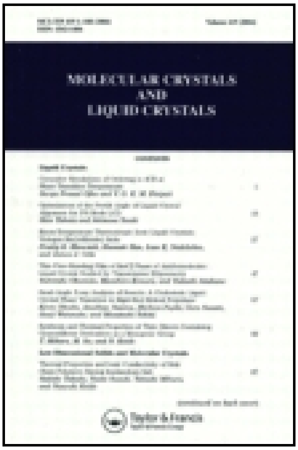

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Photoresponsive Behavior and Photochemical Phase Transition of Amphiphilic Diblock Liquid-Crystalline Copolymer

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Photoresponsive Behavior and Photochemical Phase Transition of Amphiphilic Diblock Liquid-Crystalline Copolymer

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The photoresponsive behavior of an amphiphilic diblock liquid-crystalline (LC) copolymer (P40A37) was studied in both toluene solution and spin-coated film. The LC copolymer in a film state showed slower response and relaxation than that in the solution. Significant H-aggregation in the film led to a blue shift by 16 nm at the maximum absorption. The photochemical phase transition was observed with a polarizing optical microscope (POM) upon exposure to 366-nm light. The photoinduced isotropic state remained stable at room temperature, indicating the potential application for 2-D and 3-D storage.

Keywords: amphiphilic liquid-crystalline diblock copolymer; azobenzene; liquid-crystalline polymer; photochemical phase transition; photosensitive polymers

INTRODUCTION

Owing to the covalent combination of two incompatible macromolecules, the AB-type diblock copolymers always show microphase-separated structures with cylinder, lamellar and sphere morphologies

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[1], which has attracted attention of scientific research especially in the field of nanotechnology and supramolecular chemistry. During the past two decades, azobenzene (AZO)-containing liquid-crystalline (ALC) materials, in which the AZO moiety plays both roles as a mesogen and a photosensitive chromophore, have been extensively explored as high-performance materials in information technology because they combine excellent performance of liquid crystal (LC) with photosensitive chromophores. On one hand, they possess self-organizing nature, fluidity of long-range order, cooperative motion and anisotropy in various physical properties, which can be easily controlled by optical, electrical and magnetic stimuli [2]. On the other hand, photochemical phase transition can be easily induced with a rapid optical response [3]. If the ALC molecules are introduced into diblock copolymers, the tailored copolymer might exhibit some interesting properties such as nano-scaled phase separation, LC phase and photosensitivity as well as photochemical phase transition. Furthermore, preparation of such ALC copolymers and evaluation of their properties would be an interesting and challengeable task.

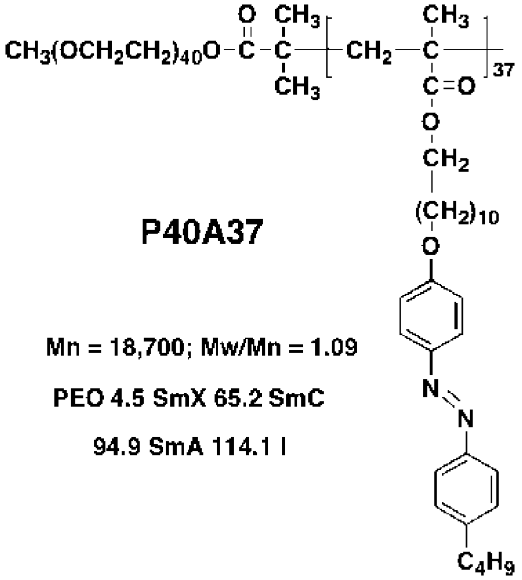
Recently, Zhao *et al.* synthesized diblock copolymers composed of polystyrene and an ALC polymethacrylate taking advantage of atom transfer radical polymerization (ATRP) method and studied the confinement effect of microphase separation on the photo-alignment, photochemical phase transition and thermochromic behavior [4,5]. Obviously, the nanostructure formed in the diblock copolymers was controlled by the ALC alignment and the ALC mobility was influenced by the nanostructure vice versa. Iyoda *et al.* reported a series of novel amphiphilic diblock LC copolymers (ADLC) consisting of flexible poly-(ethylene oxide) (PEO) as a hydrophilic segment and polymethacrylate containing an AZO moiety in the side chain as hydrophobic LC segments [6,7]. The extraordinary feature of the diblock copolymers is the microphase separation with a nano-scaled structure after annealing, e.g., a PEO cylinder regular array with 20-nm periodicity in the AZO LC matrix. Since the nano-scaled domains never scatter visible light, the ADLC can be designed to combine this nano effect with photosensitive properties of ALC polymers such as holographic recording, which may endow the inscribed gratings with controllable diffraction properties by the phase separation.

