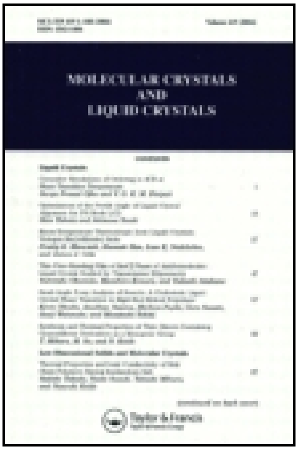

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Preparation of (Gold-Nanorod and Azo-Functionalized Polymer) Composite Films and Their Photochemical Properties

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Preparation of (Gold-Nanorod and Azo-Functionalized Polymer) Composite Films and Their Photochemical Properties

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Nano-composite films were prepared by mixing gold-nanorod (Au-nanorod) and azo-functionalized polymer in toluene, and following spin coating on a glass substrate. The compopsites films showed absorption bands around 520 and 1000 nm corresponding to the short and long axes of the Au-nanorod. Reversible change in absorbance at 1000 nm was achieved by photoalignment of molecular orientation of azo-chromophores.

Keywords: Au-nanorod; azobenzene; liquid crystal

INTRODUCTION

Much effort has been focused on synthesis of size- and shape-controlled nanoparticles, and formation of regular assemblies of the nanoparticles for applications in the fields of electronic and optical devices [1–3]. Because, the physical properties of the assemblies strongly depend on the size of nanoparticles, distance between nanoparticles, dimension of the assemblies. Recently, a few studies on the optical control and patterning of gold-nanorod (Au-nanorod) by compositing with poly(vinyl alcohol), and successive stretching and irradiation of pulsed laser were reported [4,5]. However, the patterning was irreversible because of the thermal deformation of the molecular shape of the

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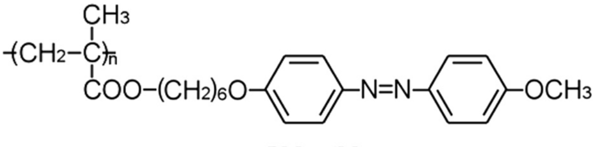
gold-nanorod. On the other hand, azobenzene dyes are well known to show photoalignment property by irradiation of polarized light [6]. In this article, we investigated the reversible control of the molecular orientation of the Au-nanorod by means of the photo-alignment effect of azobenzene groups.

EXPERIMENTAL

Azo-functionalized polymer, **PMAz6Mc**, was synthesized by conventional radical polymerization, and atom transfer radical polymerization (ATRP) in order to control the molecular weight of the polymers (Fig. 1). Radical polymerization of the methacrylate monomer having azobenzene group, **MAz6Mc**, was carried out by using 2,2′-azobisisobutyronitrile (AIBN) as a radical initiator in dimethylformamide (DMF) for 24 h at 50°C. After polymerization, the resulting polymeric material was purified by re-precipitation with tetrahydrofuran (THF) and MeOH several times. In addition, the polymer was also prepared by ATRP method as follows [7]. **MAz6Mc** was polymerized using CuCl complex with 1,1,4,7,10,10-hexamethyltriethylenetetramine as the catalyst, and ethyl-2-bromomethylpropionate as the initiator in anisole at 110°C for 24 h. After polymerization, the catalyst was removed from the sample by passing the sample through a column of activated basic alumina, and purification was performed by re-precipitation with THF/MeOH.

Au-nanorod was supplied from Mitsubishi Materials Co., and its short and longitudinal lengths were in ranges of 7–8 and 35–40 nm, respectively. Nano-composite films were prepared by mixing Au-nanorod and **PMAz6Mc** in toluene, and following spin coating



PMAz6Mc

sample	Mn	Mw	Mw/Mn	thermal property
1	28,000	64,000	2.30	G (52°C) S (89°C) N (130°C) I
2	7,500	9,000	1.20	G (48°C) S (77°C) N (120°C) I

FIGURE 1 Structure and properties of PMAz6MC. Sample 1 was prepared by using AIBN as an initiator. Sample 2 was prepared by ATRP method. Molecular weight was determined by GPC. Thermal property was investigated by DSC and POM observation.

the toluene solution on a glass substrate. In addition, a low molecular weight liquid crystal, **E44**, was added to the mixture of Au-nanorod and **PMAz6Mc**, and solid film from the mixture containing **E44** was also prepared by spin coating method on a glass substrate. **E44** was purchased from Merck Co. Absorption spectra were measured before and after irradiation of polarized UV light and non-polarized visible light.

