3764 *Macromolecules* **2010**, *43*, 3764–3769
DOI: 10.1021/ma100197z

Macromolecules
ARTICLE

Fast Photochromic Polymers Carrying [2.2]Paracyclophane-Bridged Imidazole Dimer

Atsushi Kimoto,[†] Atsuhiro Tokita,[‡] Takeru Horino,[‡] Toyoji Oshima,[‡] and Jiro Abe*,[†]

[†]*Department of Chemistry, School of Science and Engineering, Aoyama Gakuin University, 5-10-1 Fuchinobe, Sagamihara, Kanagawa 229-8558, Japan, and* [‡]*Tokyo Research Laboratory, Mitsubishi Gas Chemical Company, Inc., 6-1-1 Niijuku, Katsushika, Tokyo 125-0051, Japan*

Received January 26, 2010; Revised Manuscript Received March 17, 2010

ABSTRACT: The synthesis and photochromic behavior of the fast photochromic polymers carrying [2.2]paracyclophane-bridged imidazole dimer are demonstrated. A significant feature of this synthetic strategy is that we can modify the photochromic properties such as coloration/decoloration rate, coloring, and photosensitivity via the stepwise synthetic approach of the imidazole dimer system. Notably, the photochromic behavior of the polymers is not affected by the environment around the photochromes and copolymerization with other monomers in both solution and film, which cannot be realized in any other conventional photochromic systems. The comparable photochromic behavior of the homopolymers and copolymers in solution and film indicates that the photochromic unit is independent from the local environment, which allows effective molecular design of the photochromic monomer unit to accomplish desired photochromic properties of the polymer.

Introduction

Controlling photochromic property in bulk phase is an important and challenging issue for investigating the high-performance photochromic systems and photomechanical properties.[1,2] However, realizing universally applicable photochromic system in both solution and film includes difficulties because the photochromic reaction is generally affected by local environments, such as rigidity, viscosity, polarity, and free volume. Thus, elaborate molecular design of monomers does not always give desired photochromic properties, especially coloration/decoloration rate, in bulk phase. Applying photochromic compounds as a phototriggered switch[3−8] into stimuli-responsive materials (intelligent materials),[9−11] the equality of the photochromic behavior in solution and film is strongly required, and an enthusiastic search for such compounds is still ongoing. This article introduces a unique millisecond-order polymer photochromic system characterized by smaller interaction with other components and polymer matrices, allowing versatile functional designs. The fast photochromic polymers can be obtained via rational synthetic procedure, which enables to accomplish designer photoinduced switching polymer materials.

We recently investigated a unique series of photochromic molecules based on [2.2]paracyclophane-bridged imidazole dimer, which allow instantaneous coloration upon exposure to UV light and rapid decoloration in the dark.[12−15] The half-life of the colored species derived from the homolytic photocleavage of the C−N bond of imidazole dimer is on the order of milliseconds in solution. Another peculiar aspect of the photochromism of the imidazole dimer systems is photogeneration of imidazolyl radicals with an unpaired electron, which could modulate the magnetic property simply by turning the optical stimulation on and off.[16−18] The important aspect of paramagnetic character includes an intrinsically large molar absorption coefficient, which brings about a significant change in refractive index. This fast optical switching in both colors and spin states cannot be realized by any other currently available photochromic systems. Developing into bulk photochromism, investigation of polymeric system is of critical importance to achieve rapid photomodulation of various physicochemical properties.[19−22]

From standpoint of synthetic approach, [2.2]paracyclophane-bridged imidazole dimer can be prepared via a stepwise formation of two imidazole rings by the condensation reaction between aromatic 1,2-diketones and two aldehyde groups of *pseudogem*-bisformyl[2.2]paracyclophane as a starting material (Scheme 1). Recently, we proposed that this synthetic strategy allows rational design for achieving highly functionalized photochromes with desired performances such as thermal-bleaching rate, coloring, and photosensitivity. Herein, the stepwise synthetic approach of [2.2]paracyclophane-bridged imidazole dimer to yield a fast photochromic polymer is demonstrated.

Experimental Section

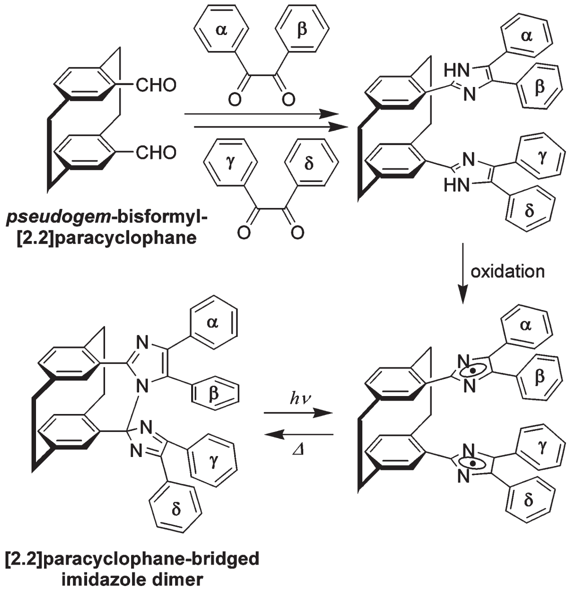
Materials. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Wakogel C-300). All reagents were purchased from TCI, Wako Co. Ltd., Aldrich Chemical Co., Inc., and Acros Organics and were used without further purification. All reaction solvents were distilled on the appropriate drying reagents prior to use.

