Mono- and Multi-layer Langmuir-Blodgett Films of Maleimide Polymers Possessing Nonlinear Optical-Active Side Chains

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Abstract: A copolymer P[OSA-MI] was synthesized by copolymerization of its corresponding monomers, N-phenyl maleimide (MI) and 2-octen-1-ylsuccinic anhydride (OSA). The polymer (poly[2-[1-(2,5-dioxo-1-phenylpyrrolidin-3-ylmethyl)heptyl]-succinic acid 4-(2-{ethyl-[4-(4-nitrophen-ylazo) phenyl]amino}ethyl) ester]) P[DR1MA-MI] was obtained from the reaction of P[OSA-MI] with 2-[4-(4-nitrophenylazo)-N-ethylphenylamino] ethanol (DR1). A stable monolayer of P[DR1MA-MI] was formed by spreading the solution of the polymer in chloroform. In Y-type Langmuir-Blodgett (LB) films prepared using this Langmuir-Blodgett method, the second harmonic waves generated from adjacent monolayers canceled each other out. In X- and Z-type LB films, the second harmonic intensity increased upon increasing the number of monolayers, but this increase was somewhat smaller than predicted by the square law. This phenomenon is due to defects or imperfect alignment of the dipoles in the LB film. The generation of second harmonic waves from Y-type LB films having an even number of monolayers supports this argument. The degree of imperfection seemed to increase as the number of layers increased. The second-order nonlinear optical properties of spin-cast films of these polymers were also measured. The largest second harmonic coefficient of the poled P[DR1MA-MI] film coated on a glass plate was 19 pm/V.

Keywords: even/odd effect, Langmuir-Blodgett technique, organic chromophores, second-order nonlinear optical effect.

Introduction

Organic materials are recognized as promising candidates to realize fast optical devices, high optical nonlinearities, and low dielectric constant.[1-5] The devices used for controlling optical signals operate on the basis of second-order nonlinear optical (NLO) effects.[6] Organic macromolecular materials with second order NLO properties have advantages over inorganic materials because they have much wider bandwidth and better processibility. Organic chromophore molecules with an electron donor on one end and an electron acceptor on the other end of a π-conjugated system exhibit high NLO properties. Such organic chromophores can be incorporated in the macromolecules as side groups or as part of the main chain.[7-15] In addition to the many interesting optical properties, azobenzene moieties are known to have high NLO properties.[16-21] Langmuir-Blodgett (LB) technique can be utilized to obtain high degree of alignment of the chromophore dipoles. Monolayer and multilayer assemblies can be deposited on glass substrates by using the LB thin film deposition method in a clean-room environment.[22-34]

In this study, a polymer (P[DR1MA-MI]) with azobenzene chromophore dipoles as pendant was synthesized and the NLO properties of its LB films as well as spin coated films were investigated.

Experimental

Materials. N-methylpyrrolidinone (NMP), pyridine, and dioxane were purified by vacuum distillation. Ethyl ether, n-

hexane, and acetone were purified by vacuum distillation over sodium and tetrahydrofuran (THF) was freshly distilled with calcium hydride. All other solvents and reagents were analytical-grade quality, purchased from Aldrich and used as received, unless otherwise described.

Synthesis of P[DR1MA-MI]. The synthetic route of P[DR1MA-MI] (poly[2-[1-(2,5-dioxo-1-phenylpyrrolidin-3-ylmethyl)heptyl]-succinic acid 4-(2-{ethyl-[4-(4-nitrophenylazo) phenyl]amino}ethyl) ester]) is shown in Figure 1. The polymerization was performed in dry THF with AIBN as an initiator. A mixture of *N*-phenyl maleimide (MI) monomer and 2-octen-1-ylsuccinic anhydride (OSA) monomer was dissolved in THF. After addition of the initiator (AIBN), the reaction mixture was heated to 60 °C while stirring and allowed to react overnight. The resulting polymer was precipitated by pouring the reaction mixture into methanol and collected by filtration. After washing the precipitate with methanol for 2 days in a Soxhlet extractor, the polymer, P[OSA-MI], was collected as white solid. Under the nitrogen atmosphere, P[OSA-MI] and 2-[4-(4-nitrophenylazo)-*N*-ethylphenylamino] ethanol (DR1) were dissolved in dioxane. After addition of pyridine, the mixture was refluxed for 4 hrs. The resulting polymer solution was poured into a large amount of cooled methanol. The polymer precipitate was collected by filtration and washed with methanol for 2 days in a Soxhlet extractor. The yield of the reddish solid polymer, P[DR1MA-MI], was 62%. The substitution ratio of DR1 estimated by NMR was approximately 30 mole%.