RESULTS AND DISCUSSION

PMAz6Mc with two different molecular weights were used in this study. The molecular weights, Mn/Mw, of the polymers were 28,000/64,000 and 7500/9000, respectively. The polymers showed smectic phase and nametic phase as shown in Figure 1.

Figure 2 shows changes in absorption spectra of **PMAz6Mc** in THF by UV and visible light irradiation. Before UV irradiation, there were two absorption bands: an intense absorption band around 350 nm corresponding to π-π^* transition, and a weak band around 450 nm corresponding to n-π^* transition. The UV irradiation caused a decrease and an increase in the absorbance at 350 and 450 nm respectively, indicating photoisomerization from trans-form to cis-form. On the other hand, the reverse photoisomerization from the cis-form to the trans-form was caused by visible light irradiation as shown in Figure 2(b). The changes in spectra shown in Figure 2 indicate clearly that that the reversible trans-cis photoisomerization can be brought about by irradiation of UV and visible light.

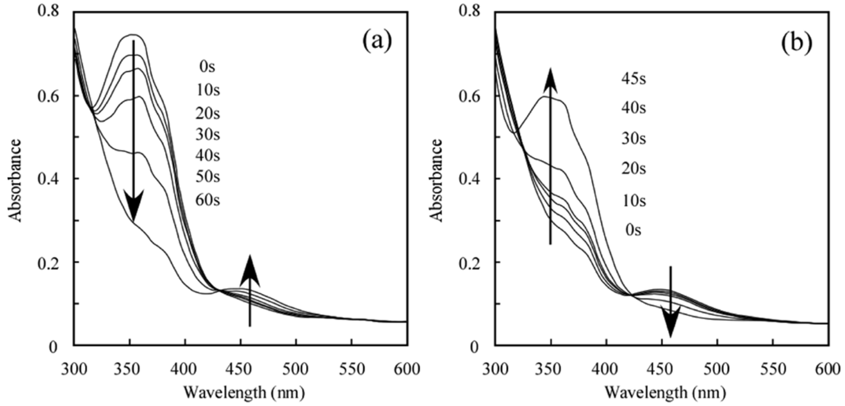


FIGURE 2 Changes in absorption spectra of the **PMAz6Mc** solid film by UV (a) and visible light (b) irradiation. Powers of the UV and visible light are 277 mW/cm^2 and 198 mW/cm^2.

Prior to explore the photochemical control the orientation of Au-nanorod in a polymeric matrix, photochemical molecular orientation of the azo-chromophores in **PMAz6Mc** was investigated by alternative irradiation of polarized UV light and non-polarized visible light. Figure 3 shows the change in polarized absorption spectra of **PMAz6Mc** solid film by the alternative irradiation. No change in the spectra with polarizer perpendicular and parallel to the polarization direction of the UV light was observed before irradiation, because of the random orientation of the azo-chromophores in the solid state. The intensities of the absorption bands with polarizer perpendicular and parallel increased and decreased respectively by successive polarized UV and non-polarized visible light irradiation. The change in the polarized absorption spectra is arose from the molecular orientation of azo-chromophores, and indicates that the direction of the molecular orientation of the azo-chromores is perpendicular to the polarization direction of the UV light [4].

Composite materials were prepared by mixing **PMAz6Mc** (Mn:28,000) and Au-nanorod in toluene, and spin coating the toluene