Generally, the holographic gratings can be recorded in ALC polymer films by interfering two coherent laser beams. In addition to surface-relief grating, the phase-type grating can be formed when the photochemical phase transition occurs [8]. Before inscribing gratings, it is necessary to study the photosensitive properties and photochemical phase transition behavior. In this paper, we report the photosensitive behavior of the ADLC, which will give us basic information for the holographic recording.

EXPERIMENTAL

Materials

As shown in Scheme 1, the diblock copolymer P40A37 with the number-average molecular weight of 18,700 and a low polydispersity ($M_w/M_n = 1.09$, measured by GPC) was used in this study. The copolymer was synthesized by the ATRP method and its thermodynamic properties were reported elsewhere [6]. Four kinds of phase transition peaks appeared in the DSC curve at 4.5, 65.2, 94.9 and 114.1°C, corresponding to PEO – smectic X – smectic C – smectic A – isotropic phase, respectively. The PEO block often shows a soft isotropic state, whereas the AZO-containing polymethacrylate block generally exhibits a hard LC phase, which enables the formation of the microphase-separated structure with two immiscible components [6]. The long methylene spacer provides the AZO chromophores with enough flexibility, giving rise to a smectic LC.



SCHEME 1 The chemical structure and properties of the amphiphilic diblock liquid-crystalline copolymer, P40A37 used in this paper.

Photosensitive and Photochemical Phase Transition Behavior

The polymer films with a thickness of about 100 nm were prepared by spin-coating a toluene solution on glass or quartz substrates. The thickness of the sample was measured with a surface profiler (Veeco Instruments Inc., Dektak 3ST). The LC property and the photochemical phase transition behavior were examined on an Olympus Model BH-2 optical polarizing microscope (POM). The UV light at 366 nm was obtained from a 500-W high-pressure mercury lamp through three glass filters (Toshiba, UV-35, UV-D36A and IRA-25). The UV-Vis spectra were measured using a JASCO V-550 spectrophotometer.

RESULTS AND DISCUSSIONS

Photoinduced change of UV-Vis spectra in the spin-coated film and the dilute toluene solution was explored at room temperature.

As shown in Figure 1(a), two absorption bands appeared in the UV-Vis spectra of the P40A37 toluene solution. Upon irradiation at 366 nm, the band around 350 nm owing to the π-π^* transition decreased, and the band at 450 nm due to the n-π^* transition increased, indicating the typical photoisomerization of the AZO. Although the photoisomerization of the spin-coated film upon irradiation at 366 nm shown in Figure 1(b) is similar to the behavior in the solution, three different points were observed. Firstly, two isosbestic points were obtained at around 415 nm and 310 nm, respectively in the toluene solution, while no isosbestic point appeared in the film. Secondly, the absorption band of π-π^* transition of trans-AZO that appeared at 334 nm in Figure 1(b) exhibited a blue shift by about 16 nm compared to the solution. Thirdly, the maximum

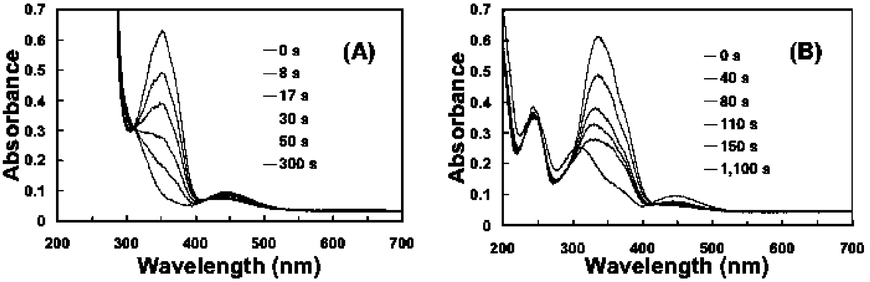


FIGURE 1 The UV-Vis spectra of P40A37 before and during 366-nm UV irradiation. (A) Toluene solution, (B) spin-coated film.

absorption peak of the film shifted to a shorter wavelength in the film upon UV irradiation unlike the solution.

Figure 2 shows the maximum absorbance as a function of irradiation time at 366 nm. We found that the copolymer in the solution underwent a faster photoreaction than in the film state. The change of the maximum absorbance (A) in the toluene solution can be best fitted by the following first-order exponential decay function.

$$A(t) = A_0 + A_1\exp(-t/T_1)$$

The value of constants, $A_0 = 0.96473$, $A_1 = 0.52999$, $T_1 = 27.294$ were obtained. In the film, however, the curve could not be fitted well by the equation mentioned above.

