Second-harmonic light generation in pyroelectric liquid-crystal polymers

Mikael Lindgren

*Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden and
Division of Laser Systems, National Defense Research Establishment, P.O. Box 1165, S-581 11 Linköping, Sweden*

David S. Hermann

Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Jonas Örtegren

Department of Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Per-Otto Arntzen

Division of Laser Systems, National Defense Research Establishment, P.O. Box 1165, S-581 11 Linköping, Sweden

Ulf W. Gedde and Anders Hult

Department of Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Lachezar Komitov, Sven T. Lagerwall, Per Rudquist, and Bengt Stebler

Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Fredrik Sahlén and Mikael Trollsås

Department of Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Pyroelectric liquid-crystal polymers were prepared by photopolymerization of binary mixtures of two monomers that exhibit a smectic C^* phase: A2c, $4''$-{(R)-$(-)$-2-[(10-acryloyloxy)decyl]oxy}-3-nitrophenyl 4-{$4'$-[(11-acryloyloxy)undecyloxy]phenyl}benzoate and A1b, $4''$-((R)-$(+)$-2-octyloxy)-$3''$-nitro phenyl 4-($4'$-[(11-acryloyloxy)undecyloxy]phenyl) benzoate.   Both liquid-crystal monomers have a NO_2 substituent to enhance the nonlinear optical properties, and one of the monomers, A2c, permits polymerization to a cross-linked polymer.   During the polymerization an electric field of approximately 25–50 V/μm was applied over the ferroelectric liquid-crystal cells.   All cases of polymers formed from the chiral smectic C^* phase showed a second-harmonic-generated signal with no external field present, indicating that polar order became fixed.   The orientation dependence of the second-harmonic-generated intensity was similar to that of the ferroelectric liquid-crystal monomer; however, some changes were observed that might be due to changes in the dielectric axes of the system.   The highest d_{16} and d_{23} coefficients were found to be in the range 0.65–0.8 pm/V and differed depending on the detailed preparation of the sample.   Experimental results of several polarization combinations of the pump and frequency-doubled light are presented and discussed.   © 1998 Optical Society of America   [S0740-3224(98)01202-8]

OCIS codes: 190.4160, 160.3710, 160.2100, 160.5470.

1. INTRODUCTION

In certain types of crystals and other ordered materials the application of an electric field results in changes of the refractive index.   The refractive-index change can be used to produce a phase shift of a polarized light wave that can cause a change in the polarization state of the light.   Thus the related phenomena constitute the fundamental means for converting a time-dependent electrical signal into an optical signal.[1,2]   Usually it is possible to exploit the same kinds of material in frequency upconver-sion, optical parametric generation, or other frequency-conversion schemes based on the nonlinear interaction of light waves, because the electro-optic coefficient is related to the d coefficient used to describe frequency conver-sion.[3,4]

A severe constraint on the electro-optic material in question is that the crystal or polymeric material must possess noncentrosymmetry.   This condition is automatically fulfilled for several crystal classes.   For a polymer in which the macromolecules usually are distributed ran-

domly, or at least in a centrosymmetric manner, the noncentrosymmetry can be induced by an applied static electric field, the so-called poling field, during the processing of the polymer system.[5] The requirements on the polymer are that it contain molecules with a permanent dipole moment and be flexible enough at a certain accessible temperature to permit the reorientation under the applied poling field. For long-term stability one requires that the polymer material be as stiff as possible at the operating temperatures.

Ferroelectric liquid crystals (FLC's) are made up of chiral molecules that have a pronounced elongated shape, giving rise to an intrinsically noncentrosymmetric system of high order.[6,7] The FLC's can form domains that possess a spontaneous polarization, and in certain systems it is possible to switch among several states, which makes these crystals useful in display technology devices and other devices based on modification of the polarization state of the light.[8] The FLC molecules can be modified to contain additional functions such as enhanced nonlinear optical activity[9,10] and the ability to be polymerized.[11–14] The synthesis and preliminary results of electro-optic and second-harmonic-generation (SHG) measurements of polymers made from monomers in a smectic C^* phase have been published recently.[11] The ability for ferroelectric switching is lost in the produced film; however, the spontaneous polarization is retained, and consequently the polymer films are pyroelectric. The new class of materials is called pyroelectric liquid-crystal polymers (PLCP's). The ability to control both orientation and function of these novel materials could be interesting to exploit further in certain device applications based on the electro-optic function, such as devices based on the photorefractive effect, spatial light modulators, and integrated electro-optically active waveguides.[15]

Here we report the nonlinear optical properties in terms of SHG of PLCP's. The samples are made from binary mixtures of monomers that have the built-in proper-ties to polymerize and to cross link and also a lateral dipole to enhance the nonlinear optical properties.

2. METHODS

A. Sample Preparation

The materials A2c and A1b, depicted in Fig. 1, were synthesized and prepared according to procedures reported elsewhere.[11,12] Conventional 4-μm test cells (EHC Co., Tokyo) were filled with monomer materials A2c and A1b in different proportions, together with a photoinitiator [2,4,6-trimethylbenzoyldiphenylphosphine oxide (BASF-AG, Ludwigshafen, Germany)]. Proper alignment and definition of the bookshelf geometry were obtained by slow cooling of the sample from ~40 to 25 °C while the cell structure was monitored in a polarization microscope. The ferroelectric switching properties could be studied simultaneously by application of a modulating voltage. The SmC^* tilt angle could be controlled and set to a desired value during the polymerization, here always 30–33°, by application of a constant dc voltage after the switching properties were checked. From the measured orientation of the optic axis the tilt angle could also be checked after the polymerization had taken place. After the polymerization the electric contacts were discon-
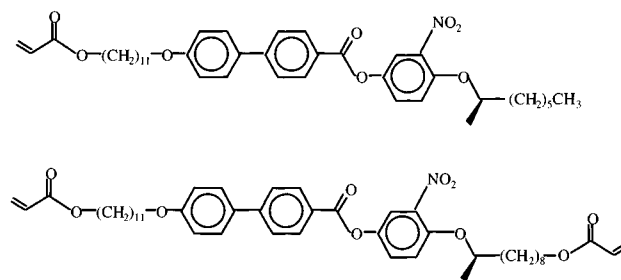

