Blue Light Guiding in a Polymeric Nonlinear Optical Langmuir–Blodgett Waveguide

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Blue light (457.9 nm) guiding with low optical loss (2–6 dB cm^{-1}) over several centimeters is reported in an all-polymeric Langmuir–Blodgett film, made by alternate deposition of an amphiphilic nonlinear optical (NLO) polymer and poly(*tert*-butyl methacrylate) on Pyrex. Low-loss optical waveguiding in the wavelength region of frequency-doubled diode lasers is of technological importance for efficient guided-mode-to-guided-mode frequency conversion schemes in waveguide format. Deposition and waveguiding were also carried out on a silicon wafer with a silicon dioxide buffer layer showing compatibility with silicon-based integrated optics. Second-harmonic generation experiments demonstrate the nonlinear activity of this polymeric material when incorporated into Langmuir–Blodgett films.

Introduction

The waveguide format is advantageous for nonlinear optical (NLO) applications, because of the high power density that can be achieved over a long propagation length.[1] The modal dispersion relations allow other phase-matching schemes between higher order modes in the waveguides, in addition to those offered by birefringence. Frequency-doubling in an optical waveguide does not necessarily require transparency to the second-harmonic wavelength if a conversion scheme such as the Čerenkov-type guided mode to substrate radiation mode is used.[2–4] But in this case the efficiency for frequency doubling is linearly proportional to the propagation length for the fundamental wavelength in the waveguide.[3] The frequency-doubled light leaks out into the substrate and, hence, the propagation loss at the second-harmonic wavelength does not limit the conversion efficiency. In the more efficient guided-mode-to-guided-mode frequency conversion scheme, the efficiency is proportional to the square of the interaction length.[1] This interaction length is determined by the phase mismatch between the fundamental and the harmonic mode and by the propagation losses for both modes.

In general, the organic molecules that exhibit high first hyperpolarizabilities β contain strong electron-withdrawing groups and strong electron-donating groups connected by a hydrocarbon chain with a higher degree of electron delocalization through π-bond linkages.[5] As a result, a charge-transfer absorption band is associated with the NLO chromophore that generally occurs in the visible range of the electromagnetic spectrum. This band does not usually extend to the near-infrared wavelengths of diode lasers, but can cause absorption at the second-harmonic wavelength. As discussed above, this limits the use of guided-mode-to-guided-mode conversion schemes. Therefore, it is desirable to increase the transparency of waveguides fabricated from such molecules by shifting the charge-transfer absorption to shorter wavelengths, ideally into the ultraviolet, resulting in a blue-transparent material. This generally requires the use of weaker electron-acceptor and -donor groups, and/or a shortening of the connecting π-bonding chain. A decrease in the molecular hyperpolarizability usually results.[6] This correlation between absorption wavelength and hyperpolarizability has been attributed to a wavelength dependence of the change in dipole moment on going from ground state to charge-transfer excited state.[7]

The bulk second-order nonlinear susceptibility depends on the orientationally averaged hyperpolarizability of all the molecules.[1] Thus, for molecules that are transparent to shorter wavelengths and therefore have smaller hyperpolarizabilities, it becomes increasingly critical to achieve a high degree of noncentrosymmetric ordering to obtain a high bulk nonlinear susceptibility. The most commonly used technique of creating noncentrosymmetric ordering in dipolar organic molecules and polymers is to use an external electric field to align the molecules.[8] The degree of ordering achieved depends on the strength of the electric field and also on the ground-state dipole moments of the molecules. However, for organic charge-transfer molecules, not only β but also the ground-state dipole moment decreases with increasing blue transparency.[7] Thus the bulk susceptibility of electric field-poled materials decreases through both these effects as the chromophore absorption wavelength decreases. In fact, it has recently been proposed that, using electric field poling, it may not be possible to achieve sufficiently high bulk nonlinear susceptibility in an organic material to obtain a usable efficiency for frequency doubling of solid-state diode lasers to 400 nm in a channel waveguide.[9] Molecular fabrication techniques, such as Langmuir–

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Blodgett (LB) assembly, are well-known to achieve a high degree of polar molecular orientational order in a thin-film structure.[10] Since this ordering results from molecular-level forces and no external electric fields are involved, the lower dipole moment of blue-transparent chromophores is not a drawback to achieving order. Thus molecular assembly may be a particularly advantageous, or even necessary, approach to preparing blue-transparent waveguide films of organic materials with sufficiently high nonlinear susceptibility for guided-mode-to-guided-mode frequency-doubling of near-infrared diode lasers.