Instruments. The structures of the synthesized compounds including the polymers were confirmed by ^{1}H-NMR and IR spectra. The ^{1}H-NMR spectra were obtained with 300 and 500 MHz ^{1}H-NMR (Varian Gemini) spectrometers and the IR-spectra were recorded using an FT-IR spectrophotometer (Nicolet 205). The thermal properties of the polymers were measured by thermogravimetry (TGA 2050, TA Instruments)
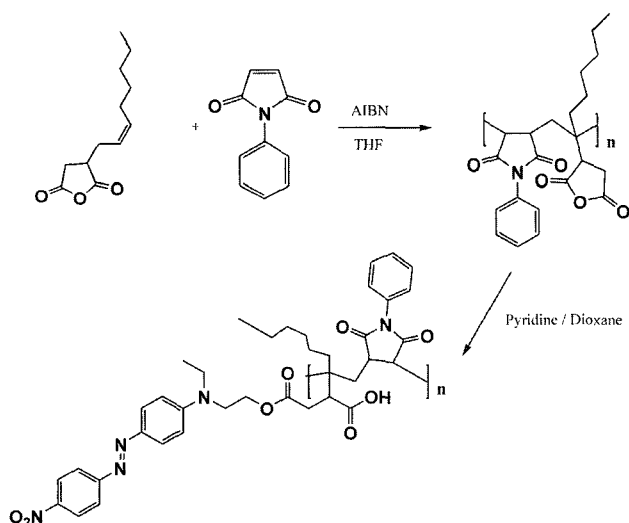
and differential scanning calorimetry (DSC 2010, TA Instruments) at a heating rate of 10 °C/min under nitrogen atmospheres. The surface morphology of LB films was observed using an AFM (Auto probe CP, Park Science Instrument).

Film Casting and Poling. Prior to film casting, the polymer solution in dichloromethane was filtered through a 0.45 μm Teflon membrane filter (Aldrich, Cat. No. Z40,003-3). The films were spin-cast at room temperature at a spin rate of 1,500 rpm and dried for 2 days under a reduced pressure at 60 °C to remove any residual solvent. The samples were poled under a high DC electric field in a corona-discharge set-up. After applying the poling voltage (6 kV), the temperature of the sample was gradually increased at a rate of 10 °C/min from room temperature to the poling temperature (150 °C) which is approximately 5 °C above the melting temperature of the polymer. The samples were maintained at the poling temperature for 30 min and cooled to room temperature. The electric field was removed after the sample reached room temperature.

Preparation of LB Film. The LB films were prepared using an alternating trough (Nima Technology, Nima 2000) equipped with a Wilhelmy plate and a surface pressure sensor. The spreading solution was prepared by dissolving P[DR1MA-MI] in chloroform (Aldrich, ACS HPLC grade) to make the concentration of 0.1%. The monolayer was formed by spreading 50-100 μL of the solution on the water subphase provided by Milli-Q system (Millipore). The subphase temperature was held constant at 25 °C. The isotherms were obtained by compressing the film at a barrier speed of 18 mm/min while recording the surface pressure as a function of the surface area. A glass plate or a silicon wafer was used as substrate to transfer the LB film. The target pressure for transfer was 35 mN/m and the dipper speed was 7 mm/min. Prior to transfer, glass plate surfaces were either hydrophilicized or hydrophobicized by dipping the substrate into aqueous solution of sodium hydroxide (2 g/dm^3) or hexamethyldisilazane, respectively. Multilayers made of up to 45 monolayers were prepared on these substrates. All three types, i.e. X-, Y- and Z-type, of LB films were prepared. The electronic spectra were recorded using a Hewlett Packard 8452A Diode Array Spectrophotometer. The NLO coefficient of the LB film was determined by Maker fringe method.

