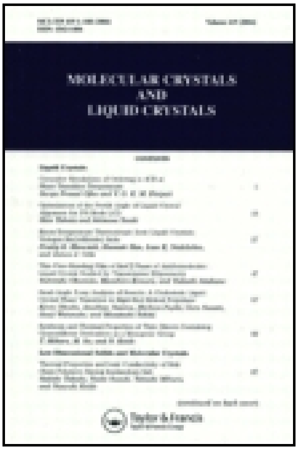

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Orientation of Main-Chain Accordion Polymers Having Different Alkyl Chains

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Orientation of Main-Chain Accordion Polymers Having Different Alkyl Chains

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The molecular orientations of homo Y-type LB films of main-chain accordion polymer having different alkyl chain (R = 12 and 16) are investigated. The homo Y-type LB films were prepared by using Miyata-type deposition system. The nonlinear optical coefficients of d33 for R = 12 and R = 16, from the result of reflected SHG intensity, are 12.0 and 8.6 pm/V. respectively. The bilayer spacing of homo Y-type LB films value from the result of wide angle X-ray diffraction (WAXD) spectra is shorter than the fully extended length of each molecule by CPK model. From the Maker-fringe for Y-type LB films, the SHG strength became the strongest when the P-P polarization was greatly slanted in the substrate. These results reveal that spontaneous polarization remains along the thickness direction. We proposed the structure of a new homo Y-type LB film which is different arrangement between odd-numbered layer and even-numbered layer.

Keywords: molecular orientation; homo Y-type LB films; accordion polymer; reflected SHG; oriented gas model

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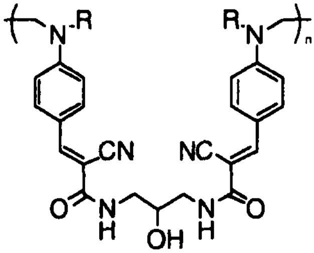
INTRODUCTION

Langmuir-Blodgett (LB) films, highly organized organic thin films, have received considerable attention in the past decade because of their potential applications such as nonlinear optical properties.[1] The LB technique is one of the best means of preparing SHG-active materials, since noncentrommetric alignment of molecules can be achieved at monolayer levels. However, conventional Y-type LB films with multilayers are generally indicates second-harmonic (SH) inactive because of the opposite orientations of the nonlinear polarizations in the adjacent layers. Hence, Y-type LB-films for NLO research have centered on the alternating a second harmonic active layer with an SH inactive space layer.[2-3] Recently, only a few, although the molecular arrangement in the Y-type LB-films shows the SHG activity originated in direction of plane of films, have been reported for the NLO properties in the homo Y-type LB-films.[4] However, the origin of SHG to the best of our knowledge, in the case of homo Y-type LB-films show the SHG activity originated in direction of thickness of films, has not been reported in details until now.[5] Recently, only a few, although the molecular arrange ment in the Y-type LB-films show the SHG activity originated in direction of plane of films, have been reported for the NLO properties in the homo Y-type LB-films.[4]



I : R = $C_{12}H_{25}$

II : R = $C_{16}H_{33}$

FIGURE 1 Structures of Accordion Polymer

We report here on a NLO properties for homo Y-type LB films of main-chain accordion polymer having different alkyl chain (R = 12 and 16) (FIGURE 1) and then the elucidation of the origin of SHG activity. [5-6]

EXPERIMENTS

Syntheses of the accordion polymer I and II were reported and described in another paper and their LB films were fabricated by the precursor method.[5-6] Reflected second-harmonic generation (SHG) intensity, wide angle X-ray diffraction (WAXD) spectra and oriented gas model analysis were carried out by the precursor method.[5]

RESULTS AND DISCUSSION

The homo Y-type LB-film polymer I and II prepared by Kuhn type LB trough did not show any SHG activity. On the other hand, homo Y-type LB-film polymer I and II prepared by Miyata type LB trough exhibited a well-defined fringe pattern resulting from SHG. The homo Y-type LB films polymer I and II shows the SHG activity originated in direction of thickness of films. Moreover, homo Y-type LB films of accordion polymer I and II are weak anisotropic showing a stronger absorption for light polarized perpendicular to the dipping direction. The nonlinear optical coefficient of d_{33} for R = 12[5] and R = 16, from the result of reflected SHG intensity, are 12.0 and 8.6 pm/V, respectively. Since the rotation angle dependence of reflected S-S (S-polarized incidence/S-polarized detection) polarization against SHG intensity was negligibly small. In case of C_2 symmetry, the simulated result of LB film polymer II is in good agreement with the experimental result. We assumed that the point symmetry of the LB film polymer II may be taken as monoclinic system with the noncentrosymmetric point group C_2. This result is same as the result of LB film polymer II. The bilayer spacing of homo Y-type LB films polymer I and II, from the result of WAXD spectra, are 36.8 Å and 41.0 Å, respectively. Since these values are shorter than the fully extended length of the accordion molecule (; the length calculated from a molecular model for polymer I and II is 54.8 Å and 61.0 Å, respectively), From the Maker-fringe for Y-type LB films polymer I and II, furthermore, the SHG strength are become the strongest when the P-P polarization was greatly slanted in the substrate. These results reveal that spontaneous polarization remains along the thickness direction. Considering that the deposition ratio of odd-numbered layer is different from that of even-numbered layer, we attained the assumption that the tilt angle of the charge transfer axis between odd- and even-numbered layer is different. From these results, we propose that molecular orientation of accordion polymer II between odd-numbered layer and even-numbered layer is different arrangement. Using a molecular-oriented gas model, studies on the orientation of the accordion polymer Y-type LB films are analyzed.[5] The tilt angles of odd numbered layer and even-numbered layer for the Y-type LB films polymer I, with regard to thickness of films, is approximately 53.0° and 37.8°, respectively.[5] While the tilt angles of odd numbered layer and even-numbered layer for the Y-type LB films polymer II, with respect to thickness of films, is approximately 57.0° and 41.2°, respectively. A possible structure for the Y-type LB films polymer II is, as a similar to a butterfly, agreed well with the that for the Y-type LB films polymer I.[5]

In conclusion, noncentrosymmetric point group for the homo Y-type LB films of accordion polymers I and II have a monoclinic system with C_2. The tilt angles with respect to surface normal for polymer I and II were somewhat different ,and then this results affected on the nonlinear optical coefficients. Using oriented gas model, we have firstly proposed a novel molecular orientation for homo Y-type LB films of accordion polymers and then the elucidated the origin of SHG activity.

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