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Second Harmonic Generation in Multilayer Langmuir−Blodgett Films of Blue Transparent Organic Polymers

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Abstract: Multilayer Langmuir−Blodgett (LB) films were fabricated with two blue transparent nonlinear optical polymers in which the orientation of the nonlinear optical chromophore in one polymer is reversed with respect to the other. The intensity of the frequency-doubled light generated in these multilayers increases quadratically, with the increasing number of bilayers indicating that the macroscopic optical nonlinearity, $\chi^{(2)}$, of the bilayer is a linear sum of the macroscopic optical nonlinearities of the individual monolayer. Also, multilayer LB films of each blue transparent polymer were made by alternate deposition with a spacer polymer, poly(*tert*-butyl methacrylate). The intensity of the frequency-doubled light generated by these multilayer films was approximately 4 times smaller than that generated by multilayer films of two blue transparent polymers with the same number of layers, indicating that the use of another nonlinear optical active polymer in the place of passive poly(*tert*-butyl methacrylate) polymer leads to considerable improvement in the frequency-doubling efficiency. Multilayer LB films of these polymers show a great potential for achieving a practical level of performance.

Introduction

Organic polymers that exhibit large optical nonlinearities are of considerable interest for application in future optoelectronic and photonic devices.[1−3] In particular, the development of materials suitable for frequency doubling of low-power diode lasers is one of the technologically important tasks.[4,5] In this regard organic polymers have received remarkable attention mainly due to their large optical nonlinearity and their synthetic diversity. Most of the organic materials that exhibit large microscopic nonlinearity, β, consist of molecular structures in which strong electron-donating and -withdrawing groups are connected through conjugated π-electron moieties. As a result, the charge-transfer band associated with such nonlinear optical chromophores, in general, falls within the visible portion of the electromagnetic spectrum.[6] Although these charge-transfer bands do not reach the fundamental wavelength of the near infrared diode lasers, they may lie within the second harmonic frequency, thereby prohibiting the frequency doubling in such materials via guided-mode-to-guided-mode-type conversions.[7,8] However, the frequency doubling via Čerenkov-type guided mode to substrate radiation mode may still be achieved, but the conversion efficiency in such a scheme is considerably reduced compared to that of guided-mode-to-guided-mode-type conversion.[9] One way to achieve the frequency doubling via guided-mode-to-guided-mode-type conversion is to increase the transparency of the nonlinear optical chromophore in the near ultraviolet spectral region by shifting the charge-transfer band into the ultraviolet spectral range. This necessitates the use of either moderate electron donor and acceptor groups or a shorter conjugation path or both. Usually, such a molecular structure will result in a considerably reduced β value and hence a lower macroscopic nonlinearity, $\chi^{(2)}$.[10] Therefore, it is necessary to use highly oriented thin films of these materials to obtain a large macroscopic nonlinearity, $\chi^{(2)}$, which depends on the orientationally averaged β values of individual molecules.

In oriented thin films (assuming $C_{\infty v}$ symmetry since this is the case with the majority of Langmuir−Blodgett (LB) films) the largest $\chi^{(2)}$ tensor component is the one along the symmetry axis *(z)* which depends on a number of parameters as shown in eq 1,[1] where N is the number density of the chromophore, $F_i(\omega_i)$

$$\chi^{(2)}_{zzz} = NF_1{}^2(\omega_1)\, F_2(\omega_2)\beta\langle\cos^3\theta\rangle \qquad (1)$$

are the appropriate local field factors, β is the molecular hyperpolarizability, and $\langle\cos^3\theta\rangle$ is the orientational factor, with θ being the angle between the symmetry axis and the direction of β. As shown in eq 1, the larger the orientation factor, $\langle\cos^3\theta\rangle$, the higher the macroscopic nonlinearity, $\chi^{(2)}$. In general, the majority of organic polymers are amorphous; therefore, it is necessary to electrically pole them to yield oriented structures prior to second-order nonlinear optical studies.[11] One difficulty with the blue transparent polymers is that they cannot be