A drawback that has long plagued LB films of chromophores inserted in monomeric amphiphiles has been a tendency to form microcrystalline domains.[11] Excessive light scattering at the grain boundaries, for both the fundamental and the harmonic waveguide modes, is then another loss mechanism in addition to absorption that affects light propagation. We have recently reported all-polymeric LB films that do not suffer from high scattering light loss.[12] But the NLO chromophore used, covalently attached to the amphiphilic polymer, had an absorption maximum around 430 nm, preventing efficient guided-mode-to-guided-mode frequency conversion. The Čerenkov-type phase-matching scheme was used to demonstrate waveguide-generated second-harmonic light at green and blue wavelengths, taking advantage of the low scattering and absorption loss at the fundamental wavelength, while avoiding the absorption of the second harmonic.[4] In the present report we have now demonstrated low-loss optical waveguiding in the blue-wavelength region with a new NLO chromophore covalently attached to an amphiphilic polymer. Noncentrosymmetric LB films have been fabricated using an inert polymer deposited alternately as an interlayer material. Second-order nonlinear activity of this film was demonstrated by second-harmonic generation. As discussed above, this low loss is a prerequisite for the use of more efficient guided-mode-to-guided-mode frequency conversion schemes. We have also deposited the LB film on a silicon wafer with a silicon dioxide buffer layer, demonstrating the compatibility with silicon-based integrated optics.

Experimental Section

Materials. The optical waveguide was made by alternate deposition of an NLO passive polymer, poly(*tert*-butyl methacrylate) (purchased from Aldrich Chemical Co., Inc.), and an NLO-active amphiphilic polymer. The NLO polymer is a random copolymer containing the NLO chromophore and hydroxyethyl acrylate in a 1:3 molar ratio. The NLO parent chromophore is 4-[(perfluorodecyl)sulfonyl]-*N*-hexyl-*N*-methylaniline, covalently attached to the acrylate polymer backbone through the flexible $-(CH_2)_6-$ spacer. The structure of both polymers is shown in Figure 1. The synthesis of the chromophore and polymer is briefly described below.

The perfluoroalkylation of 4-chlorothiophenol by 1-iodoperfluorodecane was adapted from ref 13. Oxidation of the resulting thioether using chromium trioxide gave the corresponding sulfone. The dye-bearing monomer was synthesized by aromatic substitution of the chloride at the *para* position of the thioether by *N*-methyl-*N*-(6-hydroxyhexyl)amine, made from methylamine and 6-chloro-1-hexanol. Esterification of this dye with acryloyl chloride gave the polymerizable acrylate monomer. Free radical copolymerization of the dye monomer and hydroxyethylacrylate was carried out in tetrahydrofuran solution at 60 °C using azobisisobutyronitrile as initiator. The ratio of dye monomer to hydroxyethyl acrylate in the polymer was determined to be 1:3 from the ^1H NMR spectra run on a General Electric QE-300 instrument using $CDCl_3$ as the solvent. Size exclusion chromatography (SEC) was performed by the Analytical Technology Division of Eastman Kodak Co. to obtain $\bar{M}_w$ = 12 000 and $\bar{M}_n$ = 6450.

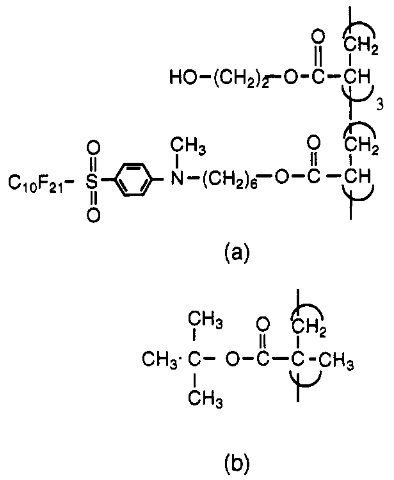

Figure 1. Molecular structure of the polymers used. (a) NLO-active polymer. (b) Poly(*tert*-butyl methacrylate).

