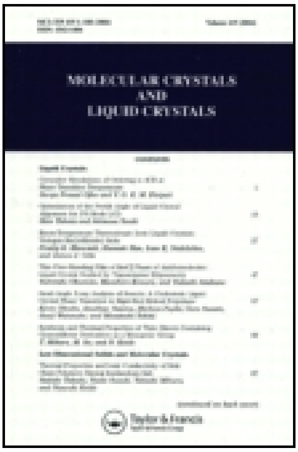

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Photochromic Behavior and Surface Properties of Vacuum-Evaporated Spiropyran Film

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Photochromic Behavior and Surface Properties of Vacuum-Evaporated Spiropyran Film

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A spiropyran derivative introduced long alkyl chain (SP-18) was evaporated on a glass plate and a polystyrene cast film containing silica particles. SP-18 films indicated reversible photochromism by UV-irradiation and standing under the dark. Change of surface properties of SP-18 film by photochromism was discussed based on wettability. Change of contact angle of water by photochromism was 35° in maximum.

Keywords spiropyran; photochromism; wettability

INTRODUCTION

Spiropyran derivatives reversibly isomerize between spiropyran-form (SP-form) and merocyanine-form (MC-form) by photo-irradiation. This phenomenon is called "photochromism". Photochromic compounds change reversibly not only their chemical structures or color but also absorption spectra, refractive indices and dipole moments by photo-irradiation. Change of these properties can be utilized in various opto-electronic devices. On the other hand, it has been widely studied to apply another properties of spiropyran compounds to new fields. Hayashida has reported that the wettability of a polystyrene (PSt) film containing spiropyran compound changes by photochromism [1]. This phenomenon will be able to apply to printing media for repetitive use, functional ink and so on. Little is known, however, about the mechanism of the wettability change by photochromism because spiropyran compound is usually dispersed in the polymer matrix. In this work, we prepared a spiropyran film by vacuum-evaporation method and investigated the wettability change of the film by photochromism.

EXPERIMENTAL

Spiropyran derivative introduced octadecyl group (SP-18) is used here. Figure 1 shows the molecular structure and photochromism of SP-18. A glass plate and a polystyrene film containing silica particles were used as the substrate. The latter substrate was prepared by following method. PSt powder was dissolved in a tetrahydrofuran (THF) with two kinds of silica particles (16nm and 1 ~ 2 μm in diameter). The THF solution was dispersed in the ultrasonic bath for 30 minutes and then the PSt film containing silica particles was prepared on glass plates by spin-coating at 3000 rpm. SP-18 was evaporated on the substrates kept at 20 °C from a fused silica glass crucible heated by a tungsten filament in a vacuum of 1.33 × 10^{-3} Pa. The film thickness was controlled 100nm.

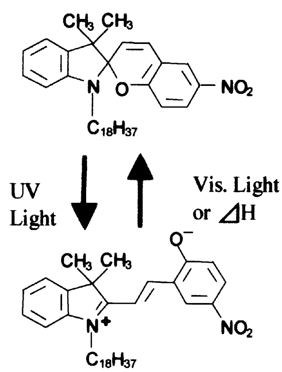

FIGURE 1 Moleculer structure and photochromism of SP-18.

RESULTS AND DISCUSSION

SP-18 film deposited on a glass plate was colorless and transparent. When the SP-18 film was exposed under UV light (λ = 365nm), the film color changed into violet. Figure 2 shows the spectral change during UV- irradiation. There are no peaks at visible range in the absorption spectrum of as-deposited SP-18 film, as shown in Fig.2 (a). The broad absorption band appears in the wavelength range of 450-680 nm after UV- irradiation. The intensity of this band increases with prolonging irradiation time as shown in Fig.2 (b)-(e).

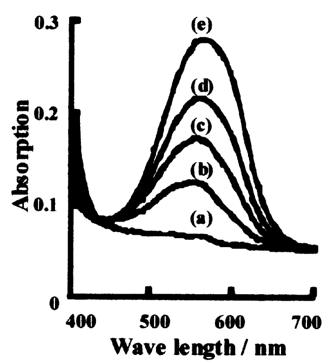

FIGURE 2 Spectral change of the SP-18 film during UV-irradiation.