Fig. 1.   Molecular structures of the liquid-crystal monomers, A1b (top) and A2c (bottom), used for polymerization to PLCP in this study.
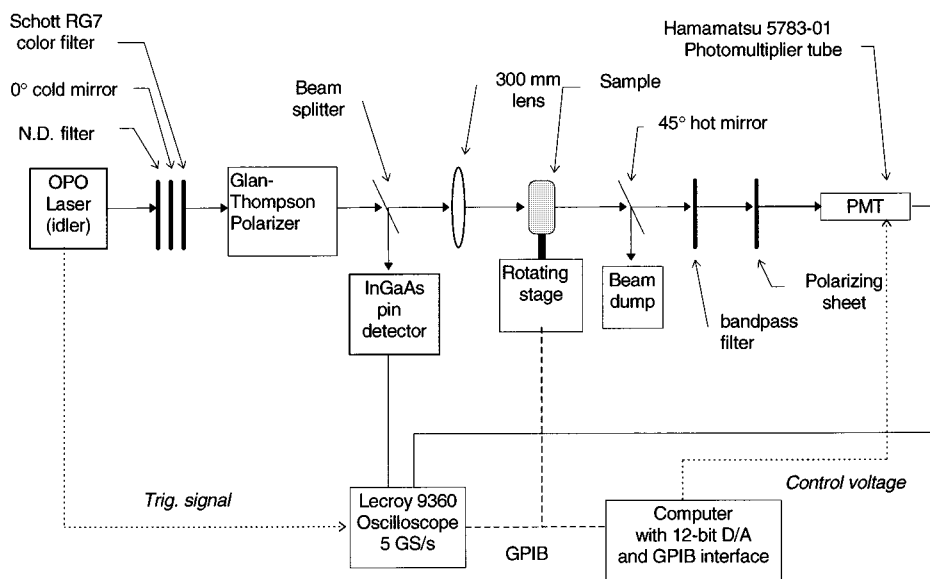

Fig. 2.   Schematic of the experimental setup used for SHG measurements.   Details on the components are given in Section 2. GS/s, gigasamples/second; GPIB, general-purpose interface bus.

nected and the sample was stored in a freezer (at -30 °C) until it was mounted for SHG measurements. All the data on PLCP's discussed in this study were collected with no external voltage applied over the cell containing the PLCP film.

B. Second-Harmonic-Generation Experimental Setup

The frequency conversion from 1100 to 550 nm was examined with a modified Maker-fringe setup for SHG.[16] A schematic of the experimental setup is depicted in Fig. 2. The idler output of a Sunlite Continuum optical parametric oscillator (opo) laser, tuned to 1100 nm, was employed as the pump beam. After adjustment to the appropriate power (approximately 6–12 mJ/7 ns) by a set of neutral-density (N.D.) filters, the spectral and polarization purity of the beam was enhanced by a combination of a cold mirror (Melles Griot), an RG7 absorption filter (Schott), and a Glan–Thompson polarizer (Newport). Approximately 1% of the beam intensity was extracted with a beam splitter and detected with a reference detector (InGaAs p-i-n diode; Newport). The pump beam was focused onto the sample by a 300- or 400-mm lens. The angle of incidence was varied by a rotation stage controlled by a Microcontrole IP28/PP28 unit. The SHG light was detected with a Hamamatsu 5783-01 photomultiplier tube (PMT) after passing through a 45° hot mirror and two narrow-bandwidth (10-and 40-nm) interference filters (Melles Griot). The signals of the reference detector and the photomultiplier were measured with a 5-GS/s oscilloscope (Lecroy 9360). The rotational stage, the oscilloscope, and the sensitivity of the PMT were all controlled by means of a GPIB bus through a Dell 486/ME computer operating under Windows 3.11.

C. Sample Positioning

A coordinate systems used to describe the orientation of a sample is shown in Fig. 3. The X, Y, Z coordinate system refers to the fixed laboratory frame, and x, y, z to the sample cell that could be oriented by various means. A thin sample holder was constructed that permitted free rotation of the sample about the y axis (ϕ). The whole sample holder could be rotated about the Z axis (θ) by use of a computer-controlled stepper motor. In addition, the sample had micrometer adjustments along Y and the whole sample holder had a coarse adjustment along X and Z. The two last-named degrees of freedom permitted the translation of the sample within the focused pump beam and kept the same spot position on a selected surface of the sample during simultaneous rotation about the Z and y axes.

In the experimental setup the pump laser beam was always propagating in the negative Y direction and polarized along the X axis. Since the incidence angle θ is varied by rotation about the Z axis, the incident beam was always p polarized. For an unwound smectic C* phase under polar alignment the C_2 symmetry axis is parallel with the plane normal (y axis). Here it will be assumed that the optical symmetry is uniaxial, and we take the z axis as the direction of the optic axis (parallel to the molecular director). With a polarizer in front of the PMT either the p or the s polarization of the SHG light was de-
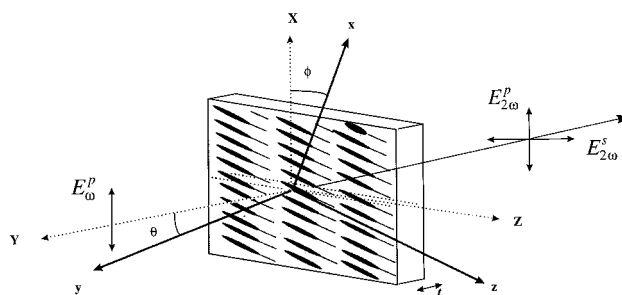

