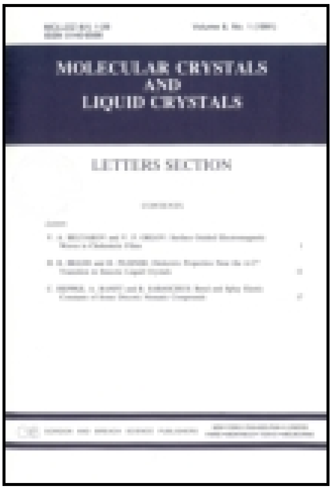

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Photo-Controlled Manipulation of Micrometer-Scale Objects on Polyethyleneglycol Thin Films with Azobenzene Compounds

Su Ma[a], Yutaka Kuwahara[ab], Hiroto Nagano[a], Nodoka Hatae[a], Tomonari Ogata[c], Sunnam Kim[a] & Seiji Kurihara[abcd]

[a] Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, Chuo-ku, Kumamoto, Japan

[b] Kumamoto Institute for Photo-Electro Organics (PHEONICS), Higashi-ku, Kumamoto, Japan

[c] Innovative Collaboration Organization, Kumamoto University, Chuo-ku, Kumamoto, Japan

[d] JST-CREST, K's Gobancho, Chiyoda-ku, Tokyo, Japan

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Photo-Controlled Manipulation of Micrometer-Scale Objects on Polyethyleneglycol Thin Films with Azobenzene Compounds

SU MA,[1] YUTAKA KUWAHARA,[1,2] HIROTO NAGANO,[1]
NODOKA HATAE,[1] TOMONARI OGATA,[3] SUNNAM KIM,[1]
AND SEIJI KURIHARA[1,2,3,4,*]

[1]Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, Chuo-ku, Kumamoto, Japan
[2]Kumamoto Institute for Photo-Electro Organics (PHEONICS), Higashi-ku, Kumamoto, Japan
[3]Innovative Collaboration Organization, Kumamoto University, Chuo-ku, Kumamoto, Japan
[4]JST-CREST, K's Gobancho, Chiyoda-ku, Tokyo, Japan

We demonstrated manipulation of micrometer-sized objects (micro-objects) by scanning light irradiation on polyethyleneglycol (PEG) thin films doped with azobenzene derivatives. 4-Ethoxy-4′-methoxyazobenzene (EMAB)-/ Disperse Red 1(DR1)-doped polyethyleneglycol films were selected as matrix. The motion of micro-objects was caused by irradiation upon UV ($\lambda = 375$ nm) and visible ($\lambda = 488$ nm) light, which suggested that the photo-responsive motion was affected by the following three factors: light intensity, the concentration of azobenzene compound in PEG, and the distance between the irradiation position and the micro-objects. Moreover, the travelling speed of micro-objects on the DR1-doped PEG film was more effective than that on the EMAB-doped PEG film under the visible light.

Keywords Azobenzene; photoisomerization; assembly technique; manipulation

1. Introduction

It is well known that azobenzene can exhibit reversible trans-form to cis-form isomerization by UV and visible (Vis) light. Owing to the interesting photoisomerization behavior, much effort has been focused on the azobenzene compounds in advanced materials [1–5] and life-science [6–8]. The azobenzene also shows comparatively photo-stability as negligible decomposition occurs even after prolonged irradiation, while trans-form and cis-form of azobenzene molecule exhibit different structural shape, which can induce changes of

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[*]Address correspondence to Seiji Kurihara, Department of Applied Chemistry & Biochemistry, Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan, Tel.: +81-96-342-3678; Fax: +81-96-342-3679. E-mail: kurihara@kumamoto-u.ac.jp

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well-ordered molecular structure, and polarity, which enables to change surface force of environments like surface tension. Consequently, with existence of azobenzene molecules, the light could create mechanical force coming from changes of the molecular structure, surface tension and so on [9–18].

