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Synthesis of photo-switchable 3-FcAB-modified polymer particles †‡

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3-Ferrocenylazobenzene (**3-FcAB**)-containing polymers were prepared using solution polymerization and emulsion polymerization. **Polymer A**, prepared by solution polymerization followed by re-precipitation, and **Polymer B**, prepared by emulsion polymerization, had spherical shapes with the outer diameters of *ca*. 300 nm and *ca*. 20 nm, respectively. Both the polymers responded to green light, UV light, and blue light in solution like monomeric **3-FcAB** and its derivatives. In the solid state, **Polymer A** exhibited both isomerization and re-orientation behaviors upon light irradiation, indicating a possibility to achieve a light-induced shape change by the re-orientation of the chromophore. On the other hand, **Polymer B** underwent simple photoisomerization behaviors, which is more preferable for developing a switching system using spectroscopic detection of the isomerization behaviors of nano-dots.

Introduction

Photochromic molecules have been intensely studied because their physical properties can easily be switched by light.¹ Integrations of these molecules have attracted much attention because of their potential application to photo-switchable molecular devices.² Azobenzene is one of the most popular photo-switchable molecules and its assemblies have been extensively investigated. Assemblies of azobenzene derivatives such as polymers,³ monolayers,⁴ and colloids⁵ have especially attracted much attention because they can achieve immobilization and high-density of the switching units.

We have reported that 3-ferrocenylazobenzene (**3-FcAB**) exhibits a redox-conjugated reversible photoisomerization in solution⁶ and on the surface of an electrode.⁷ As shown in Scheme 1, the excitation of the metal-to-ligand charge transfer (MLCT) band with 546 nm green light causes the *trans*-to-*cis* isomerization of **3-FcAB** in the reduced Fe(II) state in addition to the normal UV and blue light response (*trans*-to-*cis* isomerization by excitation of the azo π - π * band with 365 nm UV light, and the reverse *cis*-to-*trans* isomerization by excitation of the *cis*-azo n- π * band with 436 nm blue light). Once **3-FcAB** is oxidized to **3-FcAB**⁺ in the Fe(III) state, the MLCT band disappears and the *cis*-to-*trans* reverse isomerization occurs by excitation of the *cis*-azo n- π * band with the same 546 nm light. By using this feature, this compound can



Scheme 1 Redox-coupled photoisomerization of 3-ferrocenylazobenzene.

be controlled reversibly by a single green light coupled with the redox reaction between Fe(II) and Fe(III). Assemblies of this compound therefore have a possibility to achieve photo-switching without dual light sources, and this simpler photoswitch will be advantageous for construction of small size devices. The aim of this study is to introduce 3-FcAB in acrylic polymers for the purpose of integrating the functional molecule and to examine the photo-responses of the 3-FcAB-containing polymers. We have attempted two types of polymerization, one is solution polymerization and the other is emulsion polymerization,⁸ and the polymers thus obtained are Polymer A and Polymer B, respectively. Both methods afforded spherical polymer shapes but their sizes were different. We discuss the differences of the structures and characteristics of the polymers depending on the preparation methods.

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Results and discussion

Synthesis and characterization

There are many polymerization types, *i.e.*, solution polymerization, liquid phase bulk polymerization, gas phase polymerization, solid phase polymerization, suspension polymerization, and emulsion polymerization. To create size-controlled discrete polymer particles, solution polymerization and emulsion polymerization were chosen in this study.

First, we attempted solution polymerization and emulsion polymerization of 3-ferrocenyl-4'-acryloylmethoxyazobenzene, but only trace amounts of polymer were obtained. This failure can be ascribed to the involvement of the ferrocene moiety, which works as a radical scavenger.9 The polymers containing 3-FcAB were, therefore, prepared by the modification of the bromide substituted polymer compounds (Scheme 2). The solution polymerization reaction of 2-bromoethyl acrylate was carried out both in toluene and in cyclohexane. Polymerization proceeds in both solvents almost quantitatively. In the emulsion polymerization process, sodium dodecyl sulfate (SDS) was used as an emulsifier and the monomer was well dispersed in water as a stable monomer micelle, so that the mixture of the monomer and SDS in water was transparent. Because of the relatively small diameter of the formed polymer (ca. 20 nm, vide infra), the surface energy might be low enough to emulsify a large part of the monomer and the polymerization reaction was like microemulsion polymerization. The generated polymer was hardly soluble in organic solvents (~ 0.1 g per 100 mL in chloroform, THF, or toluene) and almost insoluble in methanol because of its high degree of polymerization. The surfactant must be totally removed because the existence of amphiphilic molecules disturbs the ether synthesis at the next 3-FcABmodification reaction. As the surfactant could not be removed by reprecipitation by chloroform-methanol, the polymer was washed vigorously with water and methanol. The polymer became further insoluble on removing the surfactant by washing with water.

