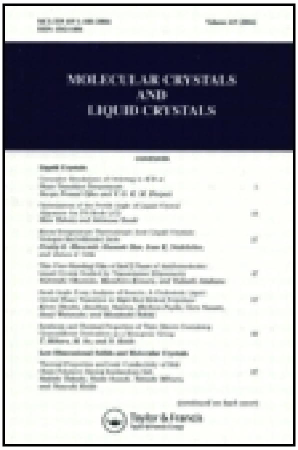

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Langmuir-Blodgett Films of Novel Diacetylene-Containing Polymers with High Second Order Nonlinear Optical Susceptibility

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Langmuir-Blodgett films of four polymers containing benzoate and cinnamate main chains and Disperse Red 19 in the side chains were prepared and characterized by means of BAM and AFM. The poly(para-benzoate) and poly(para-cinnamate) gave LB films with much higher ordered textures than the respective meta-polymers. The para-polymers apparently possess self-assembly capacity, and this is thought to be the cause of their high second order nonlinear optical susceptibility. The X-type films of the para-polymers showed second order nonlinear optical responses, suggesting that the para-polymers form self organized

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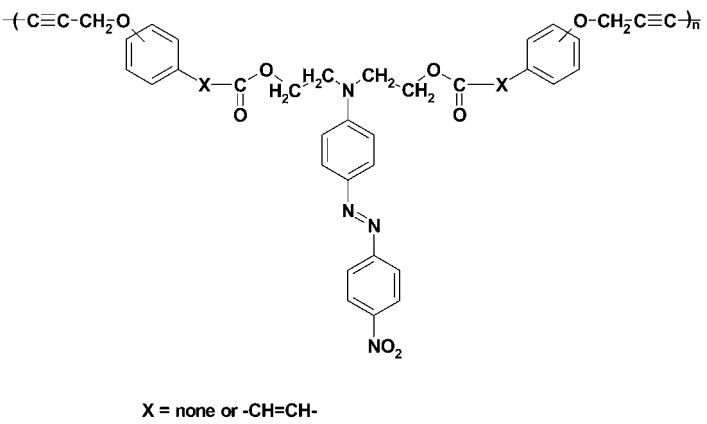
membranes with the chromophores orientated to the direction perpendicular to the substrate.

Keywords: azo-polymers; LB films; SHG

I. INTRODUCTION

Polymers containing polar chromophores have been extensively investigated in the last decades in search of materials for second order nonlinear optical (2-NLO) applications [1–4]. However, because of poor 2-NLO susceptibility and inevitable relaxation of poled chromophores, the interest in organic 2-NLO materials has gradually faded out. Recently however, the present authors have obtained series of novel polymers containing diacetylene groups in their main chains and polar chromophores as the side groups [5–7]. Their general structure is shown in Scheme 1. Thin spin coated films of some of these polymers were found to have extremely high 2-NLO coefficients (d_{33}) of 200–350 pm/V [8–9]. The emission of green 532 nm beam could be observed on naked eye during the measurements with a Q-switched Nd:YAG laser of 1064 nm, 8 ns, 10 Hz. In the previous studies, it was found that the *para*-polymers have much higher 2-NLO coefficients that the corresponding *meta*-polymers, and the relaxation of poled chromophores was much less in the former. It is thought therefore, that the high 2-NLO coefficients are due to the main chain structure favorable to orientate the chromophore groups by poling.



SCHEME 1 General structure of poly(benzoates) and poly(cinnamates).

In this work, in order to see any significant difference in the film morphology among these polymers, Langmuir-Blodgett membranes were prepared, and their morphology was investigated by atomic force microscopy (AFM) and Brewster Angle microscopy (BAM).

II. EXPERIMENTAL

The four polymers used in this work, poly(hexa-2,4-diynylene-1,6-dioxydi benzoates) and poly(hexa-2,4-diynylene-1,6-dioxycinnamates), shown in the following structure, were prepared by the methods previously reported [6–7].

Langmuir-Blodgett membranes were prepared using a LB trough NIMA 622D2 (NIMA Technology Coventry, UK) equipped with a Wilhelmy plate surface pressure sensor. Spreading solutions were prepared by dissolving the polymers in chloroform (HPLC grade) at concentration range of 0.8–1.5 mg/mL. The monolayer was formed by spreading 100–150 μL of the solution on water subphase, which had been purified by a Milli-Q system (Millipore), $\rho = 18.2\ \mathrm{M\Omega \cdot cm}$. The films were compressed after $15-20$ minutes of equilibration with a constant barrier speed of $5\,\mathrm{cm}^2/\mathrm{min}$. The isotherms were recorded at $22 \pm 1^\circ\mathrm{C}$. Multilayers were formed by depositing the monolayers at a target pressure of 25 mN/m and with a dipper speed of 5–10 mm/min. min. A transfer ratio between 0.8 and 1.0 was observed.