Measurement of Second Harmonic Generation (SHG). We used the 1064 nm output from a Q-switched Nd:YAG laser (10 Hz repetition rate, 20 ns pulse width) as a fundamental beam. Beam splitter and photodiode were used to compensate the intensity fluctuations of the fundamental beam. The polarization direction of the beam could be changed to be perpendicular (*s*-polarized) or parallel (*p*-polarized) to the table by using a half-wave plate. Only the second harmonic beam was made to enter the photomultiplier tube (PMT) by using a prism and a harmonic pass filter. The ana-

Figure 1. Syntheses of P[DR1MA-MI]

lyzer was used to confirm the p-polarization of the harmonic signal. The sample was mounted on the rotator coupled to the step motor. The output signals from photodiode and from PMT were detected with a peak detector. We used the Y-cut crystal quartz as a reference material for determining the relative strength of the second harmonic signals generated from our samples. Therefore, it was not necessary to measure the absolute intensities of the fundamental and harmonic beams.

Results and Discussion

In the DSC analysis, the glass transition temperature (T_g) and the melting point (T_m) of P[DR1MA-MI] appeared at 103 and 145 °C, respectively. The initial decomposition at ca. 250 °C in the TGA thermogram of P[DR1MA-MI] is attributable to the thermal breakdown of the diazo groups. The second weight loss in the TGA thermogram of P[DR1MA-MI] which appeared from ca. 370 °C corresponds to the main chain decomposition.

P[DR1MA-MI] formed a stable monolayer on water. The pressure-area isotherm of the monolayer is plotted in Figure 2. The monolayer of P[DR1MA-MI] showed a relatively high collapse pressure of about 48 mN/m. The transfer ratio of the LB film on a substrate at 35 mN/m was between 0.7 and 0.8. The Maker-Fringe patterns of the LB films are shown in Figure 3 through Figure 5. In Y-type LB films, the intensity of the second harmonic signal from the films with odd number of monolayers was higher than that from the films with even number of monolayers. This is because, in Y-type LB film, the dipoles in two adjacent layers are aligned in the opposite direction such that two electric fields
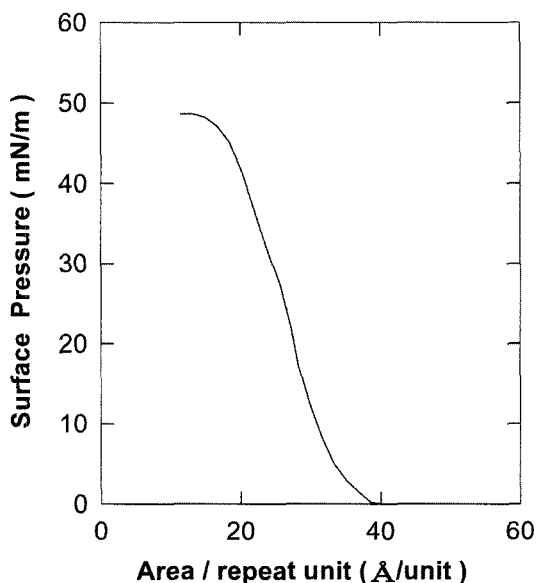
of each second harmonic signal interfere destructively. However, in the Z-type LB films, as can be seen in Figure 4, the intensity of the second harmonic signal increased with the number of monolayers. Ideally, the intensity of the second harmonic signal should be proportional to the square of the number of monolayers. However, the measured intensity was
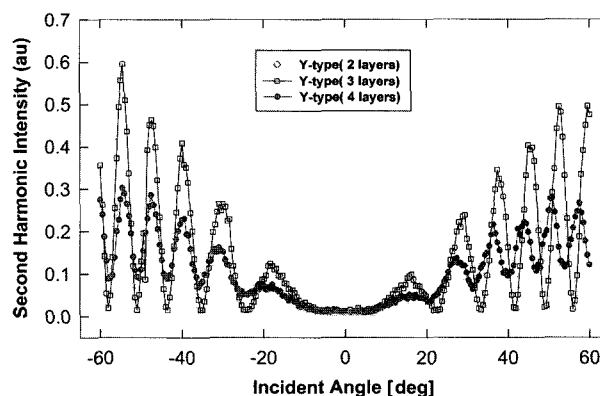

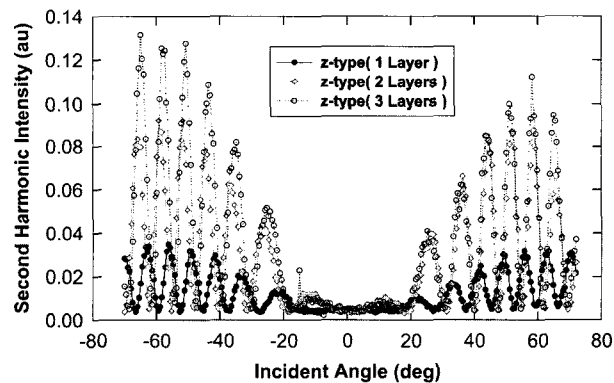**Figure 3.** Maker-Fringe pattern of the Y-type LB film of P[DR1MA-MI].