Modification of poly(2-bromoethyl acrylate) formed by solution polymerization was performed by addition of sodium

tert-butoxide and 3-ferrocenyl-4'-hydroxymethylazobenzene to give **Polymer A**. As for modification of poly(2-bromoethyl acrylate) formed by emulsion polymerization with **3-FcAB**, the reaction was carried out in suspension to give **Polymer B**. The modification reactions occurred only at the outer sphere since the solubility decreased rapidly as the reactions proceeded. 3-Ferrocenyl-4'-((2-(acryloyloxy)ethoxy)methyl)azobenzene (**Monomer**) was prepared as a reference.

IR spectra of **3-FcAB**, **Monomer**, **Polymer A**, and **Polymer B** are similar to each other, containing a peak around 1600 cm^{-1} attributable to the azo N=N stretching. A peak around 1700 cm^{-1} ascribed to the C=O stretching of the carboxyl group or the ester group in **Monomer** was slightly shifted in higher wavenumbers in the polymers because the conjugation of C=O with the double bond is lost by polymerization (Fig. S1, ESI‡). In the spectrum of **Polymer B**, the intense absorption at 1227 cm⁻¹ due to sodium dodecyl sulfate (SDS) was not observed, indicating that the amount of residual SDS was very small.

The ¹H NMR spectrum of poly(2-bromoethyl acrylate) exhibits broadening of all peaks typical to polymers with short relaxation times (Fig. S2, ESI \ddagger). On the other hand, the peaks in the spectrum of **Polymer A** are broad but the peaks of the ferrocene part are relatively sharp (Fig. S2, ESI \ddagger). This is probably because the mobility of each part of the polymer is different and the **3-FcAB** part, as a side chain of the polymer, can move freely. The exchange ratio in the **3-FcAB**-modification reaction was estimated to be *ca.* 20% for **Polymer A** from the signal integration of the ¹H NMR spectrum.

For scanning electron microscope (SEM) analysis, **Polymer A** was reprecipitated from a THF solution with an equal volume of water¹⁰ and the resulting suspension was dropped on gold-deposited mica (Au/mica), and **Polymer B** in a 1,4-dioxane solution was dropped on Au/mica. Both polymers are composed of spherical particles and the outside diameters were *ca*. 300 nm for **Polymer A** and *ca*. 20 nm for **Polymer B** as shown in Fig. 1. The diameter of **Polymer A** particles was poly-dispersed as shown in Fig. S3 (ESI[‡]), where larger particles might be generated by the aggregation of polymer



Scheme 2 Synthesis of Polymer A, Polymer B and Monomer.



Fig. 1 SEM images of the re-precipitated Polymer A on Au/mica (A) and Polymer B on Au/mica (B).

particles at the stage of solvent evaporation. On the other hand, the particles of **Polymer B** were mono-dispersed as shown in Fig. 1B. From this result, polymer particles prepared



Fig. 2 Scaled UV-vis absorption spectra of Polymer A (solid line), Polymer B (dotted line) and Monomer (dash-dotted line) in 1,4-dioxane.

by emulsion polymerization were rigid enough to be unchanged in their shapes and sizes in the sample preparation process.

Photoisomerization behaviors in solution

UV-vis absorption spectra of Monomer, Polymer A, and Polymer B are shown in Fig. 2. The exchange ratio of Polymer B in the 3-FcAB-modification reaction was estimated at *ca*. 50% from the absorbance of the spectrum assuming a molar extinction coefficient of 2×10^4 M⁻¹ cm⁻¹, which is a regular value for azobenzene derivatives. The λ_{max} value of the π - π * band is not shifted for Polymer A, whereas it is shifted to the longer wavelength by 5 nm for Polymer B, suggesting that the azobenzene chromophores are buried in the polymer and experience a more polarizable environment than dioxane.