Recently, several studies on manipulation or assemble technology, which is carried out by light irradiation, have been reported by our group [11–14] and other groups [15–18]. Diguet, et al. reported an oil droplet floated on a water bath containing azobenzene, whose polarity depended on the illumination wavelength, could be manipulated by light [16]. Varanakkottu et al. demonstrated manipulation of micron-sized particles on the air-water interface with hydrophilic azobenzene molecules was also available by light irradiation [17]. The manipulation of micrometer-sized objects (micro-objects) by light is promising to be applied in assembly technology and micron-/nano-machines.

In our previous work [11], we prepared liquid crystalline (LC) film, 5CB or E44, doped with several kinds of azobenzene dyes. In an azobenzene-including LC film under Ar^+ light ($\lambda = 488$ nm) irradiation, both trans-to-cis and cis-to-trans photo-isomerization of azobenzene moieties simultaneously occurred and subsequent disruption of molecular alignment of liquid crystals could be induced. As their result, we could carry out the precisely-controlled motion of micro-objects on the LC films with azobenzene molecules. While, when they were exposed to UV light ($\lambda = 375$ nm), we could not accurately transport the micro-objects on LC films in order to enlarge the area of disordered isotropic phase.

In this study, we investigated manipulation of micro-objects on polyethyleneglycol (PEG) films as matrix, because the PEG has advantages for not only a widely-useful polymer but also biocompatible and low-hazardous.

2. Experiment

2.1. Materials

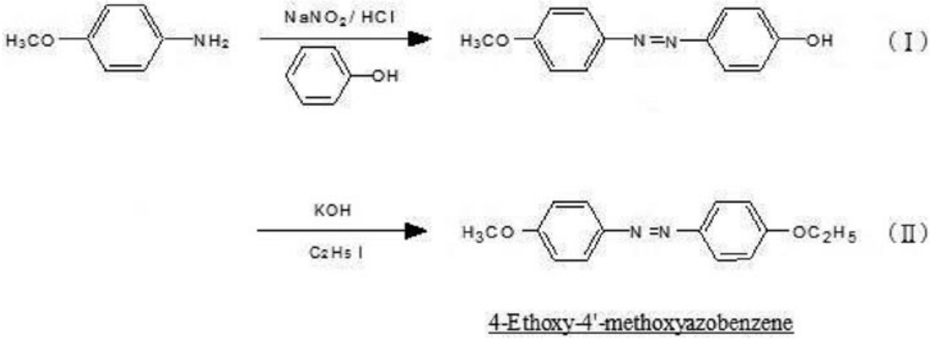
Polyethyleneglycol (PEG) with n = 300 was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Disperse Red 1 (DR1) was purchased from SIGMA ALDRICH (Japan) and were recrystallized from ethanol solution. Other reagents were purchased and used without further purification, unless stated.

2.2. Synthesis of 4-Hydroxy-4′-methoxyazobenzene

To a solution of sodium nitrite (9.52 g, 57 mmol) in water (50 mL), a mixed solution of *p*-anisidine (6.26 g, 50 mmol) in water (150 mL), acetone (50 mL) and aq. HCl (10 mL) were added dropwise at 0°C with stirring. After that, mixed solution of phenol (5.07 g, 53 mmol) and sodium hydroxide (2.35 g, 56 mmol) in water (100 mL) was added to the solution at room temperature and resulting solution was stirred for 15 h. Then, acetic acid was added to neutralize the solution. The resulting mixture was concentred by filtration. The residue after being dried was purified by silica-gel column (eluent: ethyl acetate: hexane = 3:1) to give yield of 29.7% (6.77g) as shown in Scheme 1-I.

2.3. Synthesis of 4-Ethoxy-4′-methoxyazobenzene

4-hydroxy-4′-methoxyazobenzene (0.5 g, 2.2 mmol), ethyl iodide (0.31 g, 5.5 mmol) and potassium hydroxide (0.6 g, 10 mmol) were dissolved in ethanol (10 mL). The mixed solution was stirred at 50°C for 150 min. The resulting mixture was evaporated in vacuo.