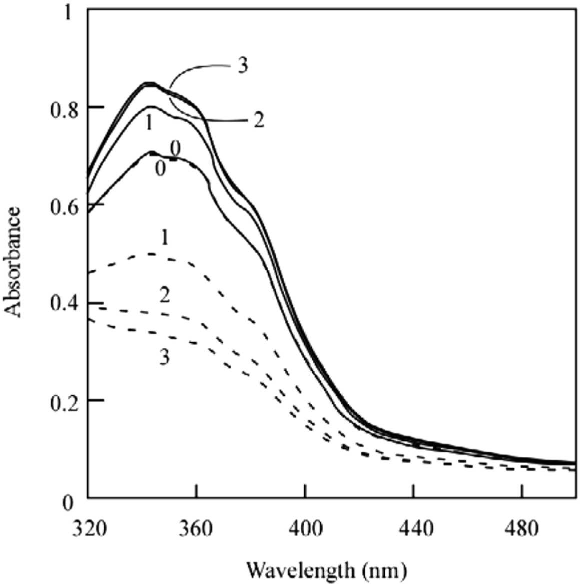


FIGURE 3 Change in polarized absorption spectra of PMAz6Mc film by successive irradiation of polarized UV light and non-polarized visible light. (——) and (- - - -) were measured with polarizer perpendicular and parallel to the polarization of the UV light, respectively. The number (0,1,2,3) indicates the successive irradiation times of both UV and visible light.

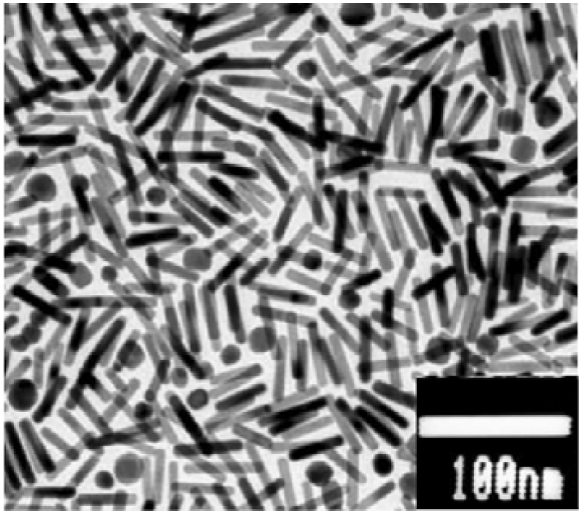


FIGURE 4 TEM image of Au-nanorod used in this study.

solution on a glass substrate. The concentration of **PMAz6Mc** and Au-nanorod dissolved in toluene were 2 and 0.5 wt%, respectively. The short and longitudinal lengths of the Au-nanorod used were respectively in ranges of 7–8 and 35–40 nm as can be seen in Figure 4. Figure 5 shows visible-NIR spectrum of the composite film (solid line). Two weak peaks around 520 and 1000 nm were observed additional to the peak around 350 nm corresponding to π-π^* transition of **PMAz6Mc**. These peaks are corresponding to short and longitudinal surface plasmon of Au-nanorod [4,5].

In Figure 5, the change in the polarized absorption spectra of the composite film by alternative irradiation of polarized UV light and non-polarized visible light was also shown. The irradiation caused the change in the polarized absorption spectra in a range from 350 nm to 400 nm, indicating the formation of anisotropic molecular orientation of azo-chromophores. On the other hand, no change was observed in a wavelength region longer than 500 nm. The size of the azo-chromophore is much smaller than the Au-nanorod, because the longitudinal molecular length of the azo-chromophore is about 3 nm (ca. 27 Å) estimated by MO calculation. Therefore, the driving force of the azo-chromophores to affect the orientation of the Au-nanorod may be small. So, we investigated the photochemical change in the orientation of the Au-nanorod in a composite film having lower concentration of the Au-nanorod. Figure 6(a) shows the change in the polarized absorption spectra of the composite film prepared from the

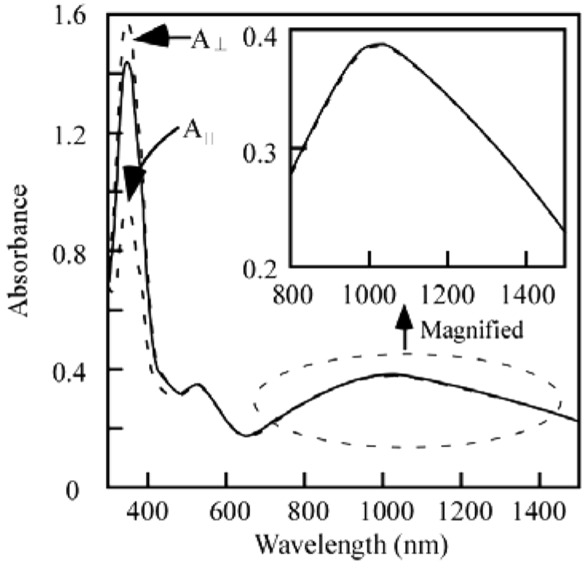


FIGURE 5 Vis-NIR spectra of a composite film of **PMAz6Mc** and Au-nanorod (80:20 in wt%). The composite film was prepared by casting toluene solution containing 2 wt% of **PMAz6Mc** and 0.5 wt% of Au-nanorod on a glass substrate.