Various substrates were tested, and silicon wafers, quartz and soda glass were used in this work. The silicon wafer was cleaned by a mixture of hydrogen peroxide solution (30%), ammonium hydroxide (30%) and purified water (1:1:1 in volume) in an ultrasonic bath at 70°C, and then washed repeatedly with purified water at room temperature in the ultrasonic bath. The quartz panes were washed with chloroform followed with acetone and ethanol. The glass plates were washed with potassium hydroxide solution in ethanol (20%) then with water repeatedly, and by the same process to that for the quartz. The cleaning processes were performed in the ultrasonic bath. The cleaned substrates (quartz and glass) were hydrophobized by treating with ferric stearate prior to deposition. Multilayers of X-type were prepared in this work.

Brewster angle microscope (BAM) images were taken with a BAM2-plus setup from Nanofilm Technologies, GmbH, using an argon laser illumination and a CCD camera for recording. The field was 620 μm in width and 500 μm in height. Atomic force microscopy (AFM) of the LB films was carried out using a NanoScope IIIa of Digital Instruments, Inc., and the images were recorded with contact mode at room temperature. The scan speed was 1.5 Hz and low scanning forces (0.3 N/m) were employed to avoid surface damage. UV/Visible absorption spectra were taken using a Varian Cary 100 Scan spectrophotometer. The 2-NLO response was measured with a Q-switch Nd:YAG laser (1064 nm, 10 Hz) using the set-up shown in the previous paper [9].

III. RESULTS AND DISCUSSION

Figure 1 shows the surface pressure-area isotherm of the four polymers. The all monolayers showed high collapse pressure of about 50 mN/m, and the large liquid-condensed region indicates that stable condensed films are formed on water. Behaviors of polymer monolayers on the subphase were examined by cycling the compression isotherms of surface pressure-area at pressure of 20 mN/m, and in all the cases reversible curves were observed, as shown in Figure 2 for poly(*para*-benzoate) for example. The results show that irreversible rearrangement does not occur by cycling.

The occupied area per molecule at the constant surface pressure of $\pi = 0$, and the condensed region are 0.4 and 0.24 nm^2, respectively. It has been generally known that azobenzene-containing fatty acids have an area of 0.25 nm^2 when standing vertically on water [10]. This suggests that the azo group of these polymers also line up vertically the nitro group being in the water and the main chains in the air.

BAM images of the Langmuir film of poly(*para*-benzoate) are shown in Figure 3. It can be seen that a high quality homogeneous film is formed

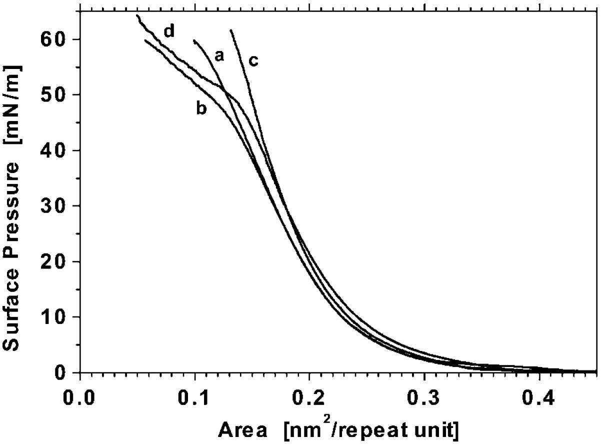


FIGURE 1 Surface pressure-area isotherms of the four polymers. a) *para*-cinnamate, b) *meta*-cinnamate, c) *para*-benzoate, d) *meta*-benzoate.

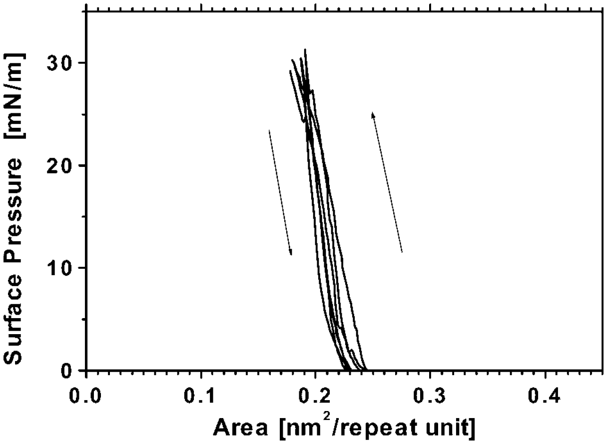


FIGURE 2 Hysteresis curves showing the reversibility of the isotherm of poly(*para*-benzoate).