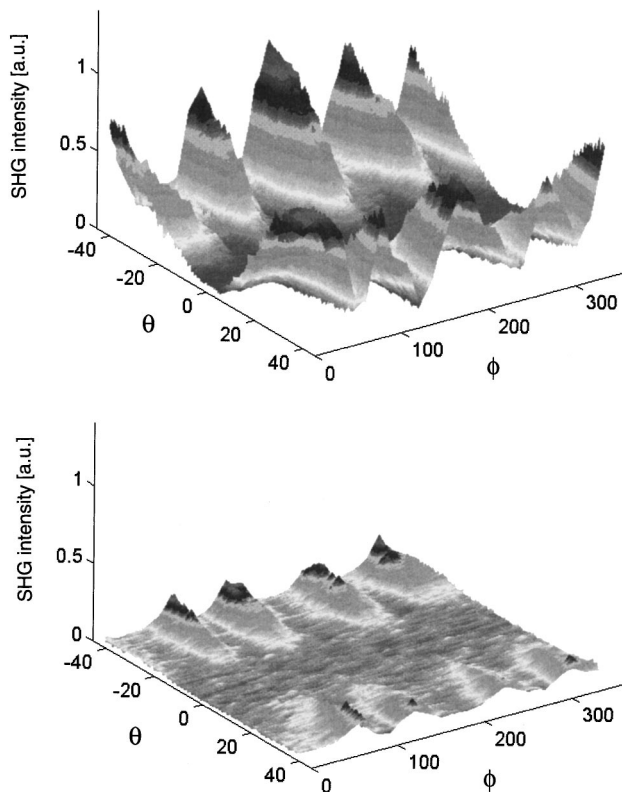Fig. 3. Schematic of a FLC or a PLCP defining the laboratory (XYZ) and the sample (xyz) coordinate frames.

Fig. 4. SHG intensity as a function of angles θ and ϕ of the A2c monomer with a 100-V field applied over the FLC cell. Top, p-(pump) to p- (detected) conversion; bottom, p-to-s conversion.

tected. Thus with the two rotational degrees of freedom of the sample it was possible to investigate all kinds of polarization combinations between the pump and the SHG light to determine the specific symmetry of the FLC or PLCP film, i.e., the interaction of two waves, ordinary (o) and extraordinary (e), at the pump frequency ω, to yield o or e waves at the second-harmonic frequency, 2ω.

D. Simulation of Transmission through a Liquid-Crystal Film

The calculation of the transmission of a p-polarized wave was made by solution of the Maxwell equations under appropriate boundary conditions for a plane wave incident upon an anisotropic thin film. The calculations were carried out with a MATLAB computer program; the boundary

and the eigenmodes of refraction were solved by numerical matrix manipulations containing all six field components simultaneously.

3. RESULTS AND DISCUSSION

A. General Orientation Dependence of the Pyroelectric Liquid-Crystal Polymer Film

The variation of the incidence angle (θ) for different settings of the sample orientation (ϕ) of an incident pump beam permits the examination of all possible polarization combinations for the conversion to second-harmonic light. Data obtained from a cell filled with the monomer A2c under an applied field of 100 V are shown in Fig. 4. By rotating the sample a full 360° turn we detected four distinct maxima of second-harmonic light for both polarization combinations, *p* and *s*, at the detector; however, the four maxima of the *p*-to-*s* conversion are shifted approximately 45° with respect to those observed for the *p*-to-*p* conversion. The magnitude of the SHG intensity at each maximum was found to depend on the applied voltage, which is as expected from previous studies of FLC monomer systems.[17,18]

The polymerization of A2c, A1b, and binary mixtures thereof, under an applied electric field, produces PLCP films. Representative SHG data of a cell with polymerized A1b monomer obtained under experimental conditions similar to those for the FLC system shown in Fig. 4 are shown in Fig. 5. The plot of SHG intensity corresponding to the *p*-to-*p* conversion expresses a behavior very similar to that for the FLC monomer case with respect to the orientation dependence; however, the plot of
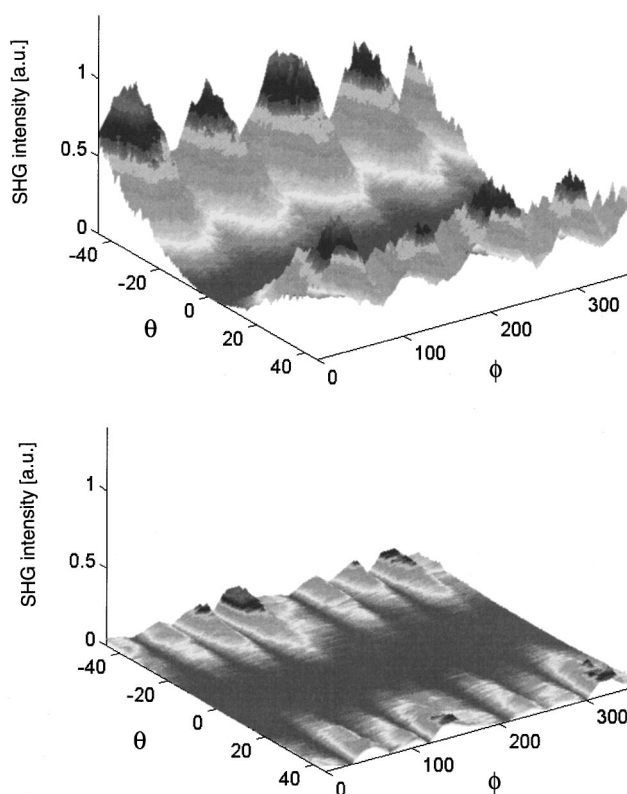