Scheme 1. Synthesis of 4-Ethoxy-4′-methoxyazobenzene (EMAB).

The residue was purified by recrystallization from ethanol to give a yield of 63% (0.35 g) as shown in Scheme 1-II.

2.4. Characterization of Synthesized Compounds

The synthesized azobenzene compounds were characterized by elemental analysis and ^{1}H-NMR spectroscopy respectively. The data of the compounds are as follows:

4-Hydroxy-4′-methoxyazobenzene: M.P. = 139.2–140.5°C; ^{1}H-NMR (400MHz, $CDCl_3$): 7.87 (2H, dd, aromatic), 7.84 (2H, dd, aromatic), 7.00 (2H, d, aromatic), 6.94 (2H, d, aromatic), 5.33 (1H, s, —O*H*), 3.89 (3H, s, —OCH_3)

4-Ethoxy-4′-methoxyazobenzene (EMAB): M.P. = 136.9–138.1°C; ^{1}H-NMR (400 MHz, $CDCl_3$): 7.87 (4H, dd, aromatic), 7.00 (4H, dd, aromatic), 4.11 (2H, q, OCH_2CH_3), 3.89 (3H, s, —OCH_3), 1.45 (3H, t, –OCH_2CH_3)*;* elemental analysis: calcd (%): C 70.29, H 6.29, N 10.93; found (%):C 70.21, H 6.33, N 10.93

2.5. Phototchemical Property of EMAB and DR1

The photoisomerization behaviour of EMAB and DR1 were examined in methanol solution by monitoring changes in the absorption spectra from a UV/Vis spectrometer (Shimazu UV-1600) at room temperature.

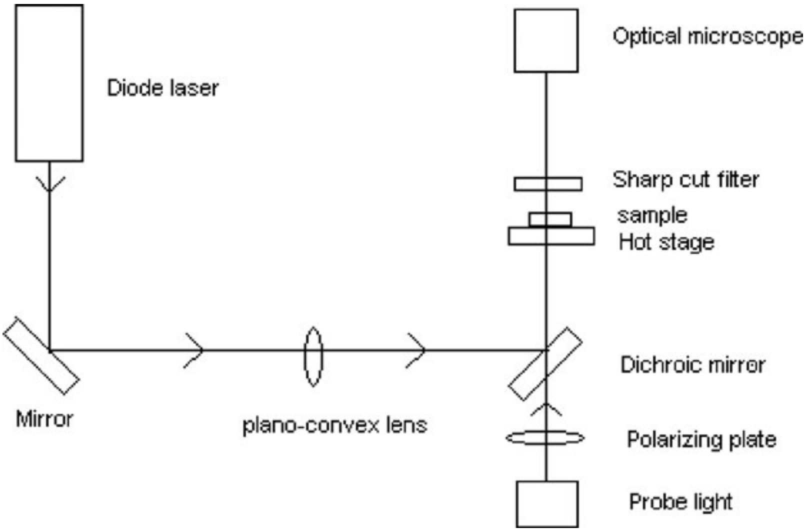
The photoisomerizations of trans-cis or cis-trans was induced by using a 500W high-pressure mercury lamp (Ushio SX-UI 5000) equipped with a cut filter (Sigma UTVAF-35U OR Sigma SCF-50S-42L) for UV (λ = 365 nm) or Vis (λ = 436 nm) light irradiation, whose intensity were 13 mW/cm^2 or 140 mW/cm^2, respectively.

2.6. Fabrication of Thin Films

EMAB- or DR1-including films of PEG were prepared on a glass substrate by the spin-coating method using THF as solvent, then glass rods (c.a. diameter = 7μm) as the micro-objects were placed on the thin film. The thickness of the films was estimated about 150 nm by measuring absorbance of dyes in the films from spectroscopy.

2.7. Manipulation of Micro-Objects

The manipulation of micro-objects on the PEG film doped with azobenzene was carried out by using UV laser ($\lambda = 375$ nm, 128 mW/cm^2) or Ar$^+$ laser ($\lambda = 488$ nm, 130 mW/cm^2/ 40 mW). The setup for imaging the motion of micro-objects on PEG film was shown as Scheme 2.