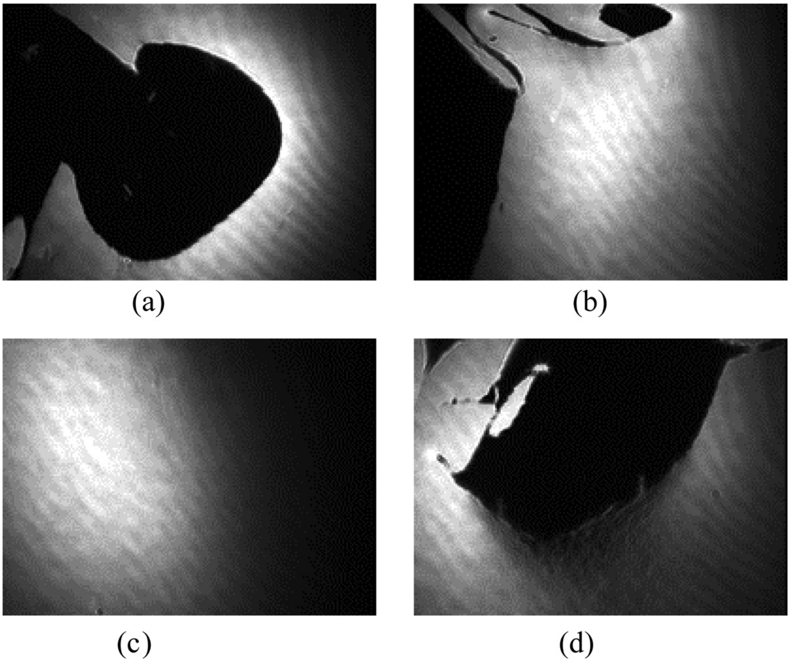


FIGURE 3 BAM images for poly(*para*-benzoate) at (a) $A = 0.329\,nm^2$, (b) $0.284\,nm^2$, (c) $0.258\,nm^2$, (d) during decompression.

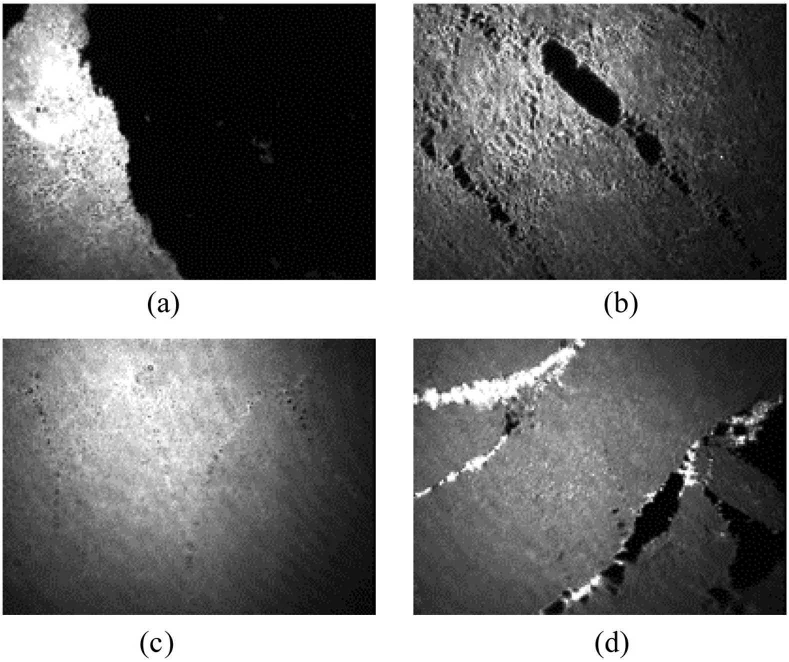
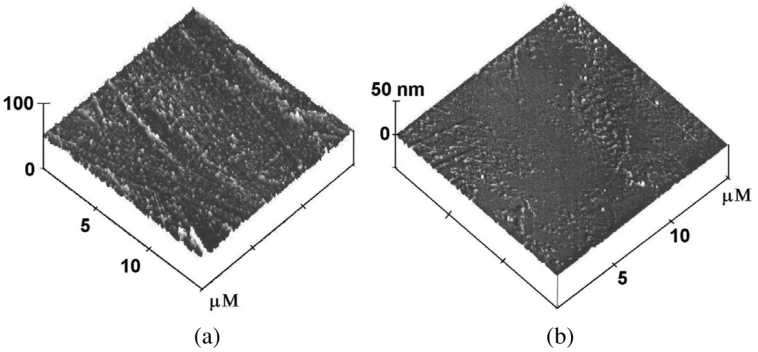


FIGURE 4 BAM images for poly(*meta*-benzoate) (a) $A = 0.466\,nm^2$, (b) $0.322\,nm^2$, (c) $0.264\ nm^2$, (d) during decompression.

