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Derivatives of azobenzene cause photoisomerization when they are illuminated with UV-vis light. We investigated the photoisomerization of azobenzene derivatives for holographic memory. Organic films containing amphiphile azobenzene derivatives can be applied in molecular devices by changing energy of molecular level, refractive index. In order to investigate of photoisomerization of azobenzene derivatives at the air/water interface, azobenzene derivatives having side chain copolymer containing methacrylic acid [poly 4-(n-methacryloyl)-Disperse Red 1-methacrylic acid (pDR1MA)] was synthesized. The film of azobenzene derivative was characterized by the measurements of Brewster Angle Microscope (BAM) images at the air/water interface and Atomic Force Microscopy (AFM) images on the glass substrate.

Keywords: organic thin films; optical memory

INTRODUCTION

Photoisomerization of azobenzene and its derivatives has received considerable attention over the past few years because of the potential

applicability in areas such as high-density optical memory elements and molecular switching devices. The isomerization process has been investigated both in solution and in thin films on the solid substrate. The photoirradiation induces polarity changes of the azo unit; the dipole moment changes from 0.5 to 3.0D as the azo unit was photoisomerized from trans to cis form as shown in Figure 1.[1,2]

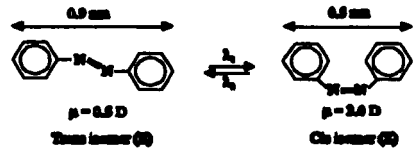


FIGURE 1. Characteristics of cis and trans isomers of azobenzene

Langmuir monolayer technique offers a convenient way to organize molecules in two dimensional surface, both at the air/water interface and on the solid substrates.[3] In this paper, an amphiphilic azobenzene derivatives having side chain copolymer containing Disperse Red 1 and methacrylic acid have been synthesized and studied by preparing ultrathin organic films.

EXPERIMENTAL

The first step was to systhesize 4-(N-methacryloyl)-Disperse Red 1 (DR1MA). The methacryloyl chloride (1 ml, 1 mmol) in THF (10 ml) was added dropwise to the cooled mixture of THF (20 ml), Disperse Red 1 (0.33g, 1 mmol) and triethylamine (0.1 ml, 1 mmol). The mixture was stirred at 0 ℃ for 1 h and followed by stirring at room temperature for 6 h more. The precipitated monomer was then filtered, dried and recrystallized from ethanol; Yield: 50%, TLC: R_f = 0.6 with eluent solution (ethyl acetate:hexane = 1:1, v/v). The second step was to synthesize poly 4-(N-methacryloyl)-Disperse Red 1-methacrylic acid (pDR1MA). The mixture of methacrylic acid (3.65 g, 50 mmol), DR1MA (0.17g, 0.5 mmol) and AIBN (0.017g) as an initiator in 30 ml of acetone-water solution (v/v = 4:1) were deoxygenated by bubbling nitrogen gas for 30 min and were stirred at 50 ℃ for 24 h. The copolymers were precipitated in ethyl acetate and recrystallized from ethanol; Yield: 25%, TLC: R_f = 0 with eluent solution (ethyl acetate:hexane=1:1, v/v). In the experimental setup of Brewster Angle Microscope (BAM; Nanofilm Tech, Germany) for the characterization of monolayers and interfacial processes, the light beam of a pulsed laser (λ =532 nm, beam diameter 1 mm) passed a polarizer set for *p*-polarization and was incident on the monolayer of pDR1MA at air/water

interface at the Brewster angle (53.15°). The reflected beam was detected using CCD camera. Also the sample deposited by the spin coating on the glass was measured to get surface images by Atomic Force Microscopy (AFM; MMAFM, Digital Instrument Int, Tapping mode, image size $1000nm^2$)

RESULTS AND DISCUSSION

BAM images of pDR1MA as shown in Figure 2 were taken in correlation with the surface pressure. BAM images of pDR1MA monolayer at the air/water interface showed the homogeneous pattern. Also BAM images of pDR1MA monolayer showed to be brighter pattern with increasing surface pressure up to 25 mN/m. This indicates that pDR1MA forms an homogeneous stable monolayer well up to approximately 25 mN/m and thereafter the collapsed monolayer disturbs the homogeneous reflection of the laser beam at the air/water interface. The monolayer of pDR1MA at the air/water interface was started to be folded by wrinkling above the surface pressure of 41 mN/m.

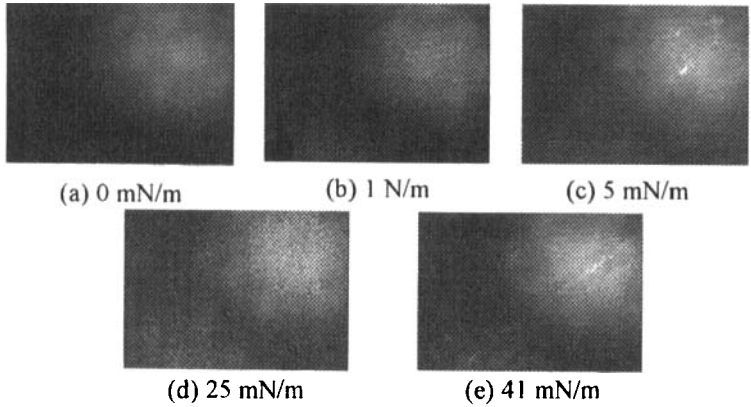
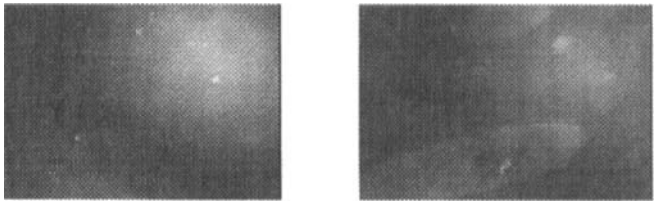


FIGURE 2. BAM images of pDR1MA monolayer versus increasing of surface pressure at the air/water interface

BAM images as shown in figure 3 were obviously different between trans and cis form of pDR1MA with different refractive index of films. As trans form was converted to cis form with UV-vis light (488 nm) irradiation,

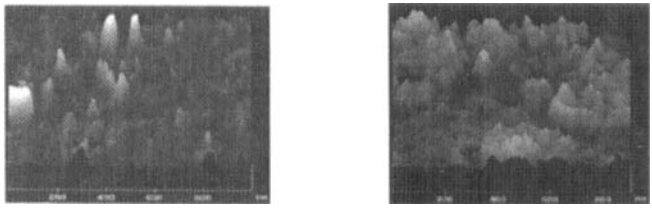
BAM images of monolayer was became to be dark. Due to the lower reflectivity of cis form than trans form, BAM image of cis form showed the darker image than that of trans form at same surface pressure.



(a) trans (b) cis

FIGURE 3. BAM images of pDR1MA monolayer of trans (a) and cis (b) at 5mN/m surface pressure, air/water interface. (a) is initial and (b) is after 1 min UV light irradiation (488 nm) (image size : 430 × 320 μm)

AFM images of trans and cis forms of pDR1MA are shown in figure 4. The AFM images of pDR1MA show that trans form was more compact structure than cis form, due to more irregular structure of cis isomer than trans isomer.



(a) (b)

FIGURE 4. AFM images of trans and cis pDR1MA films. (a) trans pDR1MA film (b) cis pDR1MA film on the glass plate.

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