Scheme 2. Schematic drawing for experimental setup of manipulation.

3. Results and Discussion

3.1. Photoisomerization Behavior of EMAB and DR1

To evaluate the isomerization of EMAB or DR1 upon light irradiation, the changes in the absorption spectra of the methanol solutions were examined under UV or Vis light irradiation, as shown in Fig.1 and Fig. 2.

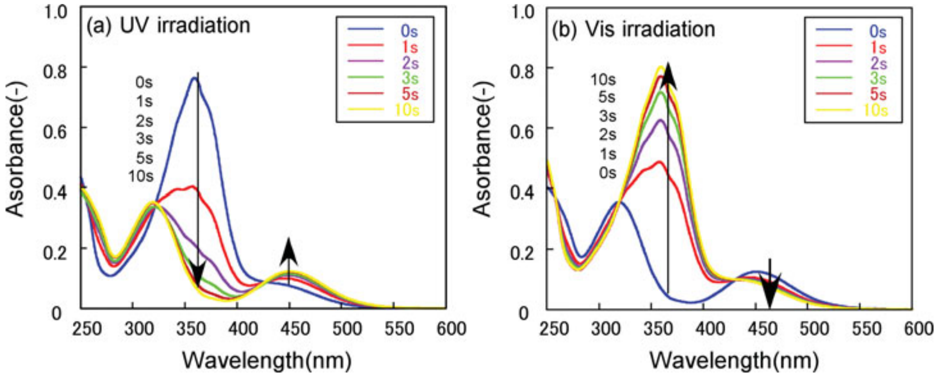


Figure 1. Changes in UV-visible spectra of EMAB in methanol by UV and visible light irradiation.

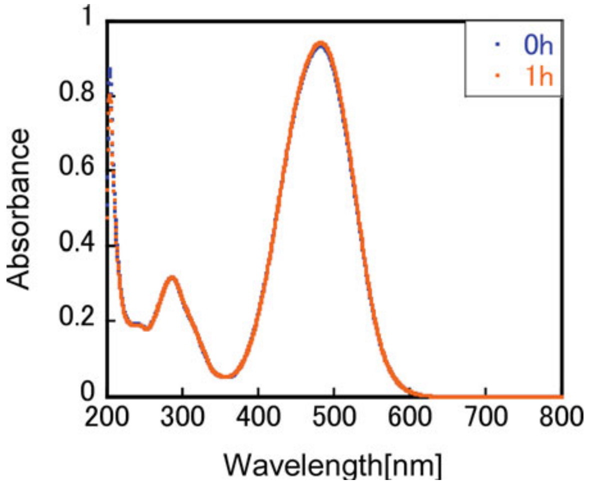


Figure 2. UV-visible spectra of DR1 in methanol before and after irradiation for 1 h.

Before UV irradiation, the UV-Vis spectrum of EMAB methanol solution exhibited a strong absorption at around 360 nm due to $\pi-\pi^*$ transition in the trans-form azobenzene, with a weak absorption at around 450 nm originating from n–π^* transition. Upon UV ($\lambda =$ 365 nm) irradiation, the absorbance decreased at 360 nm and increased a little at 450 nm, which indicated that photoisomerization from the trans-form to cis-form was induced. A photostationary state was reached after 10 s of exposition to UV light (Fig. 1a). While, upon visible light ($\lambda = 436$ nm) reverse photoisomerization was observed as shown in Fig. 1b, where an increase and a decrease of absorbance values at approximately 360 nm and 450 nm, respectively. The significant thing found from Fig. 1 was that the recovery of the initial spectrum was almost complete when it was exposed to Vis light for 10 s, whose time was the same as being exposed to UV light.