On the other hand, the film color is gradually colorless under the dark at room temperature. This indicates that the photochromic behavior of SP-18 is reversible in the film.

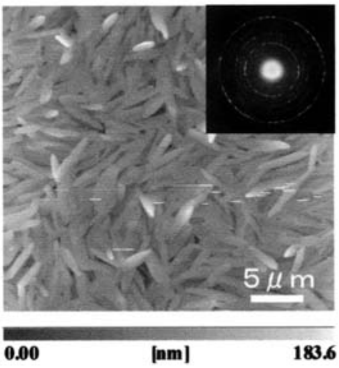

FIGURE 3 AFM image and electron diffraction pattern of the SP-18 film deposited on the glass.

Figure 3 shows the atomic force micrograph and the electron diffraction pattern of SP-18 vacuum-evaporated film. As-deposited SP-18 film is composed of rod-like crystals with a few microns in length. The electron diffraction pattern of the film indicates the ring pattern with the lattice spacings corresponding to 0.71nm, 0.60nm, 0.53nm and 0.44nm.

In general, the photochromic behavior of spiropyran derivatives is observed in the amorphous phase because a large free volume is required in the solid phase in order to avoid the steric hindrance induced by open-ring reaction. In the case of SP-18, however, the flexible alkyl chain is contained in the molecule and caused a big free volume. Thus, SP-18 indicates reversible photochromism even in the crystalline state.

The SP-18 film was evaluated by the contact angle of water. The contact angles of the SP-18 film before and after UV-irradiation for 10 minutes were 90° and 69°, respectively. The contact angle after UV-irradiation increased gradually under the dark and recovered the same value before irradiation at final. Change of contact angle of water on the SP-18 film by photochromic reaction is 21°. MC-form with open-ring form has a bigger dipolemoment than SP-form. It is reasonable to consider that MC-form is more hydrophilic than SP-form. Therefore, it seems that the origin of different wettability of the film is attributed to the change of dipolemoment caused by open-ring reaction. The remarkable change in wettability was performed using the PSt film containing silica particles as the substrate. The contact angles of SP-18 film on the PSt substrate before and after UV-irradiation are 120° and 85°, respectively, as shown in Fig.4 (a) and (b).

Recovery in contact angle under the dark is also observed in this case (Fig.4 (c)). Difference in contact angle between SP-form and MC-form achieves 35°. It is known that the contact angle is dependent on the surface morphology. The relation between contact angle and surface roughness is explained by the following Wenzel's equation;

$$\cos \theta r = r \times \cos\theta$$

where θr and θ are the contact angles on a rough surface and a smooth surface, respectively, and r is the roughness factor which is the ratio between the real and apparent area of surface. This equation indicates that the apparent contact angle on rough surface is bigger than that on the smooth surface if real contact angle is greater than 90° and this angle is smaller if less than 90°. It was found from AFM observation that SP-18 film formed along the silica particles and its surface area increased remarkably comparing to that on the glass substrate. Therefore it is concluded that an emphasized change of contact angle is attributed to the rough surface of the substrate.

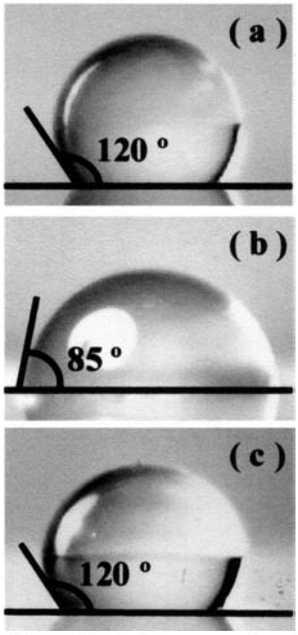

FIGURE 4 Photographs of water droplet on the SP-18 film deposited on the PSt film containing silica particles before (a) and after (b) UV-irradiaion and after straging in the dark (c).

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[1] S.Hayashida, Polymer Journal, *18*, No.3, 227(1986)