Fig. 5. SHG intensity as a function of angles θ and ϕ of the PLCP based on the A1b monomer. Top, *p*- (pump) to *p*- (detected) conversion; bottom, *p*-to-*s* conversion.
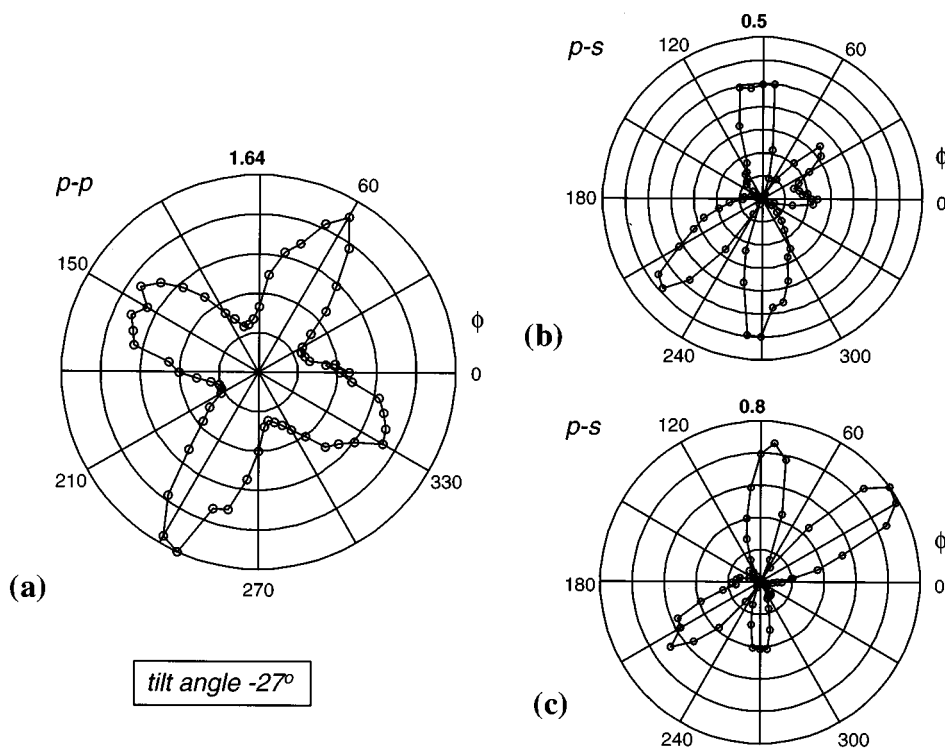

Fig. 6. SHG intensity as a function of angle ϕ with θ kept fixed. The PLCP sample is based on a mixture of A1b:A2c monomers in the proportions 60:40. (a) *p*- (pump) to *p*- (detected) conversion; (b) *p*-to-*s* conversion, $\theta = +40°$; (c) *p*-to-*s* conversion, $\theta = -40°$. The solid curves connecting the data points (circles) are included to guide the eye and have no other meaning.

the p-to-s conversion indicates a similar, but more complicated, interaction of the pump wave with the sample. The magnitude of the measured SHG intensity is approximately the same for both the unwound FLC with an applied voltage and the PLCP film, and it appears evident that some of the spontaneous polarization has been fixed in the PLCP by the polymer network.

An alternative way to express the orientation behavior of the SHG intensity of FLC or PLCP films is to plot the ϕ dependence of the detected SHG intensity while keeping θ at a fixed value. This is also a fast way to collect experimental data on the orientation dependence of a thin film, because only one parameter needs to be varied. The SHG intensity as a function of ϕ dependence, for a PLCP based on a binary mixture A1b:A2c with the proportions 60:40, is plotted in Fig. 6. We determined the tilt angle by using a polarization microscope after the polymerization reaction, and for this sample the angle was found to be $\sim 27°$. The tilt angle is also known to define two of the lobes of maximum SHG intensity in the plot of the ϕ dependence for a FLC sample in the smectic C* phase with the helix unwound by an applied electric field.[18] Thus the maximal features of the p-to-p conversion [Fig. 6(a)] correspond to orientation with the optic axis perpendicular or parallel to the plane of incidence, just as in the case with the FLC monomer. We can conclude that PLCP films and the unwound FLC have similar orders with regard to both polar order and the orientation of the molecular director.

As indicated by a comparison of Figs. 4 and 5, the p-to-s conversion seems to have an entirely different angular dependence (ϕ), as is shown more clearly in the measurements of the ϕ dependence when the s-polarized SHG light is detected. The results of a binary mixture PLCP are shown in Figs. 6(b) and 6(c) for two different angles of incidence (θ), revealing a prominent asymmetry in the angular (ϕ) distribution of the detected SHG intensity. It is noteworthy that the angular positions that yield large p-to-p conversion are always accompanied by a minimum in the p-to-s conversion.

As shown above, the maxima of the p-to-p conversion in the plot of the ϕ dependence correspond to the orientations of the sample with the director perpendicular or parallel to the plane of incidence. This fact also gives the clue on how to interpret the orientation dependence (ϕ) of the p-to-s conversion. Refraction of light into a surface of a uniaxial sample generally produces both an e and an o wave within the sample, and special cases occur when the optic axis lies within the plane of incidence or perpendicular to the plane of incidence. When the director is in the plane of the sample (parallel to the surface) and perpendicular to the plane of incidence, an o wave always remains an o wave, independently of the incidence angle (θ). Similarly, an e wave remains an e wave when the director lies in the plane of incidence. For other orientations of the director the refraction of the pump beam at the input surface always produces an e wave together with an o wave. A small fraction of the light is reflected at the first surface, and the remaining light gives rise to both e- and o-polarized second-harmonic light, depending on the wavelength, the sample thickness, and details of the anisotropic refractive index. To illustrate this phe-

nomenon we show in Fig. 7 calculations of the transmitted light for a hypothetical uniaxial liquid-crystal system with the director taken as the optic axis in the surface plane of the thin-film device. Just as in our SHG experiments, the incoming light is p polarized, and Figs. 7(a) and 7(b) show the transmitted s-polarized and p-polarized light, respectively. As indicated by the simulation presented in Fig. 7, the p-polarized light incident upon a FLC or a PLCP system yields a considerable amount of s-polarized pump light within the sample at the exit surface. Similar plots can be calculated for the light with the double frequency. These aspects need to be taken into account when one is analyzing the detailed orientation dependence of the SHG conversion efficiency.

