurement of the poled polymer films was performed under the same conditions as the LN plate. The refractive indices for the poled 3RDCVXY polymer films at 1.30 \( \mu \text{m} \) were accurately measured with a prism coupler (Metricon PC-2100) where the TE- and TM-polarized laser light was coupled into and out of the films spin coated on Si wafers. The refractive index of the poled 3RDCVXY film was 1.5481 at 1.30 \( \mu \text{m} \). In this film the difference between the refractive indices measured with the TE- and TM-polarized light was very small (<0.001). This means that the ordinary and extraordinary refractive indices of the film are nearly the same, as assumed in Eq. (16).

3RDCVXY polymer films 5 \( \mu \text{m} \) thick were poled in an electric field of 14, 21, 28, and 35 MV/m. For the 14 MV/m poled polymer film the half-intensity \( I_\text{m} \) was determined as 170 mV. The relationship between the modulation voltage amplitude \( V_m \) and the measured modulated-beam intensity \( I_m \) is shown in Fig. 6. As shown for the LN plate, the \( I_m \) value is directly proportional to the \( V_m \) value, and from the slope of this figure the \( I_m/V_m \) value is determined as \( 15.8 \times 10^{-6} \) for the polymer film. By substituting these values in Eq. (22) the \( r_{33} \) value for the 14 MV/m poled 3RDCVXY film is estimated to be 2.1 pm/V at 1.31 \( \mu \text{m} \).

The \( r_{33} \) values of the other films poled at 21–35 MV/m were determined using the same procedure as that for the 14 MV/m poled film described above. These \( r_{33} \) values are listed in Table I.

### D. Comparison of EO coefficients with second-harmonic coefficients

The \( \chi^{(2)} \) values of the poled 3RDCVXY films at 1.55 \( \mu \text{m} \) were determined from SHG measurements. The experimental setup is shown in Fig. 7. 5-\( \mu \text{m} \)-thick polymer samples were spin coated onto Si wafers and poled at 14, 21, 28, and 35 MV/m with the electrode poling method. The fundamental wave at 1.55 \( \mu \text{m} \) was generated using differential frequency generation of a second-harmonic (SH) wave at 1.06 \( \mu \text{m} \) and a tunable dye laser. The SH intensities from the
polymer films were measured as a function of laser incident angles, and \( \chi_3^{(2)} \) values were determined using a single-crystal quartz plate (\( \chi_0^{(2)} = 0.67 \text{ pm/V} \)) as a reference. The determined \( \chi_3^{(2)} \) values of the poled 3RDCVXY films are listed in Table I.

The relationship between the EO coefficient \( r_{33} \) and the \( \chi_3^{(2)} \) values measured at different frequencies \( \omega \) and \( \omega' \) is given by

\[
r_{33}(-\omega;\omega,0) = -\frac{2\chi_3^{(2)}(-2\omega';\omega';\omega')}{n_\omega f(0)} \frac{f(\omega)^2 f(0)}{f(0)^2 f(2\omega')} \times \frac{(3\omega_0^2-\omega^2)(\omega_0^2-\omega'^2)(\omega_0^2-4\omega'^2)}{3\omega_0^2(\omega_0^2-\omega'^2)^2},
\]

where \( \omega_0 \) is the frequency of the absorption peak (0.505 \( \mu \text{m} \)) of the 3RDCVXY film and \( f \) is the local field factor. In our experiments the wavelengths of the EO experiment (1.31 \( \mu \text{m} \)) and the SHG measurement (1.55 \( \mu \text{m} \)) are close to each other, but distant from the absorption peak. Therefore, in our case Eq. (24) is simplified as follows:

\[
r_{33}(\omega;\omega,0) = 2\chi_3^{(2)}(-2\omega';\omega';\omega') \frac{f(0)}{n_\omega^4} \frac{f(\omega)^2 f(2\omega')}{f(0)^2 f(2\omega')} \times \frac{(3\omega_0^2-\omega^2)(\omega_0^2-\omega'^2)}{3\omega_0^2(\omega_0^2-\omega'^2)}. \tag{25}
\]