DR1, which is push-pull-substituted azobenzene, exhibited a large peak of absorbance at 480 nm. Because of ultrafast photoisomerization and reverse-isomerization [19], no significant different spectrum of photoisomerization behavior were observed for absorption of DR1-methanol solution, even being exposed to visible light for a long time (as shown in Fig. 2). The $\varepsilon_{\mathrm{EMAB}}$ and $\varepsilon_{\mathrm{DR1}}$ were also calculated from the spectra before irradiation, which were 22,800 and 28,000 cm^{-1}mol^{-1}dm^3 at 360 and 480 nm, respectively.

3.2. Manipulation of Micro-Objects

The manipulation of micro-objects on PEG films with EMAB and DR1 was studied using UV ($\lambda = 375$ nm) and Vis ($\lambda = 488$ nm) light, respectively. Typical trapping trajectories were presented in Fig. 3-I and Fig. 3-II. When the EMAB-doped PEG thin film ($7.5 \times 10-5$ mmol/mg in PEG) was irradiated with UV light, the motion towards irradiation area (Fig. 3-I-b, Fig. 3-I-c) was induced for the dispersed glass rods on the surface of the film. After Vis irradiation, the glass rods moved away from the irradiation area (Fig. 3-II-b, Fig. 3-II-c).

In addition, the glass rods could travel farther with increase of the irradiation time. It should be emphasized that the glass rods after UV irradiation could almost travel back to

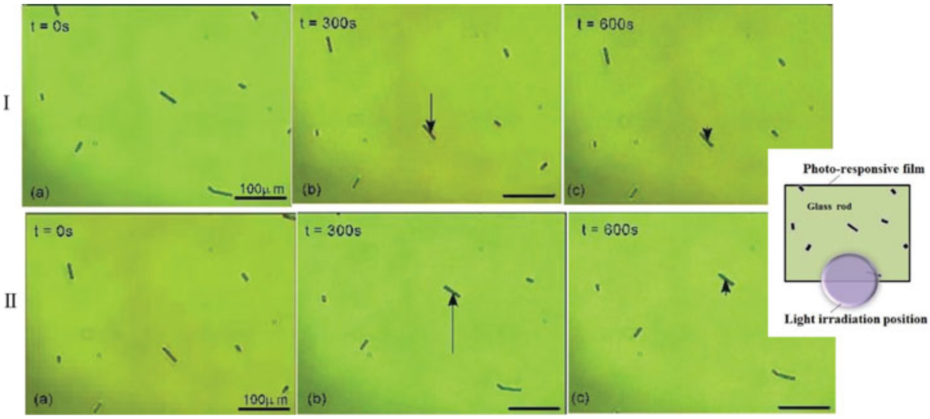


Figure 3. Photo-induced manipulation of glass rods on a PEG film doped EMAB (7.5 × 10−5 mmol/mg in PEG) and optical micrographs of glass rods on the PEG film. (I) were exposed to UV light ($\lambda = 375$ nm; light intensity = 128 mW/cm2); (II) were exposed to visible light ($\lambda = 488$ nm; light intensity = 130 mW/cm2). The time-bar marked on the pictures is the irradiation time.

the original position (Fig. 3-I-a). The time of travelling away and towards the irradiation area was almost the same.

As can be seen from Fig. 2, there was no absorption peaks found at around 375 nm in DR1-methanol solution, thus the UV light irradiation was not carried out to study the manipulation of micro-objects on DR1-doped PEG films. Rapping trajectories of micro-objects on DR1-doped PEG films upon Ar$^+$ laser ($\lambda = 488$ nm; light power = 40 mW) were presented in Fig. 4. During the irradiation, the glass rods moved to the interface between the irradiation and un-irradiation area.

In this case with DR1, the glass rods moved toward the Vis-light-irradiated area, whose motion was of opposite direction, compared with the case of the EMAB-doped PEG film. However, the motion behaviour of glass rods on the PEG film with DR1 is similar to that on LC films with DR1 [13].