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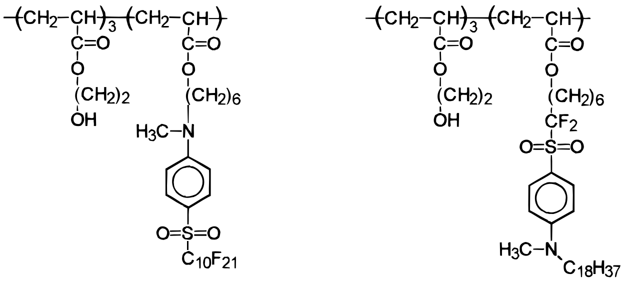
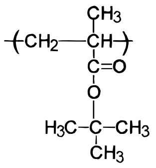


Normal Polymer **(N)** Reverse Polymer **(R)**



Poly(t-butyl methacrylate) **(P)**

Figure 1. Molecular structures of normal polymer (N), reverse polymer (R), and poly(*tert*-butyl methacrylate) (P).

efficiently oriented through the electric field poling process due to their smaller β values and their smaller ground state dipole moments.[12] However, highly oriented thin films of such polymers can be fabricated via the Langmuir–Blodgett technique, provided that appropriate amphiphilic properties are incorporated into the molecular structure.[4,5] The Langmuir–Blodgett technique, the method of transferring a molecular monolayer from an air–liquid interface onto a substrate, has been widely used for the fabrication of well-oriented molecular assemblies with the precise control of the film thickness.[13]

Often when multilayer LB films are fabricated in the vertical Y-mode, the resulting film consists of two consecutive layers with either head-to-head- or tail-to-tail-type structures, thus creating an inversion center. This can be avoided by alternate deposition of the nonlinear optical (NLO) active molecular layer with a passive spacer molecular layer. One drawback in this approach is that the density of the nonlinear optical chromophore is reduced due to the presence of passive spacer molecules. An attractive way to overcome this drawback is to employ two NLO active molecules whose charge-transfer axes are reversed with respect to the amphiphilic orientation.[14–17] The overall nonlinearity of such a bilayer LB film is expected to be equal to the linear sum of each monolayer, provided that there is no interaction between two monolayers.[17]

In this paper we report the results of the second harmonic generation studies of multilayer LB films fabricated with two blue transparent nonlinear optical polymers whose chromophores are oppositely oriented with respect to the long carbon chain. We refer to these two polymers as normal polymer (polymer N) and reverse polymer (polymer R), respectively. The molecular structures of polymers N, R, and poly(*tert*-butyl methacrylate) (P) are shown in Figure 1. These polymers (polymer N and polymer R) appear to form stable structures with no interaction between adjacent layers. In fact, previously, the phase-matched second harmonic generation (SHG) of blue light was demonstrated in a LB film waveguide fabricated with polymer N and P.[4] Although the normalized efficiency of this system was high, the actual output (~1 μW) was rather modest. During the previous study it was foreseen that the macroscopic nonlinearity of the system could be improved by replacing the passive spacer polymer, P, with an NLO active polymer in which the same chromophore is linked to the polymer backbone in a reverse orientation by means of the sulfonyl group. In this work we replace the passive polymer P with nonlinear optical polymer R. We show that the macroscopic nonlinearity, $\chi^{(2)}$, of an alternated polymer film is the linear sum of those of two corresponding polymers.

Experimental Section

The NLO polymers used in the present study are random copolymers containing the NLO chromophores and hydroxyethyl acrylate in a 1:3 molar ratio. In polymer N the NLO moiety, 4-[(perfluorodecyl)-sulfonyl]-*N*-hexyl-*N*-methylaniline, is covalently attached to the acrylate polymer backbone via a flexible hexamethylene spacer. In the polymer R, [[4-(*N*-methyl-*N*-octadecylamino)phenyl]sulfonyl]perfluoromethylene is covalently attached to the acrylate polymer backbone via a flexible hexamethylene spacer.[4,5] The synthesis of polymer N was previously reported, and the synthesis of polymer R is included as supporting information for this paper. Polymer P was purchased from Aldrich Chemical Co., Inc., and used without further purification. The ratio of the dye monomer to hydroxyethyl acrylate in polymers N and R was determined to be 1:3 from the proton NMR spectra. The results of size exclusion chromatography yield values of $\bar{M}_w = 4200$, $\bar{M}_n = 9090$ and $\bar{M}_w = 5410$, $\bar{M}_n = 3590$ for polymers N and R, respectively.