Film Fabrication. Monolayer Langmuir film formation and alternate LB deposition were carried out on an ultrapure water subphase (Millipore Milli-Q system) using a commercial two-compartment trough (KSV 5000) in a class 100 environment. The waveguide substrates were Pyrex glass slides (1 × 4 cm, 1 mm thick) made hydrophobic by silanation with octadecyltrichlorosilane. The NLO polymer was deposited at a surface pressure of 34 mN m^{-1} and a cross-sectional area per repeat unit of 0.53 nm^2. The poly(*tert*-butyl methacrylate) was deposited at 10 mN m^{-1}. Alternate deposition was repeated up to a thickness of 168 bilayers. Waveguide experiments were performed on this sample in the blue and green spectral regions, but the film thickness was below cutoff in the red and infrared. For a complete determination of the dispersion of the refractive index of the LB film, the alternate deposition was extended on the same film up to a final film thickness of 0.88 ± 0.02 μm as verified by ellipsometry and stylus profilometry. For the total number of bilayers (336), this corresponds to 2.6 nm/bilayer. Using the value of 1.0 nm for the poly(*tert*-butyl methacrylate) (ptbm) layer previously determined[4] yields a value of 1.6 nm for the NLO polymer layer. The thickness of the 168-bilayer intermediate film that was used to determine the waveguiding losses at 457.9 nm was then calculated to be 0.44 μm.

Silicon wafers (400 μm thick with a 3-μm-thick thermally grown silicon dioxide layer) have also been used as substrates. A thick LB film of 1.00 ± 0.05 μm (388 ptbm layers and 384 NLO polymer layers) has been deposited. This allowed the guiding of two modes in the deep blue (415 nm), offering the possibility of a consistency check for the thickness determination.

Optical Characterization. Prism coupling was used to perform waveguide experiments on the LB films on the Pyrex substrate at the visible wavelengths of an Ar^+-ion laser (457.9, 476.5, 488.8, 496.5, and 514.5 nm), at the 632.8-nm He/Ne laser line, and at a diode laser line (830 nm). Waveguiding over the complete useful length of the sample (approximately 3.5 cm) was observed at the Ar^+-ion laser lines for the 168 bilayer (0.44 μm) film. The optical waveguide loss was determined with a coherent fiber bundle that images the light scattered out of the waveguide onto a detector.[14] The resolution of the detection system has been calculated to be 86 μm^2.

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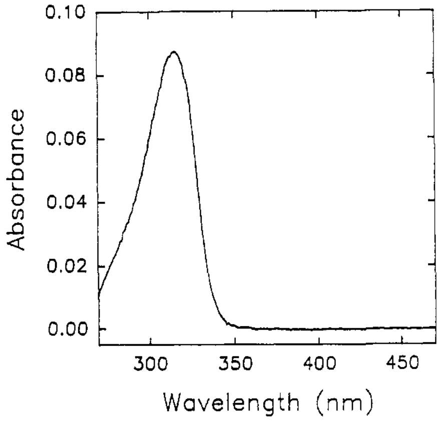

Figure 2. Absorption spectrum of an LB film consisting of eight bilayers of the NLO polymer, deposited alternately with poly(*tert*-butyl methacrylate) on each side of a Pyrex substrate.

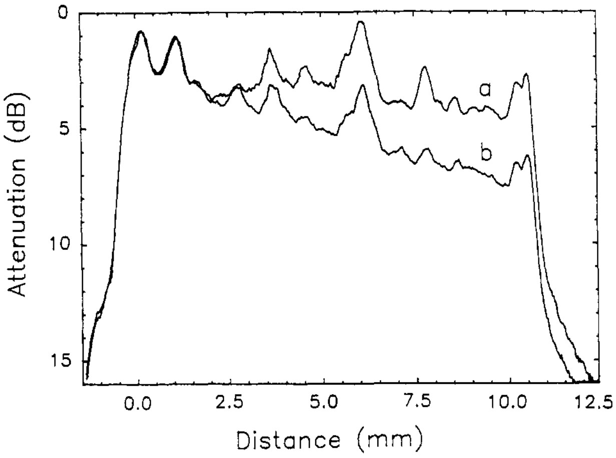

Figure 3. Waveguide attenuation in the single mode 0.44-μm-thick LB film on Pyrex at 457.9 nm. (a) TM polarization, 2.6 dB cm^{-1} loss. (b) TE polarization, 5.8 dB cm^{-1} loss.