B. Typical Results for a Series of Polymerized Samples
Polymers produced under the conditions described in Section 2 always produced SHG-active PLCP films. A series
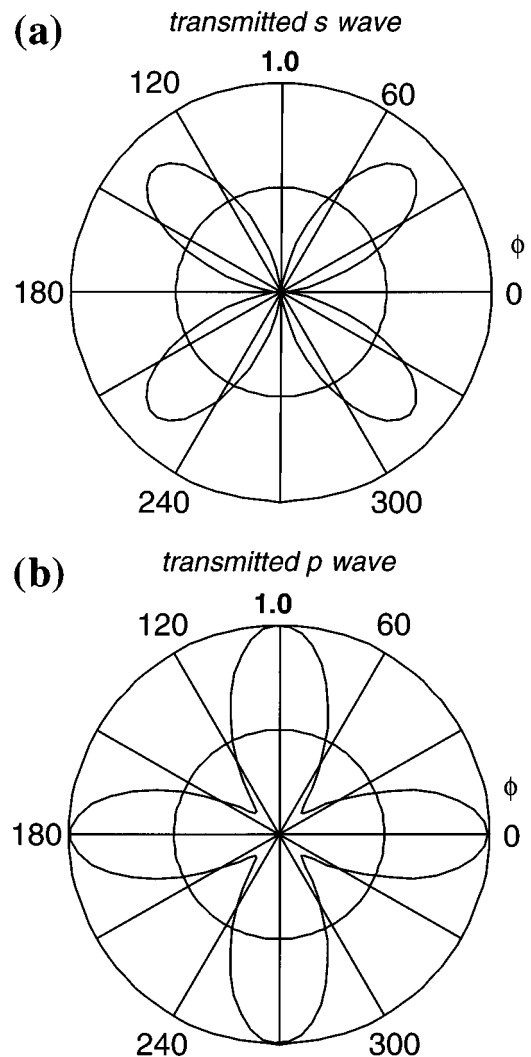

Fig. 7.   Simulation of the s- and p-transmitted light for a uniaxial liquid-crystal system with the optic axis (molecular director) as the z axis in the film plane. The incoming light is assumed to be p polarized in an experimental setup corresponding to the setup used for the SHG measurements. Parameters: $n_z = 1.57$, $n_x = n_y = 1.47$, sample thickness 4 μm, wavelength 1100 nm. $\theta = 40°$.
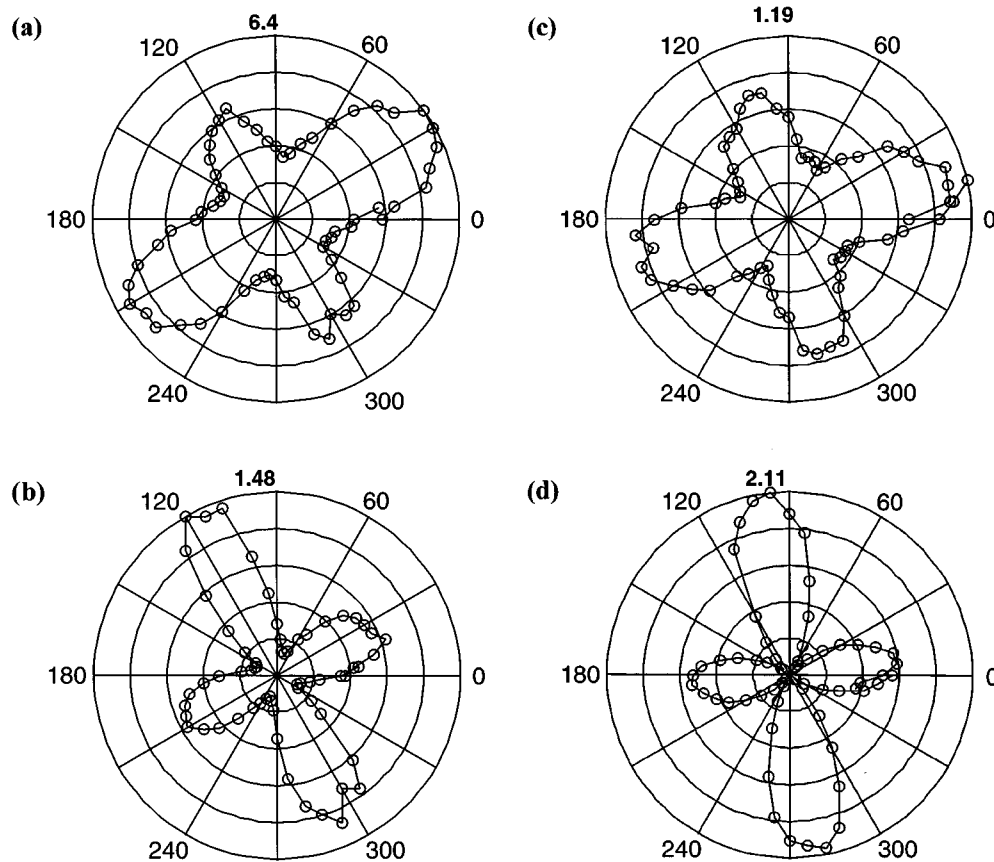
Fig. 8. SHG intensity as a function of the angle ϕ while θ is kept fixed (40°). The PLCP sample is based on (a) 100% A1b, tilt angle 31°; (b) A1b:A2c monomers with the proportions 60:40, tilt angle 25°; (c) A1b:A2c monomers with the proportions 40:60, tilt angle 17°; (d) 100% A2c, tilt angle 4°. All experiments are for *p*-to-*p* conversion. The boldface number at the top of each figure refers to the largest value of detected SHG intensity for that case. The tilt angles were measured with a polarizing microscope after the SHG measurements. The solid curves are included to guide the eye and have no other meaning.

of experiments performed under identical conditions (pump power, sample position, and orientations) is shown in Fig. 8. The angular positions of the lobe maxima corresponded very well to the tilt angle of the associated sample as measured with a polarization microscope (given in the figure caption); however, the shapes and the magnitudes of the lobes differed considerably. There can be several reasons for the variation in behavior. Because the tilt angle in the produced PLCP films deviated from the value set immediately before the polymerization reaction took place, it seems reasonable to attribute the changes in the SHG results to some kind of relaxation within the polymer system that occurs during the polymerization reaction.