Monolayer Langmuir film formation and alternate LB film deposition were accomplished in a commercial two-compartment trough (KSV5000) by using double-distilled deionized water as the subphase. Individual polymer was dissolved in chloroform (~1×10^{-3} M) and slowly spread onto the subphase. The solvent was allowed to evaporate for at least 10 min before compression began. The Langmuir film was slowly compressed to the desired transfer pressures and maintained at that pressure during the film deposition. All films except for those for ellipsometry were deposited onto silica substrates which were made hydrophobic by ~15 min of treatment with octadecyltrichlorosilane dissolved at 1 mM in a mixed solvent consisting of bicyclohexyl, carbon tetrachloride, and chloroform in a volume ratio of 0.80:0.18:0.02, respectively. In the process of alternate deposition of polymers N and R, polymer N was first deposited on the downstroke and polymer R was deposited on the upstroke at a constant surface pressure of 33 mN/m and a cross sectional area per repeat unit of 0.53 and 0.34 nm^2, respectively. Film thicknesses and refractive indices were measured ellipsometrically on multilayer samples deposited onto silanized silicon wafers using a commercial variable angle spectroscopic ellipsometer (Woollam Corp.). The thickness of a N/R bilayer was derived to be 46 Å. Assuming that the previously determined thickness of N remained at the value of 16 Å previously determined for N/P films,[5] the thickness of R is 30 Å. The refractive index of the N/R multilayer was determined to be 1.51 at 800 nm and 1.54 at 400 nm. These results were derived assuming isotropic refractive indices. Since the dichroism of N/P films has been shown to be very small,[5] this is a reasonable assumption. The drying time between successive deposition cycles was 5 min. The polymer N can be deposited with a transfer ratio of almost unity (0.95–1.03) whereas the transfer ratio of the polymer R fluctuated between 0.81 and 1.02. The alternate LB layers of polymers N and P were fabricated in such a fashion that the polymer N was first deposited on the downstroke and the polymer P was deposited on the upstroke at constant pressures of 33 and 12 mN/m, respectively. The alternate LB layers of polymers R and P were deposited at constant pressures of 33 and 12 mN/m, respectively. In this case, polymer P was first deposited on the downstroke and polymer R was deposited on the upstroke. All films were deposited at a rate of 10 mm/min.

The LB films of different thicknesses (different numbers of bilayers) were deposited on different substrates. Since the vertical deposition

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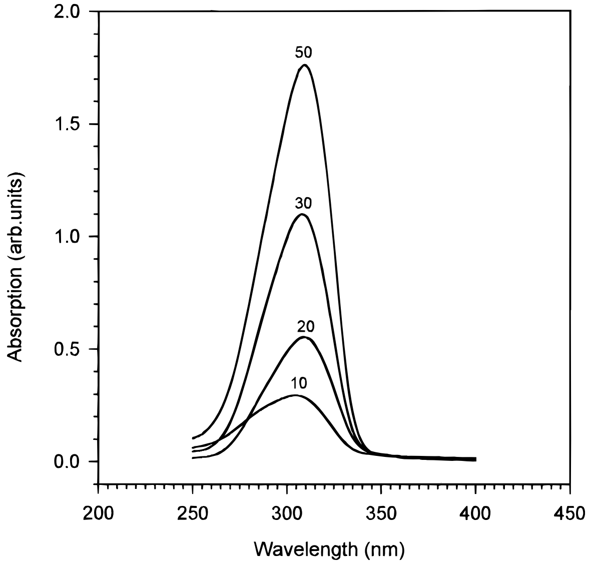

Figure 2. Absorption spectra of multilayer LB films of polymers N and R on hydrophobic S1-silica substrates. Spectra were recorded by using a bare substrate as the reference. The number of bilayers in the film is indicated next to the absorption peak.

coats both sides of the substrate, the film from one side of the substrate was removed carefully by washing it with chloroform and distilled water. Absorption spectra of LB films were recorded on a Shimadzu uv-3101PC UV−Vis−near-IR scanning spectrophotometer by using a bare substrate as the reference.