Results and Discussion

Material Properties. The chemical bifunctionality of the sulfonyl electron-acceptor group allows the incorporation of this chromophore into an amphiphilic polymer between the methacrylate backbone and the hydrophobic side chains.[15] The perfluorinated $-C_{10}F_{21}$ side chain is advantageous in several ways. First, the presence of this electron-withdrawing group at the electron-acceptor site increases the first hyperpolarizability β of the chromophore.[16] Second, a perfluorinated chain is more hydrophobic than a hydrocarbon aliphatic chain of the same length.[17] As a result, the amount of hydrophobicity necessary to build stable LB films could be achieved with shorter chains, thereby increasing the chromophore number density in the amphiphilic polymer. The alternate deposition of an NLO-active and an NLO-passive layer preserves the overall noncentrosymmetry necessary for second-order NLO applications.

The absorption spectrum of a thin film of the NLO polymer on Pyrex, using uncoated Pyrex as a reference, is shown in Figure 2. The relatively short conjugated phenyl π-electron system causes a blue shift of the absorption spectrum compared to the spectrum of the more extended stilbene or azobenzene molecules. Compared with our previous azobenzene chromophore,[4,12] a blue shift of approximately 100 nm in the absorption spectrum has been realized. On the basis of the reported measurement on the corresponding *N,N*-diethyl analog of the chromophore in this polymer,[16] a hyperpolarizability of about 9×10^{-30} esu is expected compared to a value of 70×10^{-30} esu obtained[15] for the azobenzene chromophore used in our earlier studies (both measured at 1907 nm).

Waveguiding. As stated above, the 168 bilayer film was below cutoff for the longer wavelengths.[18] Figure 3 shows the waveguide attentuation at 457.9 nm for both TE (transverse electric) and TM (transverse magnetic) polarizations. The corresponding waveguide losses are 5.8 and 2.6 dB cm^{-1}, respectively. Figure 4 is a photograph of the guided blue light (TM polarization). At longer wavelengths, the absorption losses were even lower.

To be able to calculate the refractive indexes at all wavelengths, coupling experiments were also performed on the 0.88-μm-thick film. From the observed coupling angles for both TE and TM polarization in this film, the ordinary and extraordinary refractive index, the birefringence and the dispersion were determined. Figure 5 shows the dispersion of the refractive indexes, together with a single-term Sellmeier fit to the data. The refractive index data are given in Table I and the fitting parameters are given in Table II. Resonance enhancement of the refractive index values is observed closer to the absorption band.

Additional waveguiding experiments were performed in the LB film deposited on the silicon wafer. The refractive indexes for the LB film on this substrate (also given in Table I; parameters obtained from a single-term Sellmeier fit to the data given in Table II) are lower than for Pyrex as a substrate. At 415 nm (frequency-doubled Ti:sapphire laser), two guided modes were observed in the 1.0-μm-thick film. Attenuation was high at this wavelength, presumably due to residual absorption by the chromophore. The analysis based on the coupling angles for the two modes results in a value for the refractive index and for the film thickness. This allows for a consistency check by comparison with the thickness determined from profilometry. The film thickness from waveguide experiments (1.08 μm for TE and 1.07 μm for TM polarization) is consistent with the physical thickness (1.00 ± 0.05 μm), as measured by stylus profilometry.