Here, using the Onsagar and Debye approximations, \( f(0) = (n_D^2 + 2)/(2\epsilon + n_D^2) \)

\[
f(0) = \frac{\epsilon(n_D^2 + 2)}{(2\epsilon + n_D^2)}, \tag{26}
\]

\[
f(2\omega') = (n_{2\omega'}^2 + 2)/3, \tag{27}
\]

where \( \epsilon \) and \( n_D \) are the dielectric constant and the refractive index at the Na D line (0.589 \( \mu \text{m} \)) of the 3RDCVXY film, respectively. When we assume \( n_D = n_{2\omega'} = 1.6 \) and \( \epsilon = 3.5 \), the product of the second and third terms of the right-hand side of Eq. (25) becomes 1.03. Therefore, Eq. (25) is further simplified as follows:

\[
r_{33}(-\omega;\omega,0) \sim 2\chi_3^{(2)}(-2\omega';\omega';\omega') \frac{n_\omega^4}{n_\omega^4} = 2\chi_3^{(2)}(-2\omega';\omega';\omega'). \tag{28}
\]

The \( r_{33} \) values of the poled 3RDCVXY films can be estimated by using the \( \chi_3^{(2)} \) values measured at 1.55 \( \mu \text{m} \) listed in Table I and Eq. (28). The estimated \( r_{33} \) values are also listed in Table I. These values agree well with the electro-optically determined \( r_{33} \) values if we take account of the poling-experiment error of about \( \pm 10\% \).

IV. DISCUSSION

In this section we discuss in detail the piezoelectric contribution to the linear EO effect in the poled polymers.

It was assumed in Eqs. (9) and (15) that the EO effects of the LN crystal and poled polymer films were defined at zero strain (clamped); however, an applied low-frequency electric field can actually induce strains via the piezoelectric and electrostrictive effects in a crystal or film that is free to respond (unclamped). These strains change the ordinary or extraordinary refractive indices of a crystal (or film) due to the photoelastic or elasto-optic effect. The electrically induced strain tensor is given by

\[
S_{mn} = d_{k, mn}E_k + \gamma_{31, mn}E_kE_l, \tag{29}
\]

where the linear and quadratic terms are the piezoelectric and electrostrictive effects, respectively. Among these effects the linear EO (or Pockels) effect is influenced only by the piezoelectric effect. It is well known that in a LN crystal the linear EO coefficients \( r_{33} \) and \( r_{33} \) determined under the unclamped condition are about 10\% larger than those in the clamped condition.\(^2\) Both the electro-optically determined and the known \( r_{33} \) values for the \( z \)-cut LN plate described above are unclamped values.

Next, we examine the piezoelectric contribution to the linear EO effect in the poled polymers. Taking the piezoelectric effect into account, the relationship between the \( r_{33} \) values under unclamped and clamped conditions is simply expressed as follows:

\[
r_{33}^U - r_{33}^C + \rho_{33} d_{33}, \tag{30}
\]

where \( r_{33}^U \) and \( r_{33}^C \) are the \( r_{33} \) values under unclamped and clamped conditions, respectively, \( \rho_{33} \) is the photoelastic constant, and \( d_{33} \) is the piezoelectric coefficient. The photoelastic constants of a wide variety of materials lie in the range from about 0.1 to 0.6.\(^2\) The \( \rho_{33} \) value of 3RDCVXY polymer has not yet been measured; however, we assume that the \( \rho_{33} \) value is the same as that \((-0.3)\) for polystyrene polymer.\(^2\)

On the other hand, the piezoelectric (strain) constant \( d_{33} \) has not been determined for 3RDCVXY, whose base polymer is poly(methylmethacrylate) (PMMA). However, the \( d_{33} \) value for the PMMA polymer has already been determined as \( 4.4 \times 10^{-17} \text{ C/N} \);\(^3\) therefore, we assume that the \( d_{33} \) values of the 3RDCVXY and the PMMA polymers are the same. This \( d_{33} \) value is very small, compared with that \((6 \times 10^{-12} \text{ C/N})\) of the LN crystal. As a result, we conclude that the piezoelectric contribution to the linear EO effect can be completely ignored in the poled 3RDCVXY polymers.