The optical second harmonic generation measurements were made with the output of a dye laser (20 mJ per pulse, 6 ns pulse width, λ = 800 nm) pumped by a Q-switched and frequency-doubled Nd:YAG laser, incident on the samples at 45°. The frequency-doubled light was separated from the fundamental using an IR cutoff filter and a monochromator and was subsequently detected by a photomultiplier tube. The signal from the photomultiplier tube was amplified and processed with a boxcar integrator and a personal computer. Lateral scans across the films were performed to check the homogeneity of the samples. When the LB films coated on both sides of the substrates were used for the SHG measurements, the signal was recorded as a function of the angle of incidence. All measurements were made with a fundamental laser beam which is polarized in the plane of incidence.

Results and Discussion

Polymer N contains a perflourinated carbon chain which not only enhances the microscopic nonlinearity, β, but also introduces a more hydrophobic character in the molecule than that of a hydrocarbon chain of the same length. Because of this increased hydrophobicity, molecules bearing shorter carbon chains can be used to build stable LB films with higher chromophore densities. The absorption spectra of multilayer LB films on silica substrates are shown in Figures 2 and 3. All films exhibit absorption peaks which are well separated from the SHG wavelength; therefore, no resonance enhancement is expected in observed NLO effects.

All films (10, 20, 30, and 50 bilayers) exhibit SHG activity. The SHG signal of the multilayers exhibited the well-known interference pattern as the angle of incidence was scanned (Figure 4).[18] The SHG signal was too weak to be measured for samples which contained less than five bilayers. It was necessary to use at least 10 bilayers in order to obtain a good signal-to-noise ratio. The frequency-doubled light was found to always be polarized in the plane of incidence regardless of the polarization of the fundamental beam, indicating a $C_{\infty v}$ symmetry for the NLO chromophore orientation.

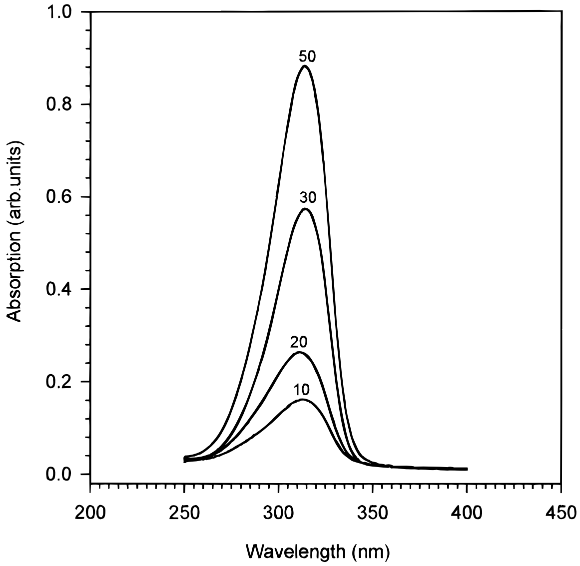

Figure 3. Absorption spectra of multilayer LB films of polymers N and P on hydrophobic S1-silica substrates. Spectra were recorded by using a bare substrate as the reference. The number of bilayers in the film is indicated next to the absorption peak.