The photoisomerization behavior of **Polymer A** and **Polymer B** in 1,4-dioxane were observed by UV-vis spectroscopy and the results are shown in Fig. 3. The photoisomerization behaviors are summarized in Table 1. They show photo-responses with three different wavelength lights at 365, 436 and 546 nm, similar to **3-FcAB** and its derivatives. The smaller amount of the generated *cis* molar ratio by 546 nm

 Table 1
 Summary of the electronic spectral changes and isomerization behaviors of 3-FcAB in polymers

				%cis molar ratio	
Sample	π – π */nm	MLCT/nm	%MLCT	UV	Green
(Polymer A)					
1,4-Dioxane	326	440	8	59	15
Solid ^b	344	450	20	10	5
(Polymer B)					
1.4-Dioxane ^a	330	436	9	54	17
Chloroform ^a	325	441	18	10	9
Solid ^b	339	450	15	12	5

^{*a*} Polymer was dissolved by ultrasonication. ^{*b*} A 1,4-dioxane solution was cast on a glass plate.



Fig. 3 UV-vis absorption spectra of **Polymer A** (A) and **Polymer B** (B) in 1,4-dioxane (orange line) and its 546 nm (green line), 365 nm (purple line), and 436 nm (blue line) photo-irradiated spectra. Inset: differences in the UV-vis absorption spectra between before and after 546 nm (green line), 365 nm (purple line), and 436 nm (blue line) irradiation.

green light irradiation of **Polymer A** (15%) and **Polymer B** (17%) compared with **3-FcAB** (35%) can be interpreted to be because of the substituent effect,^{6b} because the absorption at 546 nm is weaker. The rate constant of thermal *cis*-to-*trans* isomerization of **Polymer B** at 20 °C was $3(1) \times 10^{-5} \text{ s}^{-1}$, which is comparable to that of **3-FcAB** (5(1) $\times 10^{-5} \text{ s}^{-1}$).

To achieve the reversible isomerization controlled by single green light, the stability and light-response of the *cis*isomer in the ferrocenium state are very important. The isomerization behaviors of **Polymer A** and **Polymer B** in the oxidized state were examined by the UV-vis spectral measurements. At first, **Polymer A** and **Polymer B** in dichloromethane were irradiated by 546 nm green light to generate their *cis*isomers. From the UV-vis spectra of these solutions, the ratios of the photogenerated *cis*-isomers were estimated to be 20% for **Polymer A** and 11% for **Polymer B**. After the light irradiation, 10 eq. of iodine were added to the solution to oxidize the polymers from ferrocene to ferrocenium. The oxidized *cis*-isomer was stable in the dark (the rate constants of thermal *cis*-to-*trans* isomerization of **Polymer A** and **Polymer B** at 20 °C in the oxidized states were

 $3.3(5) \times 10^{-5} \text{ s}^{-1}$ and $5(1) \times 10^{-5} \text{ s}^{-1}$, respectively). The solutions of the oxidized polymers were placed in the dark and were irradiated by 546 nm light. The UV-vis absorption spectra and their time-course change in the dark and upon 546 nm light irradiation are shown in Fig. 4. The azo $\pi - \pi^*$ band of the polymers in the trans-form appeared at 326 nm and 350 nm for Polymer A and Polymer B, respectively, whereas λ_{max} of the band of the oxidized monomer in the trans-form was observed at 312 nm.† The large shift of the azo $\pi - \pi^*$ band in **Polymer B** is supposed to be induced by the aggregation of the 3-FcAB part in the polymer by the hydrophilic effect like an inverse micelle, because the ferrocene part was ionized and became hydrophilic by oxidation. From the spectral changes, it is suggested that the oxidized cisisomer in the polymers was converted to the trans-isomer with green light. The amount of increase of the absorbance at the azo $\pi - \pi^*$ band was about the same as that of decrease in their reduced state. This fact suggests that the cis-isomers generated by the green-light irradiation in their reduced states were totally converted to the trans-isomers by the irradiation of green light.