C. Estimate of the *d* Coefficients
The simulation of the transmitted light (Fig. 7) indicated the problem of using all sample rotation angles (ϕ) when analyzing the SHG data. It is of course possible to modify the refractive-index anisotropy in the calculation and obtain angular distributions of the transmitted *s*- and *p*-polarized pump light that agree with the angular distribution, and approximately the relative magnitude, of the lobes of the *p*-to-*p* and the *p*-to-*s* converted SHG light, for example, by assuming a biaxial dielectric tensor that can take an arbitrary orientation (tilting the molecu-

lar director or other canonical directions or both). However, for SHG conversion efficiency one must in addition take into account the anisotropy of the *d* tensor that describes the nonlinear interaction of two pump beams to yield the second-harmonic light. For an arbitrarily oriented biaxial thin film this is a nontrivial task and is beyond the scope of the present study. Here we use a simpler analysis based on data obtained with the optic axis oriented perpendicular to the plane of incidence or with the optic axis within the plane of incidence. This means that the fundamental light does not change its polarization as it propagates within the sample.

To estimate the absolute value of certain elements in the *d* tensor data were recorded under the same experimental conditions, using a reference sample at the same position as the sample cell containing the PLCP film. From an analysis based on the work of Jerphagnon and Kurtz[16] the following expression was used for the transmitted second-harmonic power:

$$P_{2\omega} = CP_\omega{}^2 d_{\text{eff}}{}^2 t_\omega{}^4 T_{2\omega} \left(\frac{1}{n_\omega{}^2 - n_{2\omega}{}^2} \right)^2$$

$$\times \sin^2\left[\frac{2\pi l}{\lambda} (n_\omega \cos\theta_\omega - n_{2\omega}\cos\theta_{2\omega}) \right], \quad (1)$$

where C is a constant for the specific laser equipment and contains factors such as the beam size and the amplification of detector signals. The apparatus constant C can include as well the power of the pump light, P_ω, if the experiment is carried out under the same laser beam conditions. $T_{2\omega}$ and t_ω are the transmission factors, λ is the wavelength of the fundamental beam, and l is the thickness of the sample.[16] The angles θ_ω and $\theta_{2\omega}$ describe the propagation direction with respect to the surface normal of the fundamental and the second-harmonic beams, respectively (within the nonlinear sample). Transmission factors and related expressions for thin poled films have also been discussed by Kuzyk *et al.*[19] Those authors pointed out that in the thin-film limit, that is, when the sample thickness is small compared with the coherence length of the nonlinear interaction, defined as $l_c = \lambda/[4(n_\omega - n_{2\omega})]$, the last two factors in Eq. (1) yield essentially unity. This situation is expected for the PLCP samples reported on here and is also supported experimentally because no or little tendency of fringes is shown in the associated plot of transmitted second-harmonic intensity versus incidence angle of the PLCP films. For the reference sample this situation does not occur.

The d_{eff} coefficient expresses the coupling between the two interacting polarized waves and a specified polarization of the generated SHG light, and generally it depends on the orientation of the sample and the incidence angle. Formally, it can be written as

$$d_{\text{eff}} = \hat{e}_{2\omega}\widetilde{d} : \hat{e}_\omega \hat{e}_\omega, \qquad (2)$$

where $\hat{e}$ are unit vectors that describe the polarization state of the interacting waves and $\widetilde{d}$ is a third-rank tensor with components determined by the symmetry of the system.[20] In the case of C_2 point-group symmetry, which applies to the FLC's and PLCP's discussed here, the $\widetilde{d}$ tensor is given by

$$\widetilde{d} = \begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & d_{16} \\ d_{16} & d_{22} & d_{23} & 0 & d_{14} & 0 \\ 0 & 0 & 0 & d_{23} & 0 & d_{14} \end{bmatrix}, \qquad (3)$$

where we have assumed Kleinman symmetry and used contracted notation. The interactions that can be measured with the x and z axes in the plane of incidence are

x axis in the plane of incidence:

$$d_{\text{eff}} = d_{16}(\sin 2\theta_\omega \cos \theta_{2\omega} + \cos^2 \theta_\omega \sin \theta_{2\omega})$$
$$+ d_{22} \sin^2 \theta_\omega \sin \theta_{2\omega} \qquad p - p, \qquad (4a)$$

$$d_{\text{eff}} = -d_{14} \sin 2\theta_\omega \qquad p - s; \qquad (4b)$$

z axis in the plane of incidence:

$$d_{\text{eff}} = d_{23}(\cos^2 \theta_\omega \sin \theta_{2\omega} + \sin 2\theta_\omega \cos \theta_{2\omega})$$
$$+ d_{22} \sin^2 \theta_\omega \sin \theta_{2\omega} \qquad p - p, \qquad (4c)$$

$$d_{\text{eff}} = d_{14} \sin 2\theta_\omega \qquad p - s. \qquad (4d)$$

The refractive indices for the fundamental and the second-harmonic beams, n_ω and $n_{2\omega}$, respectively, were modified for the anisotropy of the samples and interaction of the e and o waves; the details are given in the caption

to Fig. 9. For the PLCP polymer samples the factor $T_{2\omega}$ was set to 1, and t_ω was calculated only for the first air–glass interface, multiple reflections and the eventual influence of the thin indium tin oxide and polyimide layers of the FLC cell were neglected. The angles θ_ω and $\theta_{2\omega}$ were set equal for the PLCP sample. The necessary constants used to calculate the second-harmonic power of reference samples, in our case ~0.5-mm-thin slices of z-cut LiNbO$_3$, were taken from the literature.[20]