To understand the difference in the photoresponsive behavior of P40A37 between the film and the solution state, absorbance difference (AD) diagrams of Figure 1 (a and b) were evaluated. The AD diagrams are conveniently used to know if a reaction involves a single process in term of starting material(s) and product(s) [9].

Figure 3(a) shows the AD diagrams of the toluene solution. Here ΔA_{350} is the absorption difference at 350 nm between the original state and any state during photo-irradiation, and ΔA is the absorption difference at any wavelength. The value of ΔA increased linearly at one wavelength, supporting that the P40A37 in the solution undergoes just one kind of photoreaction without any side reactions. It is reasonable to conclude that only AZO chromophores photoisomerization is

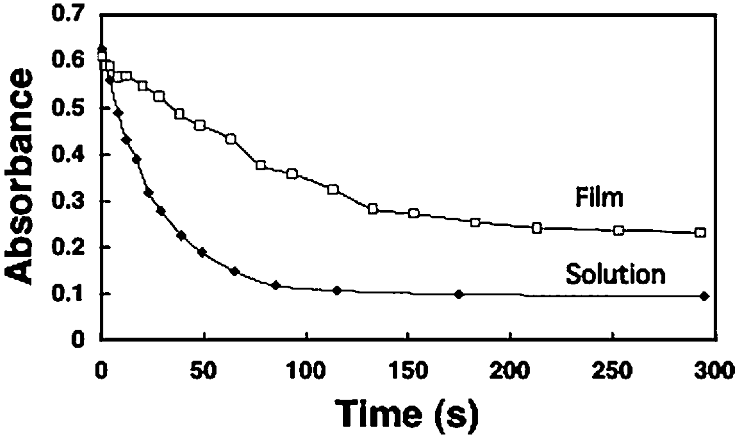


FIGURE 2 Change in the maximum absorption of UV-Vis spectra as a function of UV irradiation time.

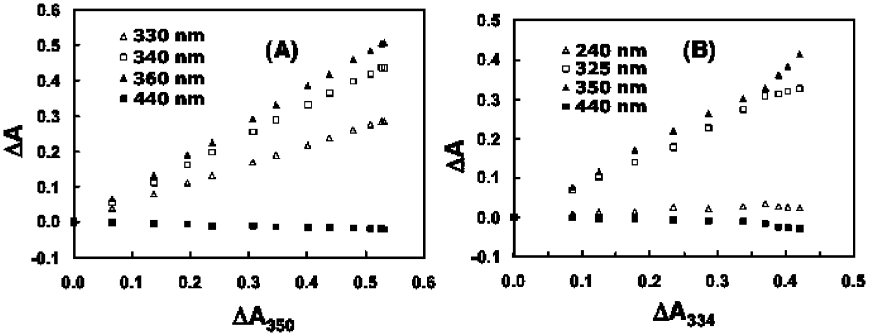


FIGURE 3 Absorption difference (AD) diagrams of P40A37 before and during the 366-nm UV irradiation. (A) Toluene solution: absorption differences (ΔA) at 330, 340, 360, 440 nm were plotted against ΔA at 350 nm. (B) Spin-coated film: absorption differences (ΔA) at 240, 325, 350, 440 nm were plotted against ΔA at 334 nm.

involved upon irradiation at 366 nm. On the other hand, the AD diagrams of the spin-coated film exhibited nonlinear curves, as shown in Figure 3(b), demonstrating that other reactions occurred at the same time as the photoisomerization. It is well known that H- or J-aggregation exists in the solid state of AZO-containing polymers [10]. In general, the H-aggregation often leads to a blue shift in absorption spectra, whereas a red shift is induced by the J-aggregation. The blue shift of about 16 nm in the UV-Vis spectrum observed in the polymer film manifests the existence of significant H-aggregation of AZO chromophores in the film state.

The fraction of cis-AZO isomer (F) can be determined from the absorbance by the following equation [11,12],

$$F = 1.05 \times (1 - A/A_{dark})$$

where A_{dark} = the initial absorbance at 334 nm for the polymer film or 350 nm for the toluene solution, and A is the absorbance in the photostationary state of AZO chromophores during photo irradiation. Irradiation of 366-nm light yielded 73% of the cis-AZO isomer in the photostationary state after 1,100 s. In contrast, the cis-AZO isomer of 89% was produced after 300 s in the toluene solution. Compared to the solution state, the spin-coated film showed a lower conversion from the trans to the cis isomer in the photostationary states, owing to the existence of both steric hindrance and the H-aggregation in the solid state.