Fig. 4 UV-vis absorption spectra of **Polymer A** (A) and **Polymer B** (C) oxidized with 10 eq. of iodine in dichloromethane followed by 546 nm irradiation, where absorption of iodine was subtracted, and the corresponding time course change in absorbance at 350 nm (B and D, respectively), where \bullet and \bigcirc indicate before and after starting 546 nm light irradiation. Inset of A and C: differences in the UV-vis absorption spectra between before and after 546 nm light irradiation.

Photoisomerization behaviors in the solid state

The photoisomerization behaviors of **Polymer A** and **Polymer B** in the solid state were also examined. Samples were deposited on Au/mica, SEM images of which show spherical particles with the outside diameter of *ca*. 300 nm for **Polymer A** and *ca*. 20 nm for **Polymer B** (*vide supra*, Fig. 1). In the UV-vis absorption spectra of **Polymer A** and **Polymer B**, the π - π * band was 14 nm and 19 nm shifted to a longer wavelength, respectively (Fig. 5). The shifts are ascribed to the formation of J-aggregates of **3-FcAB** in the polymers.

Photoirradiation caused spectral changes, which indicate that the polymers underwent photo-response against UV, green and blue light, although the cis molar ratios with UV and green light were decreased because of the J-aggregation of the chromophores (Fig. 5). The photoisomerization behaviors of these polymers are different. As shown in Fig. 5A, the π - π * band of **Polymer A** was not simply decreased with light irradiation. The spectral changes of the π - π * band can be deconvoluted to two components. One component is a simple decrease of the original $\pi - \pi^*$ band of the *trans*-isomer. The other is a generation of the new $\pi - \pi^*$ band of the *trans*-isomer at a shorter wavelength region. The latter can be ascribed as a generation of H-aggregated chromophores. Therefore, these spectral changes suggest that the aggregation state of the polymer was changed by light irradiation. The driving force of these changes might be a re-orientation of the chromophores by a continuous shape change caused by light irradiation. On the other hand, the spectral changes of **Polymer B** can be interpreted as simple trans-to-cis and cis-to-trans isomerization behaviors. These results suggest that the orientation of the chromophore in **Polymer B** was not affected by light irradiation because of its rigid structure. From these isomerization behaviors, it can be concluded that Polymer A has a possibility to detect the isomerization behavior by the re-orientation of the chromophores in the solid state, and

Polymer B is more preferable for a spectroscopic detection of the isomerization behaviors.

Conclusions

3-FcAB was introduced to the polymers prepared by solution polymerization and emulsion polymerization, and the prepared polymer particles with the outer diameters of *ca*. 300 nm and *ca*. 20 nm, respectively, were isomerized by UV, blue, and green light both in solution and in solid state. Moreover, the polymers can be controlled by the green-light-response and by the redox reaction of their ferrocene parts (Scheme 3). Therefore, it is concluded that these polymer particles are possible candidates to act as nano-sized photo-memories or switches.

Experimental

General

Ultra pure water was generated from a water purification system (Yamato, Autopure WD500). Solvents and reagents were used as received from the commercial sources, and otherwise noted. 2-Bromoethyl acrylate¹¹ and 3-ferrocenyl-4'-hydroxymethylazobenzene⁷ were prepared according to the literature. All the reactions in this section were done under a nitrogen atmosphere.

Synthesis

3-Ferrocenyl-4'-acryloylmethoxyazobenzene. 3-Ferrocenyl-4'-hydroxymethyl-azobenzene (0.603 g, 1.52 mmol) and triethylamine (1 mL, 0.73 g, 3.6 mmol) were dissolved in 20 mL of dehydrated dichloromethane under an argon atmosphere. Acryloyl chloride (1 mL, 1.12 g, 12.4 mmol) was added dropwise to the solution at 0 °C. The resulting mixture was stirred for 2 h at room temperature. 50 mL of 3% HCl-water was added and the organic layer was collected and



Fig. 5 UV-vis absorption spectra of **Polymer A** (A) and **Polymer B** (B) in the solid state (orange line) and their changes with 546 nm (green line), 365 nm (purple line), and 436 nm (blue line) light irradiation. Inset: differences in the UV-vis absorption spectra between before irradiation and after 546 nm (green line), 365 nm (purple line), and 436 nm (blue line) light irradiation.