As can be seen from Eqs. (4a) and (4c), there is a third power dependence of the $\sin \theta$ factor for the d_{22} component, compared with a linear dependence for the d_{16} and d_{23} components. Testing various values for the d_{22} component revealed that the $\sin^3 \theta$ curve did not agree; however, good fits to the experimental data could be obtained by use of the values 0.80 and 0.65 pm/V for the d_{16} and the d_{23} components, respectively [Figs. 9(a) and 9(b)], where the absolute values could be obtained by a comparison of the SHG intensity produced in a 530-μm LiNbO$_3$ sample (Fig. 10) that has the same conditions as for the
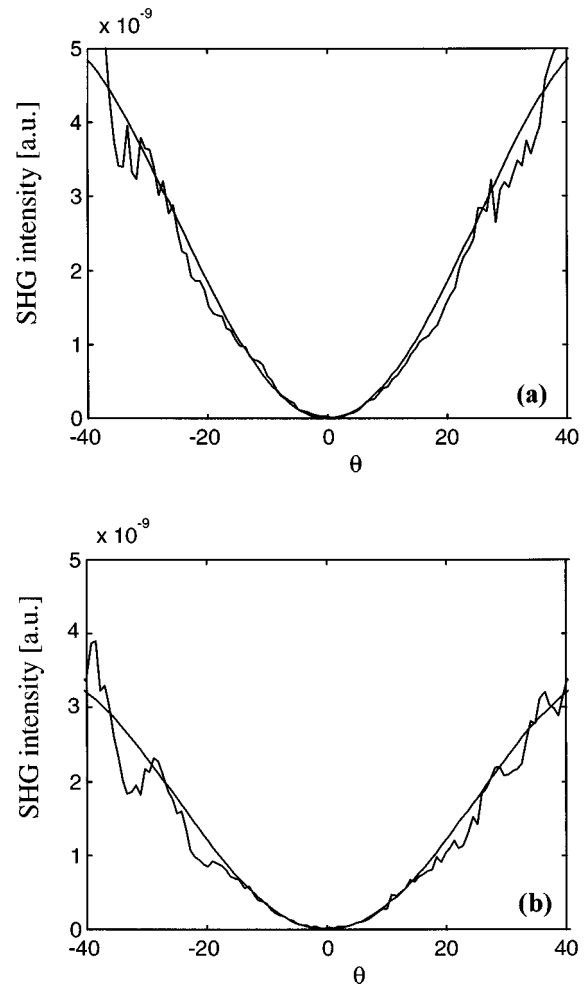

Fig. 9. Fits of the measured SHG intensity of a PLCP made from 100% A1b, tilt angle 31°, from Eqs. 4(a) and 4(c). The refractive indices were taken as $n_o{}^\omega = 1.47$, $n_e{}^\omega = 1.57$, $n_o{}^{2\omega} = 1.52$, $n_e{}^{2\omega} = 1.62$, $n_{\text{glass}}{}^\omega = 1.46$, and $n_{\text{glass}}{}^{2\omega} = 1.5$. $\lambda_{\text{pump}} = 1.1$ μm, film thickness 4 μm. The angles were approximated according to $\theta_{2\omega} = \theta_\omega$, and the θ-dependent refractive index for the e wave was neglected [i.e., $n_e(\theta) = n_e$].
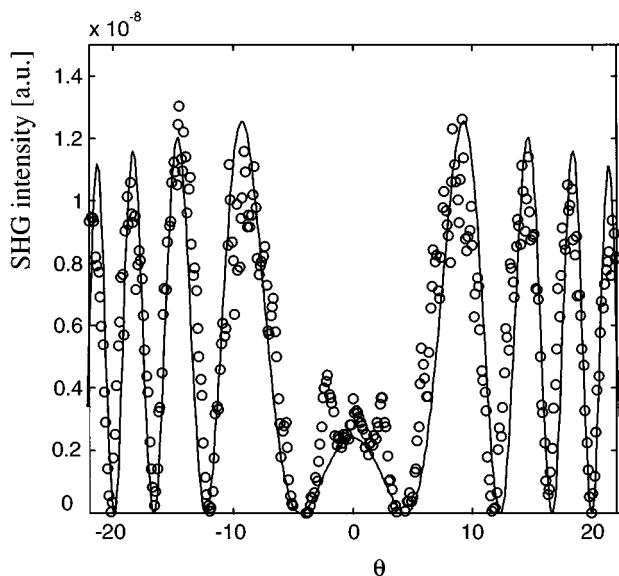
Fig. 10. Fits of the measured SHG intensity of a z-cut LiNbO$_3$ sample. The experiment was made for the p-to-s conversion with the x axis in the plane of incidence. The refractive indices corrected for temperature were taken from Ref. 20, along with a d_{22} coefficient of 2.76×10^{-12} m/V.

pump beam. The sample is here the PLCP associated with the pure A1b monomer, which gave the largest SHG signal. The parameters used in the fits are given in the respective figure captions. To obtain the magnitude of the d_{22} component we have to find an orientation where the d_{16} and the d_{23} components cancel out; however, this leads us from away from the two orientations where the formulas, Eqs. (4), are valid. The approximate magnitudes of the d_{16} and d_{23} coefficients of other samples can be obtained by comparison with the polar plots in Fig. 8, where the maximum values of the associated SHG intensities are given. The polar plot of Fig. 8(a) is for the same sample as the fit in Fig. 9; however, note that the polar plots of SHG intensity of Figs. 8(b) and 6(a) correspond to different samples that have the same composition.