Figure 4. Maker-Fringe pattern of the Z-type LB film of P[DR1MA-MI].

Figure 2. Surface pressure-area isotherm of P[DR1MA-MI] monolayer.
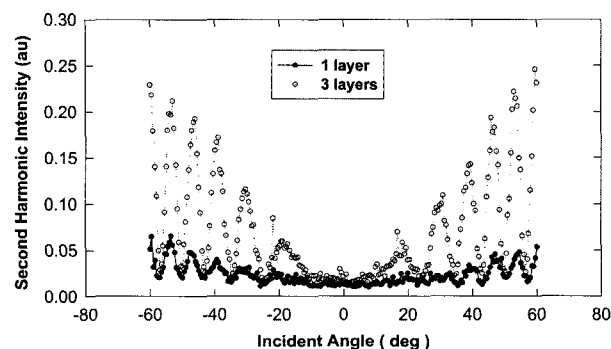
Figure 5. Maker-Fringe pattern of the X-type LB film of P[DR1MA-MI].

somewhat lower than what was expected by the square law. This is presumably due to defects or imperfect alignment of the dipoles in the LB film. This argument is also supported by the fact that the second harmonic signal from Y-type LB films with even number of monolayers does not cancel completely. The intensity of the second harmonic signal from a multiplayer sample with 45 monolayers in Y-type was comparable to that from a 3-layer sample. It is also caused by cancellation of the polarization in Y-type LB films. The degree of imperfection seemed to increase as the number of layers increased. In X-type LB films, the increase in the intensity of second harmonic signal with the number of monolayers was somewhat greater than that in Z-type LB film (Figure 4). However, the increase was still lower than what was expected by the square law.

The polymer P[DR1MA-MI] was readily soluble in CHCl₃ and could be processed into film with good optical quality by spin casting. The electronic absorption spectra of a P[DR1MA-MI] film spin-coated on ITO substrate before and after poling are shown in Figure 6. The order parameter values of the chromophore dipoles estimated from the decrease in absorbance after poling were 0.29 and 0.65 for the films coated on glass plate and coated on ITO plate, respectively. The angular dependence of the SHG signal of P[DR1MA-MI] films coated on glass plate and coated on ITO were measured and the results are shown in Figure 7 and Figure 8, respectively. The poled films showed stable second-harmonic generation. The second harmonic intensity from P[DR1MA-MI] film coated on ITO plate was greater than that observed from the one coated on glass plate by a
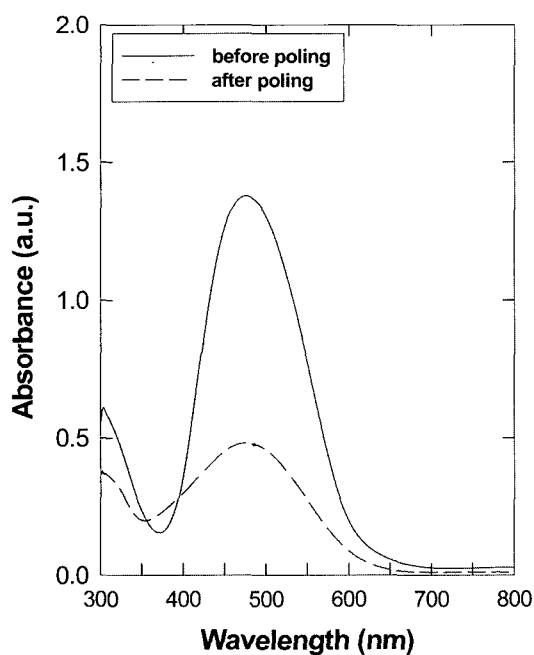
factor of two. This difference is mainly caused by the position of the anode during poling. In case of glass substrate, we put a piece of copper plate under the glass substrate and used as anode during poling. In case of ITO substrate, the ITO coating was used as the anode. The macroscopic second-order susceptibilities, d_{31} and d_{33}, of P[DR1MA-MI] film were determined from the relative second harmonic intensities of the film with respect to the values obtained from a 3 mm thick Y-cut quartz plate. For the determination of the effective
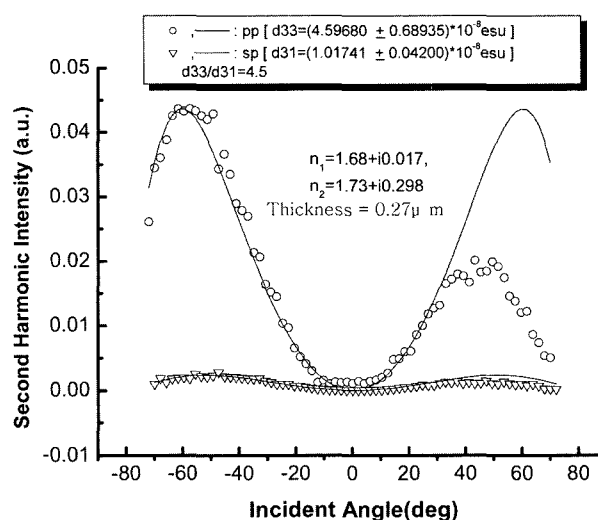