V. CONCLUSION

A simple reflection technique proposed by Teng and Man as well as independently by Schildkraut for measuring the EO coefficient of nonlinear optical polymeric films is applied to measure the \( r_{33} \) values of both \( z \)-cut lithium niobate crystal and diazo-dye-substituted polymer (3RDCVXY) films. The measured \( r_{33} \) value of the lithium niobate crystal is in excellent agreement with the known value, and the observed \( r_{33} \) values of the poled 3RDCVXY films agree well with those predicted from SHG measurements. The piezoelectric contribution to the linear EO effect can be completely ignored in the poled 3RDCVXY polymers.

ACKNOWLEDGMENTS

We gratefully acknowledge helpful discussions with M. Yaita, T. Nagatsu, S. Tomaru, and T. Watanabe. We wish to thank T. Kaino, S. Inoue, H. Kozawaguchi, and H. Hiratsuka for their continuous encouragement.
APPENDIX: DERIVATION OF PHASE SHIFT

Suppose a laser beam is obliquely incident into a crystal (thickness \(d\)) at an angle \(\theta\), and then reflected back from the bottom of the crystal, as shown in Fig. 1. In the following calculation, the size of the beam is ignored. The refractive indices of the crystal for the optical field components parallel (p wave) and perpendicular (s wave) to the plane of incidence are \(n_p\) and \(n_s\), respectively. Then, the refraction angles of each wave indicated as \(\alpha_p\) and \(\alpha_s\) for \(p\) and \(s\) waves are related to the incident angle \(\theta\) as

\[
\sin \theta = n_p \sin \alpha_p = n_s \sin \alpha_s \quad \text{(Snell’s law)} \tag{A1}
\]

\[
S_s - S_p = n_p (AB' + BC') - n_p (AB + BC + CD) = 2d (n_p \cos \alpha_p - \tan \alpha_s \sin \theta - n_p \cos \alpha_p + \tan \alpha_p \sin \theta)
\]

\[
= 2d (n_p \cos \alpha_s - n_s \sin^2 \alpha_s / \cos \alpha_s + n_p \cos \alpha_p + n_p \sin^2 \alpha_p / \cos \alpha_p) = 2d (n_s \cos \alpha_s - n_p \cos \alpha_s)
\]

\[
= 2d (n_s - n_p).
\]

From Eq. (A5) we can obtain the definition of optical path \(S_i\) for \(s\) and/or \(p\) waves as follows:

\[
S_i = 2dn^i (i = p \text{ or } s). \tag{A6}
\]

Therefore, the phase shift of the \(p\) or \(s\) wave component is given by

\[
\phi = (2 \pi / \lambda) S_i = (4 \pi d / \lambda) n^i.
\]

In this configuration (Fig. 1), the optical paths \(S_s\) and \(S_p\) for \(s\) and \(p\) waves differ from each other. The length of each path is given as follows:

\[
AB + BC = 2d / \cos \alpha_p. \tag{A2}
\]

\[
AB' + B'C' = 2d / \cos \alpha_s. \tag{A3}
\]

\[
CD = 2d (\tan \alpha_s - \tan \alpha_p) \sin \theta. \tag{A4}
\]

By using Eqs. (A1)–(A4), the difference in the optical paths \(S_s\) and \(S_p\) can be expressed as

\[
S_s - S_p = 2d (n_s - n_p), \tag{A5}
\]