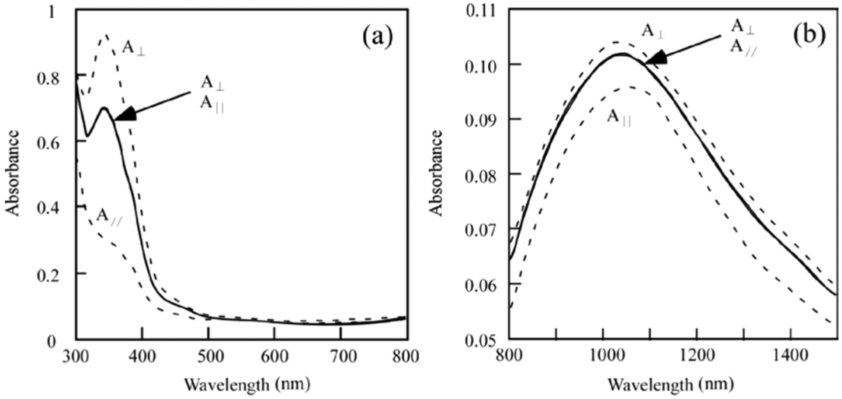


FIGURE 6 Changes in Vis and NIR spectra of the composite film of **PMAz6Mc** and Au-nanorod by irradiation of polarized UV and and non-polarized visible light three times. This composite film was prepared by casting toluene solution containing of 2 wt% of **PMAz6Mc** and 0.065 wt% of Au-nanorod on a glass substrate.

toluene solution containing 2 w% of **PMAz6Mc** (Mn:28,000) and 0.065 wt% of Au-nanorod by alternative irradiation of the polarized UV light and non-polarized visible light three times. Contrary to the former composite film, absorption bands with polarizer perpendicular ($A_{\perp}$) and paralle ($A_{\|}$) in a range from 800 nm to 1500 nm were increased and decreased respectively by the alternative irradiation. The absorption band in this region is corresponding to the longitudinal surface plasmon of Au-nanorod. This change in the polarized absorbance in this wavelength region indicate the the Au-nanorod align perpendicular direction to the polarization direction of the UV light. In addition, irradiation of circularly polarized UV light recovered the initial polarized absoption spectra. Namely, no change in the spectra was observed again after irradiation of the circularly polarized UV light. This implies that the reversible control of the orientation of the Au-nanorod in the composite film could be achieved photochemically. The orientation direction of Au-nanorod is parallel to the molecular orientation of the azo-chromophores. In order to clarify the influence of the molecular orientation of the azo-chromophores on the photochemical orientation of the Au-nanorod, the change in dichroic ratio (**DR**) of both the azo-chromophores and Au-nanorod were estimated according to the following equation.

$$\mathbf{DR} = \frac{(A_{\perp} - A_{\|})}{(A_{\perp} + 2A_{\|})}$$

Where, $A_{\perp}$ and $A_{\|}$ are absorbances with polarizer perpendicular and parallel to the polarization direction of polarized UV light. **DR** of both the azo-chromophores and the Au-nanorod were found to increase by alternative irradiation of polarized UV light and non-polarized visible light as shown in Figure 7. However, the change in **DR** of the Au-nanorod is much smaller than that of the azo-chromophores.