Figure 4. Photo-induced manipulation of glass rods on a PEG film doped DR1 (7.5 × 10−5 mmol/mg in PEG). The time-bar marked on the pictures is the irradiation time. The circle in fine imaginary line is the irradiation area; the circle in bold imaginary line is the position of glass rods.

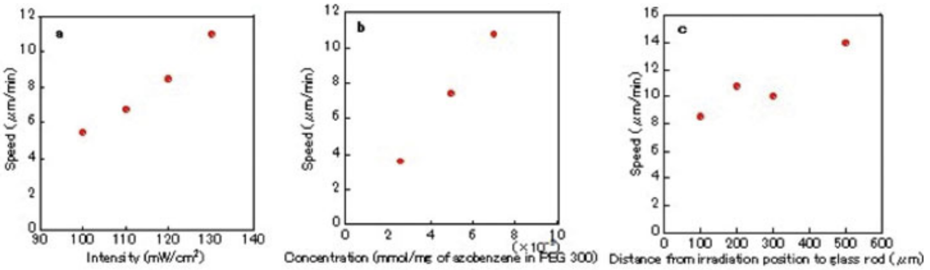


Figure 5. Effect factors on travelling speed. (a) Effect of intensity on travelling speed, where C = 7.5 × 10−5 mmol/mg, D = 200 μm; (b) effect of concentration on travelling speed, where I = 128 mW/cm2, D = 200μm; (c) effect of distance on travelling speed, where I = 128 mW/cm^2, C = 7.5 × 10−5 mmol/mg.

3.3. Effective Factors on Travelling Speed

To verify the effect of various factors: light intensity (*I*), the concentration (*C*) of azobenzene compound in PEG, and the distance between the irradiation position and the micro-objects (*D*), the travelling speed (*v*) was evaluated for the PEG film with EMAB under different conditions upon UV light. As can be seen in Fig. 5, the travelling speed increased with the increase of the light intensity and the concentration of EMAB in PEG, while there was no clear relationship between the *v* and *D*. Especially, we found linear relationship between the *v* and *C* according to the data measured in Fig. 5 (b). The regression to zero of *C* (in eq. 1) indicates that azobenzene compounds are necessary to manipulate the micro-objects.

$$v = 1.4714C \ (\mathrm{R}^2 = 0.9992) \tag{1}$$

where R is linearly dependent coefficient. In addition, in case of the condition for C = 7.5 × 10^{-5} mmol/mg and *D* = 200 μm at 40 mW, the *v* was 34 μm/min on the DR1-doped film. This *v* value was higher than that, 11μm/min, on the EMAB-doped PEG film. It is suggested that the DR1-doped PEG film could be more effective for the travelling speed of micro-objects compared to the EMAB-doped PEG film by light irradiation. The photoisomerization of push-pull-substituted DR1 could be much faster than that of EMAB [19]. Therefore, the relatively stronger force would be induced from the photoisomerization, which lead to relatively higher travelling speed of glass rods on the DR1-doped film. The potential of the photo-manipulation considerably depends on the photo-responsive nature of each azobenzene derivative.

The above-mentioned motion behaviour on the PEG film is similar to that on LC films in our previous work [13]. We already suggested that disordered behaviours of well-ordered LC molecules affected the motion of micro-objects. However, the PEG films could not have the ordered molecular structure. Although those mechanisms are unclear, it is considered that a gradient in surface tension between irradiated and non-irradiated area would generate and cause liquid flow like Marangoni flow [17].

4. Conclusions

The motion of micro-objects on PEG films was caused due to photo-responsivity of azobenzene molecules under UV or visible light irradiation. The motion was affected by three factors: light intensity, the concentration of azobenzene compound and the distance between the irradiation position and the micro-objects. Moreover, DR1 (push-pull type azobenzene)-doped PEG film was more effective for the travelling speed of glass rods compared to the EMAB (non-push-pull type azobenzene)-doped PEG film upon the external stimulus. We succeeded in potential photo-manipulation of micrometer-sized objects by using azobenzene derivatives including PEG film which is a widely-useful, biocompatible and low-hazardous polymer.

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