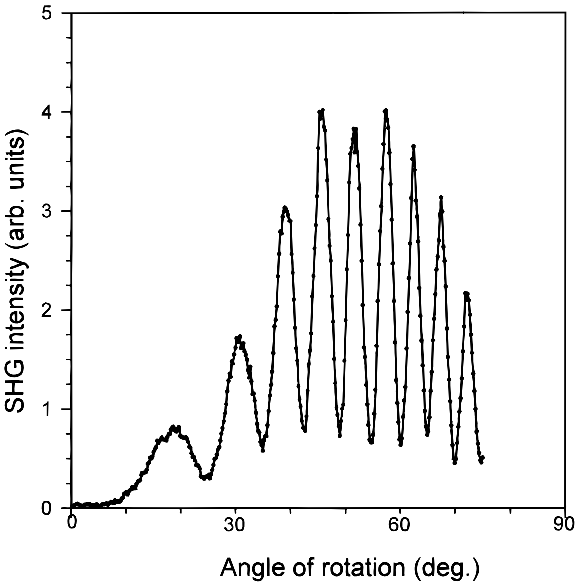

Figure 4. SHG interference pattern obtained from a 50 bilayer LB film of polymers N and R, coated on both sides of the hydrophobic silica substrate. The film was rotated around an axis parallel to the dipping axis. Both the fundamental and the frequency-doubled beams were polarized in the plane of incidence.

Within the electric dipole approximation, the SHG intensity generated in a thin film can be written as[19]

$$I^{2\omega} \propto [\chi^{(2)}]^2 \propto [N]^2 \qquad (2)$$

As shown in eq 2, the SHG intensity generated in the sample should show a quadratic increase with the increasing film thickness. In fact this behavior is clearly shown in Figure 5. The best fit to the experimental data points yields a straight line with a slope of 1.94. The fulfilment of eq 2 indicates that the film deposition occurs uniformly, preserving the chromophore orientation within successive bilayers. The multilayer LB films prepared by alternate deposition of polymer N with space polymer P, and polymer R with space polymer P, also

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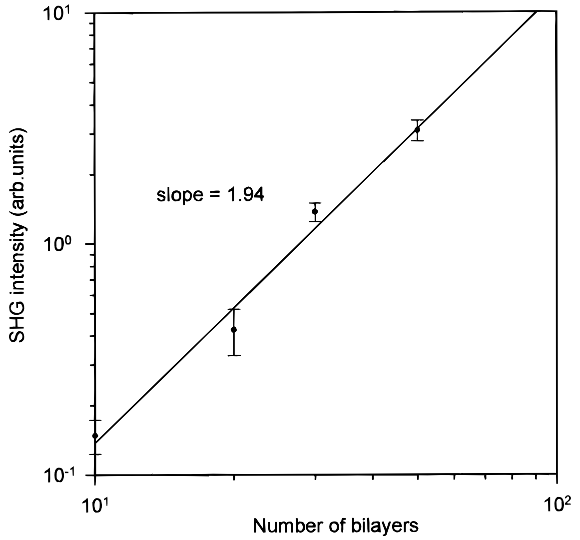

Figure 5. Second harmonic intensity in different bilayer samples of polymer N and polymer R measured at an incidence angle of 45°.

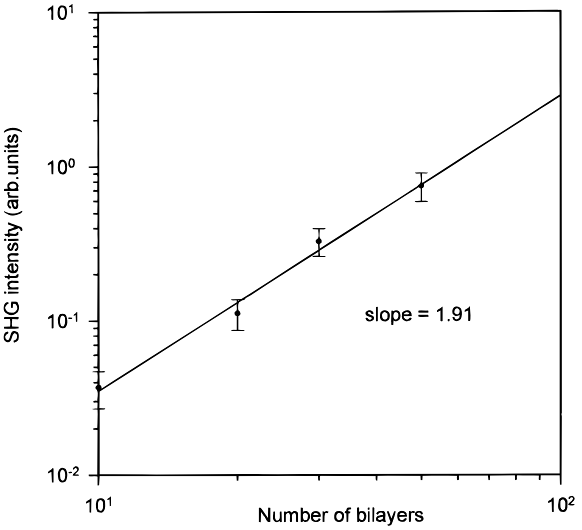

Figure 6. Second harmonic intensity in different bilayer samples of polymer N and polymer P measured at an incidence angle of 45°.

exhibit the SHG behavior described in eq 2 (Figure 6). This indicates that individual polymer N and/or R can be used to fabricate oriented multilayer films with the use of the poly(*tert*-butyl methacrylate) spacer polymer.