For poled polymer films with axial symmetry (poling axis along z) there is a relation between two of the tensor components: $d_{13} = (1/3)d_{33}$.[21] Taking the same relation for the polar orientation in our PLCP system (y axis), we can estimate the d_{22} coefficient from the d_{16} and d_{23} coefficients to be approximately 2–2.5 pm/V. The detailed relations between the d tensor elements of the PLCP must await further experimental and theoretical studies of both the molecular hyperpolarizabilities and structural order.

The d_{14} component is so small that it cannot be fitted with accuracy because essentially no s-polarized SHG intensity could be detected with the x and z axes in the plane of incidence (Fig. 6).

4. CONCLUSIONS AND SUMMARY

PLCP monomers made from binary mixtures of multifunctional FLC's have been produced and prepared for SHG studies. The dependence of the SHG intensity on the orientation of the samples reveals a clear similarity to the experiment of the associated FLC monomer with an applied voltage. The results of a series of PLCP samples produced under similar conditions showed that the magnitudes of the polar order and the tilt angles vary. The highest d_{16} and d_{23} components were obtained for a PLCP based on 100% A1b and estimated to be approximately 0.65–0.8 pm/V.

REFERENCES

1. M. Bass, ed., *Devices, Measurements and Properties,* Vol. II of *Handbook of Optics* (McGraw-Hill, New York, 1995).
2. A. Yariv and P. Yeh, *Optical Waves in Crystals* (Wiley, New York, 1984).
3. Y. R. Shen, *Principles of Nonlinear Optics* (Wiley, New York, 1995).
4. D. S. Chemla and J. Zyss, eds., *Nonlinear Optical Properties of Organic Molecules and Crystals* (Academic, New York, 1987).
5. K. D. Singer, J. E. Sohn, and S. J. Lalama, "Second harmonic generation in poled polymer films," Appl. Phys. Lett. **49**, 248–250 (1986).
6. R. B. Meyer, L. Liébert, L. Strzelecki, and P. Keller, "Ferroelectric liquid crystals," J. Phys. (France) Lett. **36**, L69–L71 (1975).
7. N. A. Clark and S. T. Lagerwall, "Submicrosecond bistable electro-optic switching in liquid crystals," Appl. Phys. Lett. **36**, 899–901 (1980).
8. M. Schadt, "Linear and nonlinear liquid crystal materials, electro-optical effects and surface interactions. Their application in present and future devices," Liq. Cryst. **14**, 73–104 (1993).
9. K. Schmitt, R.-P. Herr, M. Schadt, J. Funfschilling, R. Buchecker, X. H. Chen, and C. Benecke, "Strongly nonlinear optical ferroelectric liquid crystals for frequency doubling," Liq. Cryst. **14**, 1735–1752 (1993).
10. D. M. Walba, M. B. Ros, N. A. Clark, R. Shao, K. M. Johnson, M. G. Robinson, J. Y. Liu, and D. Doroski, "An approach to the design of ferroelectric liquid crystals with high second order electronic nonlinear optical susceptibility," Mol. Cryst. Liq. Cryst. **198**, 51–60 (1991).
11. M. Trollsås, C. Orrenius, F. Sahlén, U. W. Gedde, T. Norin, A. Hult, D. Hermann, P. Rudquist, L. Komitov, S. T. Lagerwall, and J. Lindström, "Preparation of a novel cross-linked polymer for second-order nonlinear optics," J. Am. Chem. Soc. **36**, 8542–8548 (1996).
12. F. Sahlén, M. Trollsås, A. Hult, U. W. Gedde, D. Hermann, P. Rudquist, L. Komitov, and S. T. Lagerwall, "Spontaneous polarization of novel chiral and non-chiral liquid crystalline acrylate monomer mixtures," submitted to Liq. Cryst.
13. M. Trollsås, F. Sahlén, U. W. Gedde, A. Hult, D. Hermann, P. Rudquist, L. Komitov, S. T. Lagerwall, B. Stebler, J. Lindström, and O. Rydlund, "Novel thermally stable polymer materials for second order nonlinear optics," Macromolecules **29**, 2590–2598 (1996).
14. A. Hult, F. Sahlén, M. Trollsås, S. T. Lagerwall, D. Hermann, L. Komitov, P. Rudquist, and B. Stebler, "A pyroelectric liquid crystal polymer (PLCP) for second harmonic generation," Liq. Cryst. **20**, 23–28 (1996).
15. L. A. Hornak, ed., *Polymers for Lightwave and Integrated Optics—Technology and Applications* (Dekker, New York, 1992).

16. J. Jerphagnon and S. K. Kurtz, "Maker fringes: a detailed comparison of theory and experiment for isotropic and uniaxial crystals," J. Appl. Phys. **41**, 1667–1681 (1970).

17. M. Ozaki and K. Yoshino, "Dynamic response of second harmonic generation in ferroelectric liquid crystals," Jpn. J. Appl. Phys. **28**, L1830–L1832 (1989).

18. B. Park, M. Lim, J.-H. Lee, J.-H. Kim, and S.-D. Lee, "Nonlinear optical anisotropy associated with polar ordering in ferroelectric liquid crystals," Ferroelectrics **179**, 231–240 (1996).

19. M. G. Kuzyk, K. D. Singer, H. E. Zahn, and L. A. King, "Second-order nonlinear-optical tensor properties of poled films under stress," J. Opt. Soc. Am. B **6**, 742–752 (1989).

20. V. G. Dmitriev, G. G. Gurzadyan, and D. N. Nikogosyan, *Handbook of Nonlinear Optical Crystals*, 2nd ed. (Springer-Verlag, Berlin, 1997).

21. K. D. Singer, M. G. Kuzyk, and J. E. Sohn, "Second-order nonlinear-optical properties in orientationally ordered materials: relation between molecular and macroscopic order," J. Opt. Soc. Am. B **4**, 968–976 (1987).