Compared with the previous LB films of our azobenzene-substituted amphiphilic polymer,[12] the values for the refractive indexes are, in general, relatively low. This is explained by the blue shift of the absorption spectrum of the chromophore and by the presence of the low index $-C_{10}F_{21}$ chain. The low off-resonance refractive index complicates waveguide fabrication by the Langmuir–Blodgett deposition technique, since the cutoff thickness for waveguiding in an asymmetric waveguide is larger for a lower refractive index in the waveguide core, increasing the number of layers that must be deposited.[18]

Our ability to demonstrate low-loss waveguiding by LB films of NLO polymers in the wavelength region of the second harmonic of diode lasers is of importance for the application of efficient waveguide conversion schemes. The refractive index can be tailored to some extent by the amount of perfluorinated chain in the NLO polymer and by choice of the NLO passive interlayer amphiphile. The

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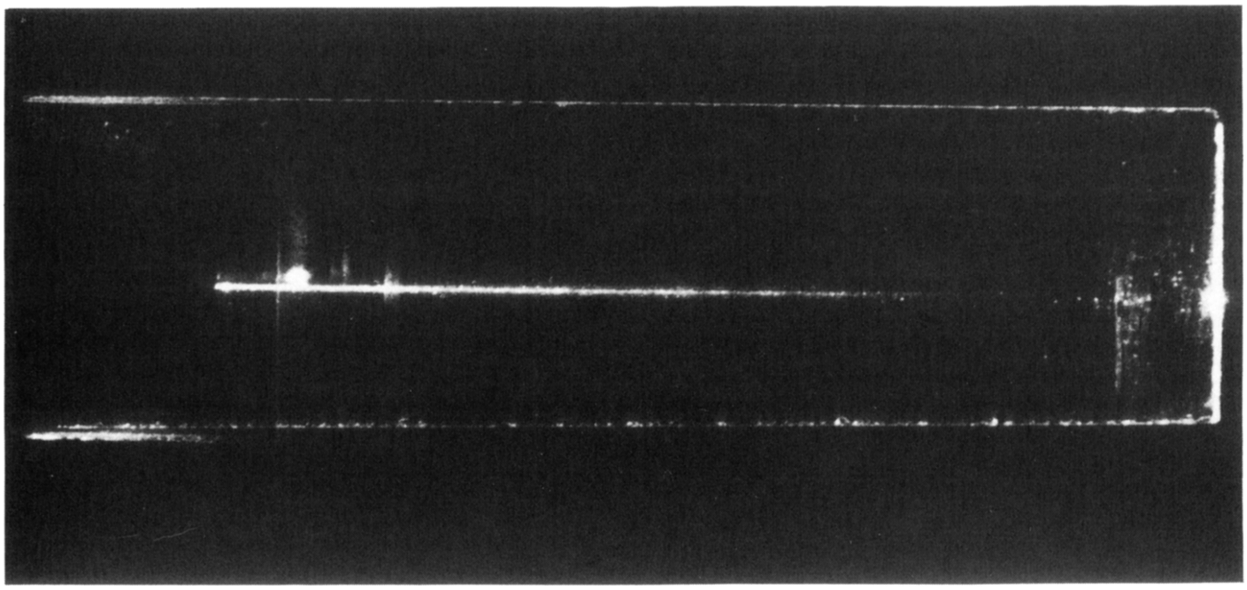

Figure 4. Photograph of the waveguiding in the single mode 0.44-μm-thick LB film on Pyrex at 457.9 nm.

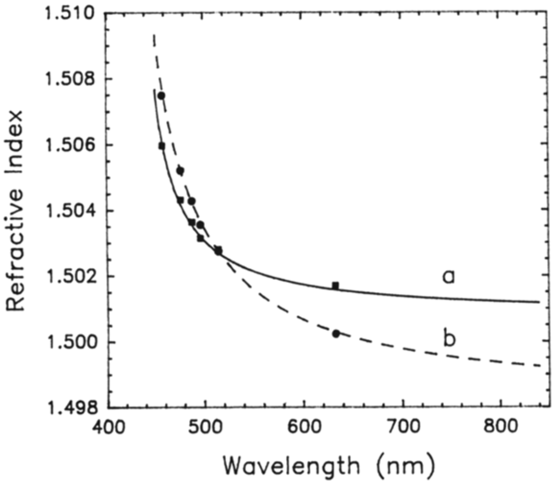

Figure 5. Dispersion of the refractive index of the all-polymeric waveguide, as obtained from prism-coupling experiments in the 0.88-μm-thick film on a Pyrex substrate. (a) Extraordinary refractive index. (b) Ordinary refractive index. The points are experimental data (given in Table I); the lines are single term Sellmeier fits to the data (fit parameters given in Table II).