If the macroscopic nonlinearity, $\chi^{(2)}$, of a alternated film obeys a simple addition, then it can be expressed as[19]

$$\chi^{(2)}_{\mathrm{NR}} = \chi^{(2)}_{\mathrm{N}} + \chi^{(2)}_{\mathrm{R}} \tag{3}$$

where $\chi^{(2)}_{\mathrm{NR}}$ is the macroscopic nonlinearity of an alternated film and $\chi^{(2)}_{\mathrm{N}}$ and $\chi^{(2)}_{\mathrm{R}}$ are the macroscopic nonlinearities of polymers N and R, respectively. The macroscopic nonlinearities, in turn, can be related to the experimentally measured SHG intensity $I^{2\omega}$ as[19]

$$\sqrt{I^{2\omega}_{\mathrm{NR}}} = \sqrt{I^{2\omega}_{\mathrm{N}}} + \sqrt{I^{2\omega}_{\mathrm{R}}} \tag{4}$$

If the simple additivity is followed, the SHG intensities in these LB layers should satisfy the relationship shown in eq 4. In order to test the validity of eq 4, we prepared several different samples as described in the Experimental Section. We measured the SHG intensities of 10 and 20 bilayer samples which were fabricated with polymers N and R, N and P, and R and P. These measurements were performed by using the samples which contained LB films only on one side of the substrates. As many as 15 data points were recorded for each sample by laterally scanning the sample. It was noticed that from location to location the amplitude of the SHG signal fluctuated by as much as ±20%. Since the IR dye in the dye laser deteriorates with time, each sample was measured two times. The data presented in Table 1 represent the average value of 20 data points for various 10 and 20 bilayer films together with the square root of the corresponding SHG intensities.

Table 1. SHG Intensities of Different Bilayer Samples Measured at an Incidence Angle of 45°

type of bilayer	$I^{2\omega}_{10\ \text{bilayer}}$	$I^{2\omega}_{20\ \text{bilayer}}$	$\sqrt{I^{2\omega}_{10\ \text{bilayer}}}$	$\sqrt{I^{2\omega}_{20\ \text{bilayer}}}$
polymers N and R	0.148 ± 0.024	0.425 ± 0.097	0.3847	0.6519
polymers N and P	0.037 ± 0.006	0.112 ± 0.021	0.1924	0.3347
polymers R and P	0.034 ± 0.007	0.128 ± 0.018	0.1844	0.3578

It is very apparent from Table 1 that, within the experimental uncertainties, eq 4 is fully satisfied. The intensity of the SHG signal generated in films that were fabricated by alternate deposition of polymers N and R is approximately 4 times larger than the SHG intensity generated in films that were fabricated by alternate deposition of either polymer N or R with polymer P. An optical waveguide consisting of a multilayer LB film of polymers N and P generates a SHG power of ∼1 μW at 410 nm for 50 mW of fundamental power at 819 nm.[4] Also, this waveguide exhibits a very low optical loss. As measured with a charge-coupled-device array, the optical attenuation was between 1.5 and 2.0 dB/cm at a wavelength of 457.9 nm for both TE (transverse electric) and TM (transverse magnetic) polarizations.[4] The macroscopic optical nonlinearity of the film was found to be 8 and 10 pm/V at 860 nm for $\chi^{(2)}_{xxz}$ and $\chi^{(2)}_{zzz}$, respectively. It is reasonable to expect the SHG intensity to be enhanced by a factor of 4 for a waveguide fabricated by alternate deposition of polymers N and R. The refractive index of such films of polymers N and R measured in the present experiments is sufficiently high in comparison to films of N and P (1.51 and 1.47,[4] respectively, at 800 nm), that the low-index buffer layer previously required for optical isolation can be omitted.[4] Since this spin-coated buffer layer is probably the origin of the relatively short phase-matched interaction length previously measured, its removal from the system may also lead to a substantial increase in the waveguided second harmonic conversion from films of N and R through an increased interaction length. Fabrication of an optical waveguide of polymers N and R is currently being pursued.

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Supporting Information Available: Text and schemes describing the synthesis of polymer R (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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