Scheme 3 Photochromic behaviors of Polymer A and Polymer B

dried with sodium sulfate. After removing the solvent, orange oil was purified by silica-gel column chromatography with chloroform-hexane (from 1:9 v/v to 1:1 v/v) as eluent and the second fraction was collected. Needle crystals were obtained by recrystallization with methanol-hexane at -30 °C. Yield: 0.620 g (0.138 mmol, 90.6%). ¹H NMR for 3-ferrocenyl-4'-acryloylmethoxyazobenzene (400 MHz, CDCl₃) δ (ppm) 8.01 (s, 1H, C₆H₄), 7.94 (d, J = 8.2 Hz, 2H, C₆H₄), 7.73 (d, J = 7.8 Hz, 1H, C₆H₄), 7.58 (d, J = 7.8 Hz, 1H, C₆H₄), 7.52 (d, J = 8.2 Hz, 2H, C₆H₄), 7.42 (dd, J = 7.8 Hz, 7.8 Hz, 1H, C₆H₄), 5.99 (m, 1H, =CH₂), 5.35 (d, J = 17.0 Hz, 1H, =CH), 5.25 (d, J = 10.5 Hz, 1H, =CH₂), 4.77 (s, 2H, C₅H₄), 4.62 (s, 2H, CH₂), 4.38 (s, 2H, C₅H₄), 4.09 (s, 5H, C₅H₅).

3-Ferrocenyl-4'-((2-(acryloyloxy)ethoxy)methyl)azobenzene.

3-Ferrocenyl-4'-hydroxymethylazobenzene (1.057 g, 2.67 mmol) was dissolved in 20 mL of dehydrated tetrahydrofuran under an argon atmosphere. To this orange solution, sodium tert-butoxide (0.294 mg, 2.62 mmol) was added and the color of the solution immediately changed to dark brown. 2-Bromoethyl acrylate (0.873 g, 4.88 mmol) was added to the solution, and the mixture was stirred for 22 h. Water (20 mL) was added and the organic layer was collected and dried with anhydrous sodium sulfate. After removing the solvent, orange oil was purified by silica-gel column chromatography with chloroform-hexane (3:1) as eluent and the second fraction was collected. Yield: 0.537 g (1.08 mmol, 40.5%). ¹H NMR for 3-ferrocenyl-4'-((2-(acryloyloxy)ethoxy)methyl)azobenzene (400 MHz, CDCl₃) δ (ppm) 8.02 (t, $J = 1.8, 1H, C_6H_4$), 7.95 $(d, J = 8.4 Hz, 2H, C_6H_4), 7.73 (d, J = 7.8 Hz, 1H, C_6H_4),$ 7.60 (d, J = 7.8 Hz, 1H, C₆H₄), 7.54 (d, J = 8.4 Hz, 2H, C_6H_4), 7.43 (dd, J = 7.8 Hz, 7.8 Hz, 1H, C_6H_4), 6.49 (dd, J =17.2 Hz, 1.2 Hz, 1H, =CH), 6.21 (dd, J = 17.2 Hz, 10.4 Hz, 1H, ==CH₂), 5.89 (dd, J = 10.4 Hz, 1.2 Hz, 1H, ==CH₂), 5.29 $(s, 2H, CH_2), 4.75 (s, 2H, C_5H_4), 4.47 (t, J = 6.0, 2H, O-CH_2),$

4.37 (s, 2H, C₅H₄), 4.07 (s, 5H, C₅H₅), 3.55 (t, J = 6.0, 2H, O–CH₂).

Polymerization of 2-bromoethyl acrylate in solution

2-Bromoethyl acrylate (1.74 g, 9.72 mmol) was dissolved in toluene (10 mL, HPLC grade, KANTO CHEMICAL Co. Inc.) and the solution was degassed with nitrogen for 15 min. 2,2'-Azobisisobutyronitrile (0.027 g, 0.16 mmol) was added to the solution and the solution was stirred for 22 h at 60 °C. The solution was then cooled by water and hexane was added to precipitate the formed polymer. The resulting gel-like material was filtrated and washed by hexane. Yield: 1.61 g (92.5%). ¹H NMR for poly-(2-bromoethyl acrylate) (400 MHz, CDCl₃) δ (ppm) 4.40 (br, 2H, O-CH₂), 3.55 (br, 2H, Br-CH₂), 2.45 (br, 1H), 2.03 (br, 1H), 1.75 (br, 1H).