Table I. Refractive Indexes for LB Film As Obtained from Waveguiding Experiments[a]

Pyrex			silicon wafer with silicon dioxide buffer		
wavelength (nm)	n_{ord}	n_{ext}	wavelength (nm)	n_{ord}	n_{ext}
457.9	1.5075	1.506	415.0	1.5013	1.4995
476.5	1.5052	1.5043	441.6	1.491	1.489
488.0	1.5043	1.5036	632.8	1.472	1.474
496.5	1.5036	1.5031	830.0	1.466	1.471
514.5	1.5027	1.5028	1064.0	1.464	1.471
632.8	1.5002	1.5017			

[a] The estimated uncertainty on the reported values is 0.0005 for Pyrex as a substrate and 0.001 for the film on the silicon wafer.

low refractive index requires a larger LB film thickness for waveguiding to occur. Although the 0.44-μm-thick film was below cutoff at 830 nm, at 457.9 nm, the mode is relatively well-confined, as is shown in Figure 6 for the TE polarization. The power fraction guided in the LB film is 0.42. The observed waveguide loss of 5.8 dB cm^{-1} for the TE mode than represents an intrinsic loss in the LB film L_{LB} of 14 dB cm^{-1}.[4] The power fraction guided in the LB film for the TM mode is 0.23. This lower guided fraction for the TM polarization is caused by the lower extraordinary refractive index at this wavelength. For this polarization, the observed waveguide loss of 2.6 dB cm^{-1} results in an intrinsic loss L_{LB} of 11 dB cm^{-1}.

Table II. Parameters from a Fit to a Single-Term Sellmeier Equation of the Form $n^2 = A + S\lambda^2/(\lambda^2 - \lambda_0^2)$[a]

	Pyrex		silicon wafer with silicon dioxide buffer	
parameter	n_{ord}	n_{ext}	n_{ord}	n_{ext}
A	2.237 (0.004)	2.250 (0.002)	1.969 (0.02)	2.12 (0.01)
S	0.008 (0.002)	0.003 (0.001)	0.163 (0.07)	0.029 (0.004)
λ_0	400 (10)	420 (10)	265 (15)	361 (5)

[a] The values in parentheses are the estimated uncertainties in the retrieved parameters.

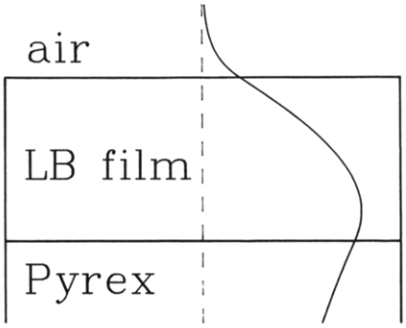

Figure 6. Modal field distribution for the TE$_0$ mode at 457.9 nm in a 0.44-μm-thick LB film on a Pyrex substrate. Refractive indexes: air, 1.0; LB film, 1.5075; Pyrex, 1.481. Effective index for the waveguide mode: 1.483. Fraction of guided power in LB film: 0.42. Fraction of guided power in substrate: 0.58.

The observed birefringence and higher waveguide attenuation for the TE polarization close to the absorption band of the chromophore seem to indicate that the orientation of this chromophore is characterized by a fairly large tilt angle so that the transition moment has a substantial component in the plane of the film. A more quantitative study of the orientation of the NLO chromophore in the LB film, including polarized absorption and second-harmonic generation experiments, is underway. A tilt angle of 49° measured by second-harmonic polarization was recently reported for a similar fluoropolymer chromophore incorporated as a side chain into a polymer and deposited as an LB film.[19] To maximize the second-order nonlinear susceptibility, the NLO chromophore should have a relatively small tilt angle with respect to the normal to the plane of the film to preserve the necessary noncentrosymmetry.