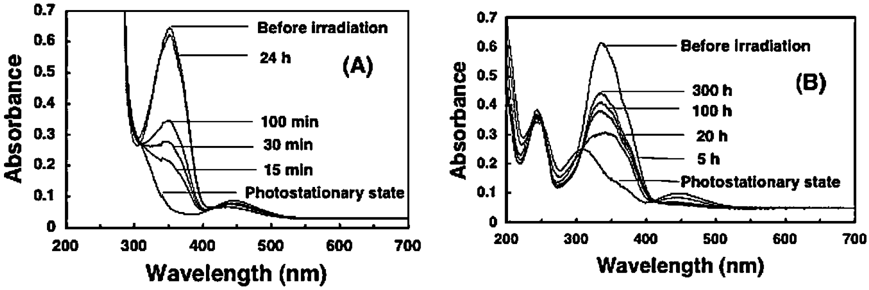


FIGURE 4 The relaxation of UV-Vis spectra of P40A37 in dark condition. (A) Toluene solution, (B) spin-coated film.

Then the relaxation processes in the spin-coated film and the toluene solution were examined. Figure 4 shows the absorption spectra after turning off the UV light.

Kept in the dark, the cis form of AZO chromophores in both the film and the solution slowly relaxed to the trans form, and the UV-Vis spectra recovered to the original shape. After being stored 300 h in the dark, the amount of the cis-AZO isomer in the film decreased to 30%, which is less than half of the content in the photostationary state (73%). For the toluene solution, the UV-Vis spectra relaxed more rapidly than those in the film. One day later, the absorption restored almost to the initial shape.

Considering the molecular structure of the copolymer P40A37, the n-butyl substituents are connected at the p-position of AZO moiety, which makes the overlap of the molecular orbital between the π-π^* and n-π^* transition poor. Such AZO moieties have a relatively long lifetime of the cis isomer [13,14].

It is well known that the trans-AZO could be an LC mesogen since the molecular shape is rod-like, whereas the cis-AZO never shows any LC phase because of its bent shape [2]. This phenomenon has been used for the photochemical phase transition in the ALC materials or ALC dispersed LC systems [3]. The present material, P40A37, shows a smectic phase from room temperature to 114.1°C. Exposure of the film to unpolarized 366-nm light at the intensity of 60 mW/cm^2 induced the LC to isotropic phase transition, resulting in the disappearance of the birefringence observed with a polarizing optical microscope (POM), as shown in Figure 5.

The upper part of the image without UV irradiation displayed the smectic texture; whereas the lower part irradiated for 10 min exhibited a dark view, which means that an isotropic state has been induced

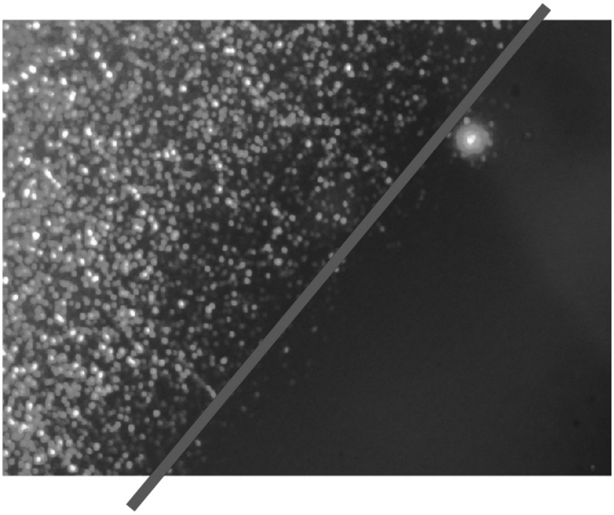


FIGURE 5 POM image of the spin-coated P40A37 film. The upper part is unirradiated area and the lower part was irradiated at 366 nm with 60 mW/cm^2 for 10 min.

by the photochemical phase transition. Besides, the light yellow color of the film became darker owing to the enhancement in the absorption of the n-π^* transition at around 450 nm. Although the trans-AZO isomer could be restored by thermal isomerization in the dark at room temperature as shown in Figure 4(b), the irradiated area still remained isotropic under observation of POM since the molecular motion is restricted in the polymer, the initial alignment can not recover even after all cis-AZO isomers go back to the trans-AZO isomers. Further experiment shows that LC cannot be restored even in visible environment without being irradiated by 488-nm laser beams because of the high viscosity of the smectic LC phase.

CONCLUSION

We studied the photosensitive property of an amphiphilic diblock liquid-crystalline copolymer (P40A37). The copolymer showed quicker response and slower relaxation behavior in the film state than those in the toluene solution. Under 366-nm light irradiation, only photoisomerization occurred in the polymer solution, whereas the additional H-aggregation was involved in the film. The photochemical phase transition from an LC to an isotropic phase was triggered in the polymer film. The isotropic state induced was stable even in the bright-light environment, giving us a hint for photonic applications such as phase-type gating based on the photochemical phase transition.

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