Polymerization was also carried out in cyclohexane. 2-Bromoethyl acrylate (1.22 g, 6.80 mmol) was dissolved in 7 mL of cyclohexane, degassed by nitrogen for 15 min, azobisisobutyronitrile (0.0127 g, 0.077 mmol) was added, and stirred for 18 h at 60 $^{\circ}$ C. The solution became clouded as the polymerization reaction proceeded. Yield of the polymer was quantitative.

Polymerization of 2-bromoethyl acrylate by emulsion polymerization

Ultra pure water (20 mL) in a 50 mL round-bottom flask was degassed by nitrogen for 15 min and sodium dodecyl sulfate (2.004 g, 6.95 mmol) was dissolved. 2,2'-Azobisisobutyronitrile (0.023 g, 0.14 mmol) was dissolved in 2-bromoethyl acrylate (0.812 g, 4.54 mmol) and the mixture was poured into the round-bottom flask and stirred for 5 min to emulsify the monomer. The resulting clear solution was heated to 60 °C and the solution became creamy white. The solution was heated for 20 h, and aqueous ammonium chloride was added to salt out the formed polymer. The ball-like polymer was washed with water and methanol vigorously. Yield: 0.732 g (36.5 %).

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Modification of poly(2-bromoethyl acrylate) formed by solution polymerization (Polymer A)

Poly(2-bromoethyl acrylate) (0.261 g) was dissolved in 10 mL of anhydrous tetrahydrofuran. To the solution, alkoxide solution (sodium *tert*-butoxide (92 mg, 0.82 mmol) and 3-ferrocenyl-4'-hydroxymethylazobenzene (0.309 g, 78.0 mmol, 0.53 eq. *vs.* poly(2-bromoethyl acrylate)) in 20 mL of anhydrous tetrahydrofuran) was added dropwise for 10 min. The resulting mixture was stirred for 3 h, and saturated aqueous ammonium chloride (20 mL) was added. The organic layer was extracted by dichloromethane and dried over anhydrous sodium sulfate. The mixture was purified by silica gel column chromatography with chloroform as eluent and the first fraction was collected. Yield: 0.305 g. IR (cm⁻¹): 2922, 2851, 1696, 1603, 1506, 1451, 1414, 1385, 1205, 1156, 1105, 1034, 1012, 870, 825, 797, 712, 689, 504.

Modification of poly(2-bromoethyl acrylate) formed by emulsion polymerization (Polymer B)

Poly(2-bromoethyl acrylate) (49 mg) was dispersed in 10 mL of anhydrous tetrahydrofuran, heated to 40 °C, and stirred for 30 min. To the solution, alkoxide solution (sodium *tert*-but-oxide (67 mg, 0.60 mmol) and 3-ferrocenyl-4'-hydroxymethyl-azobenzene (196 mg, 0.495 mmol, 1.8 eq. vs. poly(2-bromoethyl acrylate)) in 10 mL of anhydrous tetrahydrofuran) was added dropwise for 10 min. The suspension was stirred at 45 °C for 2 h, cooled to room temperature and the insoluble component was filtrated and washed with water and methanol. Yield: 25 mg. IR (cm⁻¹): 2951, 2871, 1734, 1701, 1603, 1452, 1386, 1160, 820, 688, 497. ¹H NMR: (400 MHz, CDCl₃) δ (ppm) 8.01 (s, 1H, C₆H₄), 7.86 (d, J = 7.2 Hz, 2H, C₆H₄), 7.43 (dd, J = 7.2 Hz, 1H, C₆H₄), 7.34 (d, J = 7.2 Hz, 2H, C₆H₄), 4.75

(s, 2H, C₅H₄), 4.41(br), 4.36 (s, 2H, C₅H₄), 4.07 (s, 5H, C₅H₅), 3.55(br), 2.46(br), 2.47(br) 1.77(br), 1.26(br).

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