Figure 7. Angular dependence of SH signal of the poled P[DR1MA-MI] film spin-coated on glass plate at 1,500 rpm. (d_{33} = 19 pm/V, poling condition: 6 kV, 150°C, 30 min). The second harmonic intensity is the relative value to that obtained from Y-cut crystal quartz.
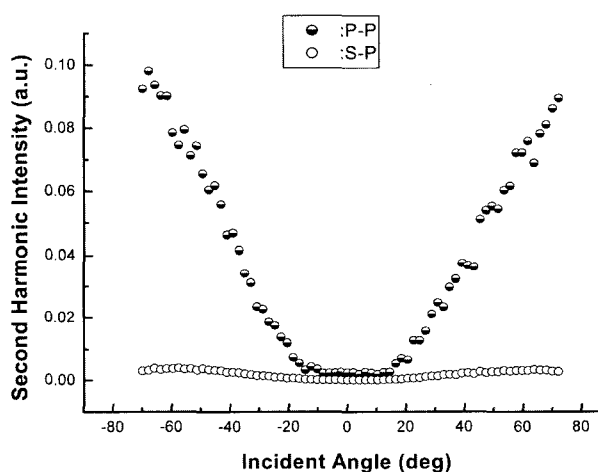

Figure 8. Angular dependence of SH signal of the poled P[DR1MA-MI] film spin-coated on ITO glass at 1,500 rpm. (Poling condition: 6 kV, 150°C, 30 min). The second harmonic intensity is the relative value to that obtained from Y-cut crystal quartz.

Figure 6. Electronic absorption spectra of the P[DR1MA-MI] film spin-coated on ITO substrate.

second harmonic coefficient, not only correction for the absorption at 532 nm was made, but also the refractive indices and the film thickness were necessary.[6] The refractive indices and thickness of P[DR1MA-MI] film coated on glass plate were measured simultaneously to be $n_1 = 1.68 + i0.0017$ at 1064 nm, $n_2 = 1.73 + i0.298$ at 532 nm, and 0.27 μm by optical transmission technique.[33] As a result, d_{31} was determined to be 4.3 pm/V from the second harmonic intensity generated by the s-polarized fundamental beam. When this value was included to the analysis of the second harmonic intensity generated by the p-polarized fundamental beam, the largest coefficient, d_{33} was determined to be 19 pm/V. However, it was impossible to determine the nonlinear coefficients for the sample coated on ITO because of the uncertainty in the optical thickness of the ITO layer.

Conclusions

The polymer P[DR1MA-MI] was obtained by incorporating DR1 as side group to P[OSA-MI]. LB films of the polymer were prepared from the monolayer of P[DR1MA-MI] obtained by spreading the solution of the polymer in chloroform. In order to obtain high SH intensity, it is important to make Z- or X-type LB film as destructive interference lowers the SH intensity in the Y-type LB film. From the projection of the SH intensity with respect to the number of monolayers, it was evident that defects or imperfect alignment of the dipoles in the LB film increased with the number of monolayers. In the spin-coated and poled film of P[DR1MA-MI], second harmonic coefficient (d_{33}) of 19 pm/V was observed.

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