The presence of the silicon dioxide layer with lower refractive index on a silicon wafer with higher refractive index results in additional possible modes of light propagation in the oxide layer, due to the high reflectance of the silicon/silicon dioxide interface. These modes are substrate-radiation modes, often also called leaky modes.[20,21] These modes are not really useful for NLO applications, since only an evanescent field is in the NLO-active LB film. The only use for the leaky modes could be in guiding the second-harmonic generated in a guided-mode-to-substrate-radiation-mode process, very much like the Čerenkov-type conversion scheme. Here, the second-harmonic would not be radiating in the substrate but would propagate as a leaky mode. The waveguide loss of such a leaky mode has to be carefully controlled through the thickness of the oxide layer.[22] This thickness is also important for decoupling the modal field from the damping effect of the silicon. Thermal growth of the silicon dioxide buffer layer limits this thickness to about 3 μm. For the small difference in refractive index between the present LB film and the oxide buffer layer, this may not be enough for efficient decoupling of the fundamental guided mode or for lowering the waveguide loss of the leaky mode at the second-harmonic wavelength.

Frequency Doubling. Second-harmonic generation experiments on the 0.88-μm-thick LB film on a transparent Pyrex substrate were performed in the transmission formate as a function of incidence angle and fundamental input polarization.[12] The result of this experiment is shown in Figure 7. From the high contrast for the interference fringes over a wide range of incidence angles, it is concluded that the deposition is uniform over the whole substrate and on both sides of the substrate. Figure 7 shows the intensity of the second-harmonic for both *p* and *s* fundamental input polarization and *p* output polarization. No *s*-polarized output could be observed. From the ratio of these signals, calculated at a fringe maximum near 45° incidence, a polar tilt angle of the chromophore was calculated, under the simplifying assumptions that the major component of the hyperpolarizability lies along the 1,4 substitution axis of the chromophore, and that the tilt of all the molecules lie within a narrow distribution. Using equations in the literature,[23] a polar tilt angle θ of 42° from the normal to the film plane is calculated. This then allows an estimate of the susceptibility of the film to be calculated from the oriented gas equation relating the molecular hyperpolarizability, chromophore density, and orientation factor to the bulk nonlinear susceptibility in a manner previously detailed.[12] A chromophore density of 7×10^{20} cm^{-3} was used in this calculation, derived from the cross-sectional area of 0.53 nm^2 and bilayer thickness of 2.6 nm. From the polar tilt angle an orientation factor ($\cos^3 \theta$ for $\chi^{(2)}_{zzz}$) of 0.4 is calculated. Using $\beta = 9 \times 10^{-30}$ esu,[16] a value for $\chi^{(2)}_{zzz} \approx 8 \times 10^{-9}$ esu or 3 pm V^{-1} is estimated. Since the value of β used in this calculation was obtained at 1907 nm, this bulk susceptibility also refers to that wavelength which is very far from resonance. A value 5–10 times higher can be anticipated at a fundamental wavelength near 800 nm[24] but requires actual measurement to quote more precisely.

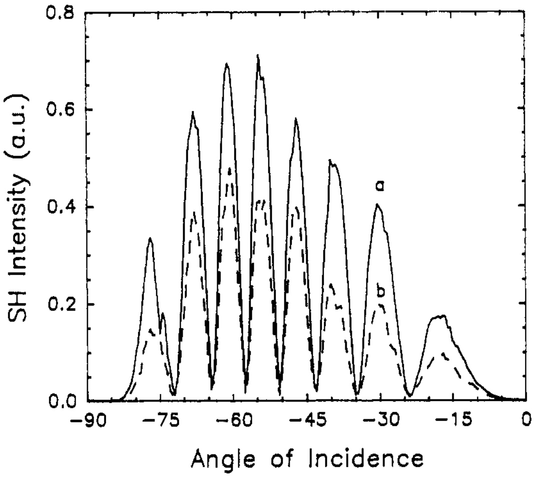

Figure 7. Interference pattern of second-harmonic intensity as a function of fundamental incidence angle, obtained from the 0.88-μm-thick LB film on a Pyrex substrate in transmission format. (a) *p*-polarized input, *p*-polarized output. (b) *s*-polarized input, *p*-polarized output.

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