It is assumed that the photochemical orientation of the Au-nanorod is influenced by mobility or fluidity of the polymeric matrix. Because, the size of the Au-nanorod is much larger compared to that of the azo-chromophore. Consequently, change in the orientational order of the Au-nanorod forces the flux of the polymeric materials in the composite film. Thus, the effects of the molecular weight of **PMAz6Mc** and additive of low molecular weight LC, **E44**, to **PMAz6Mc** on the photochemical orientation of the Au-nanorod was explore by monitoring change in **DR**. **DR** of the Au-nanorod in the composite film containing **PMAz6Mc** with lower molecular weight is higher than that of the composite film containing **PMAz6Mc** with higher molecular weight as can be seen in Figure 8(a) up to the **E44** content of 10 wt%. In

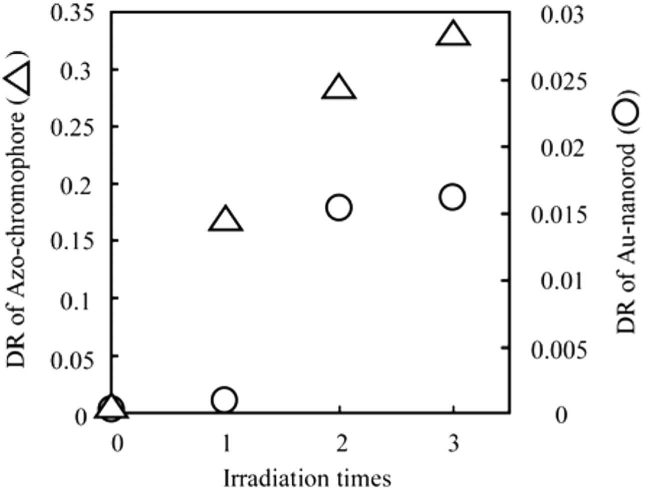


FIGURE 7 Changes in dichroic ratio of azo-chromophores and Au-nanorod of the composite film of **PMAz6Mc** having Mn of 28,000 and Au-nanorod by irradiation of alternative polarized UV light and visible light. The composite film was prepared by casting toluene solution containing of 2 wt% of **PMAz6Mc** and 0.065 wt% of Au-nanorod.

addition, **DR** of the Au-nanorod was increased with increasing the content of **E44** as shown in Figure 8(b). These results indicate that the mobility and fluidity of the composite films is one of important factors influencing the photochemical orientation of the Au-nanorod. However, the composite film containing **E44** of 20 wt% showed much

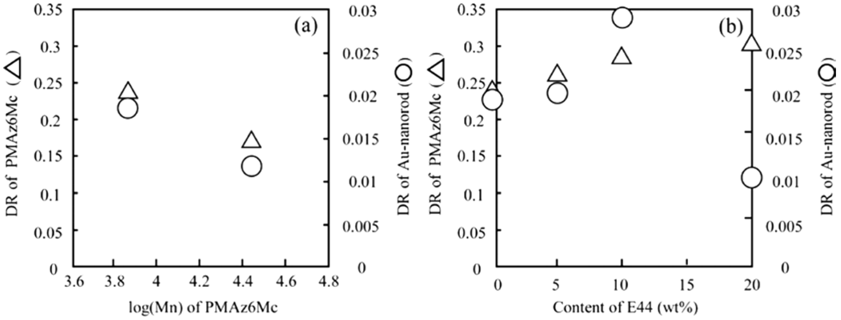


FIGURE 8 Effects of molecular weight of **PMAz6Mc** and addition of **E44** on the change in **DR**. **DR** after the alternative irradiation of polarized UV light and non-polarized visible light three times.

smaller **DR** compared with the composite films containing **E44** lower than 20 wt%. The composite film containing higher than 20 wt% of **E44** is too fluid to force the molecular orientation of the Au-nanorod dispersed in the film.

CONCLUSIONS

Composite films of azo-functionalized polymer and Au-nanorod were prepared and their photochemical properties were investigated. The composite films showed absorption bands around 520 and 1000 nm corresponding to short and longitudinal surface plasmon of Au-nanorod. The change in the orientational direction of the Au-nanorod was investigated by measuring polarized absorption spectra with/without alternative irradiation of polarized UV light and non-polarized visible light. **DR**s as measure of orientational order for the azo-chromophores were around 0.3, while **DR**s of the Au-nanorod were in a range from 0.01 to 0.03. The orientational order of the Au-nanorod was found to depend on the fluidity of the composite films. Although the orientation of the Au-nanorod could be achieved by the alternative irradiation, the order of the orientation was not high.

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