(a–c), and at the end of compression the film starts to collapse (d). The poly(*meta*-benzoate) on the other hand, showed BAM images much less homogeneous although the film was obtained, as shown in Figure 4(a–c). The collapsing feature (d) was quite different from that of the poly(*para*-benzoate). The difference is due to the main chain structures. The same tendencies were observed for the poly(*para*-cinnamate) and poly(*meta*-cinnamate). It can be concluded that the *para*-polymers have much more ordered structure than the corresponding *meta*-polymers. The large difference in the 2-NLO coefficients between the *para*- and *meta*- polymers [8–9], are in accordance with the BAM images.

Figure 5 shows the AFM images of the bilayer films of polybenzoates. In the case of the *para*-benzoate, the film presents a full coverage of the surface with three particular angular distributions, 53.4, 26.9 and 51.1 degrees, between domains from left to right as seen in Figure 5(a). It can be said that this polymer clearly shows auto-assembly nature. On the other hand the *meta*-benzoate (Fig. 5(b)) did not show any regular texture.

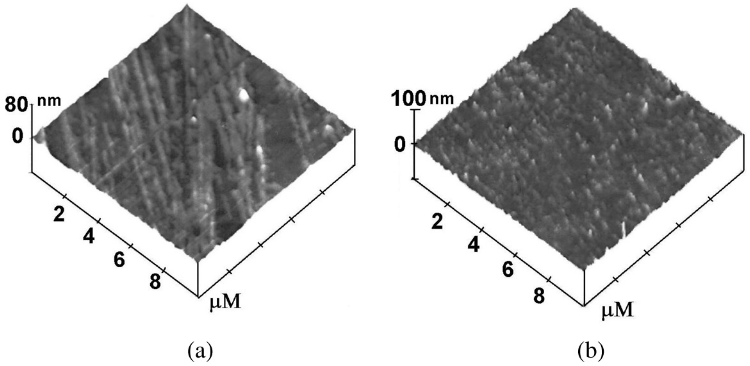


(a) (b)

FIGURE 5 AFM images of 2-layer LB films of poly(*para*-benzoate) (a) and poly(*meta*-benzoate) (b).

Figure 6 shows the AFM images of cinnamate bilayer films. Here again a very aligned texture is observed for poly(*para*-cinnamate), although the surface is not completely covered with the polymer (Fig. 6(a)). The fibers show a preferential arrangement although the angular distribution goes from 120 to 136 degrees measured from a horizontal line. The image of the *meta*-polymer, on the other hand was more irregular although there can be seen a slight alignment in a particular direction (Fig. 6(b)).

2-NLO responses of the films of *para*-polymers are shown in Figure 7. The films were X-type and not poled, but the responses are fairly strong. This suggests that the chromophores are well orientated



(a) (b)

FIGURE 6 AFM images of 2-layer LB films of poly(*para*-cinnamate) (a) and poly(*meta*-cinnamate) (b).

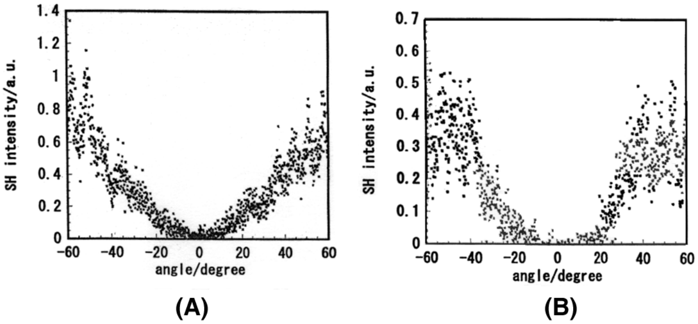


FIGURE 7 2-NLO responses of 32 layer films of poly(*para*-cinnamate) (**A**) and poly(*para*-benzoate) (**B**).

perpendicularly to the film. It is known that many X- or Z-type membranes are unstable, and they undergo membrane inversion to form Y-type films with time lapse. In the case of this work, however, the films are polymer films, and the inversion cannot take place unless the whole layer moves to be turned over. Therefore, the layers seem to be more stable than those consisting of simple amphiphilic molecules. The *meta*-polymers did not give detectable SHG signal because they do not form self-organized films when many layers are piled.

IV. CONCLUSION

From the above results it can be concluded that the poly(*para*-benzoate) and poly(*para*-cinnamate) have highly ordered structure than the corresponding *meta*-polymers. These two *para*- polymers apparently possess self-assembly nature, and the *meta*-polymers seem to have a random morphology. Preliminary results on 2-NLO responses of these X-type LB membranes, also indicates that the *para*-polymers have an ordered morphology, while the *meta*-polymer films did not show appreciable 2-NLO responses. These observations clearly explain why the 2-NLO coefficients of the spin-coated films of *para*-polymers were found to be 4 to 5 times greater than the corresponding *meta*-polymers [8,9].

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