Measurements. The NMR spectra were recorded on a JMN-ECP500A (JEOL) spectrometer, and the chemical shifts are quoted in ppm relative to tetramethylsilane. The UV−vis absorption spectra were measured on a UV-3150 (Shimadzu) spectrometer. The FAB mass spectra were measured with an MStation MS-700 (JEOL) spectrometer by using 3-nitrobenzyl alcohol as a matrix. Molecular weights and polydispersities of the polymers were estimated with gel permeation chromatography (GPC) analysis performed in tetrahydrofuran (THF, 1.0 mL/min) at 40 °C using a Shimadzu GPC apparatus, with a Shimadzu RID-10A detector and a Shodex KF-806 L column. The GPC was calibrated with narrow polydispersity polystyrene standards (Shodex STANDARD SM-105). The laser flash photolysis experiments were carried out with a Unisoku TSP-1000 time-resolved spectrophotometer.

---

*Corresponding author: Tel +81-(0)42-759-6225; Fax +81-(0)42-759-6225; e-mail jiro_abe@chem.aoyama.ac.jp.

Scheme 1. Synthetic Approach of Functionalized [2.2]Paracyclophane-Bridged Imidazole Dimer

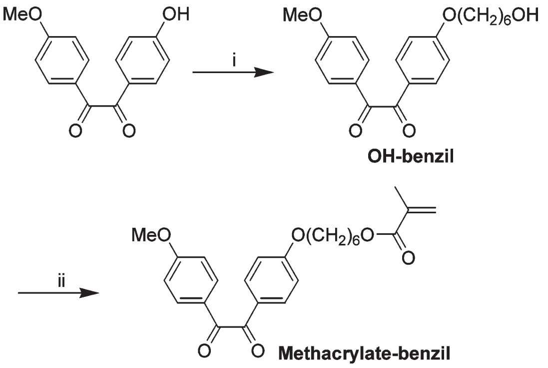


A Continuum Minilite II Nd:YAG (Q-switched) laser with the third harmonic at 355 nm (ca. 8 mJ per 5 ns pulse) was employed for the excitation light. The probe beam from an OSRAM HLX64623 halogen lamp was guided with an optical fiber scope to be arranged in an orientation perpendicular to the exciting laser beam. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a prior to the laser flash photolysis experiments. The vis−NIR absorption spectra of the absorption spectra of the colored species in film state were obtained using Fastevert S-2600 multichannel spectrometer (Soma Optics Ltd.) using a halogen lamp as the probe beam. The sample was cooled to 253 K using a liquid nitrogen cryostat USP-203-A (Unisoku, Inc.) in order to decelerate the recombination reaction. After UV irradiation was carried out using a Keyence UV-400 series UV-LED (UV-50H type), equipped with a UV-L6 lens unit (365 nm, irradiation power 300 mW/cm^2) for 2 s, the absorption spectrum was immediately measured.

Synthesis of OH-benzil. To a suspension of 4-hydroxy-4′-methoxybenzil (4.00 g, 15.6 mmol), potassium carbonate (3.02 g, 21.8 mmol), and potassium iodide (0.052 g, 0.312 mmol) in degassed *N,N*-dimethylformamide (55 mL) was added 6-chloro-1-hexanol (3.1 mL, 23.4 mmol). The reaction mixture was heated under a N_2 atmosphere at 80 °C for 12 h and poured into water. After extraction using ethyl acetate, the organic layer was washed with water and brine and dried over Na_2SO_4. To a solution of the crude mixture in dichloromethane, a large amount of hexane was added to give OH-benzil as pale yellow powders (5.47 g, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.95−7.92 (m, 4H), 6.97−6.94 (m, 4H), 4.04 (t, J = 6.5 Hz, 2H), 3.88 (s, 3H), 3.66 (t, J = 6.5 Hz, 2H), 1.84−1.81 (m, 2H), 1.62−1.59 (m, 2H), 1.52−1.44 (m, 4H), 1.32 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.88, 193.83, 165.19, 164.79, 132.71, 126.70, 126.46, 115.06, 114.62, 68.65, 63.17, 55.97, 32.96, 29.33, 26.13, 25.84. FAB-MS: *m*/*z* 357 [M + H]$^+$.

Synthesis of Methacrylate-benzil. To a solution of OH-benzil (3.56 g, 10.0 mmol), triethylamine (3.0 mL, 22.0 mmol), and *p*-hydroquinone (22 mg, 0.20 mmol) in dichloromethane (20 mL) was added methacryloyl chloride (2 mL, 20.0 mmol) at 0 °C. The reaction mixture was stirred under a N_2 atmosphere at room temperature for 6 h and poured into water. After extraction using dichloromethane, the organic layer was washed with water and brine and dried over Na_2SO_4. The crude mixture was purified with silica gel column chromatography using dichloromethane as eluent to give Methacrylate-benzil as pale yellow powders (4.71 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.96−7.92 (m, 4H), 6.98−6.94 (m, 4H), 6.09 (s, 1H), 5.55 (s, 1H), 4.16 (t, J = 7.0 Hz, 2H), 4.04 (t, J = 7.0 Hz, 2H), 3.89 (s, 3H), 1.94 (s, 3H), 1.84−1.73 (m, 2H), 1.57−1.39 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 193.87, 193.82, 167.85, 165.18, 164.75, 136.82, 132.71, 126.69, 126.48, 125.57, 115.04, 114.62, 68.58, 64.90, 55.96, 29.25, 28.87, 26.08, 25.99, 18.66. FAB-MS: *m*/*z* 425 [M + H]$^+$.

Scheme 2. Synthesis of Methacrylate-benzil[a]



[a] Reagents and conditions: (i) 6-chloro-1-hexanol, potassium carbonate, potassium iodide, DMF, 80 °C, 12 h; (ii) methacryloyl chloride, triethylamine, CH_2Cl_2, rt, 6 h.

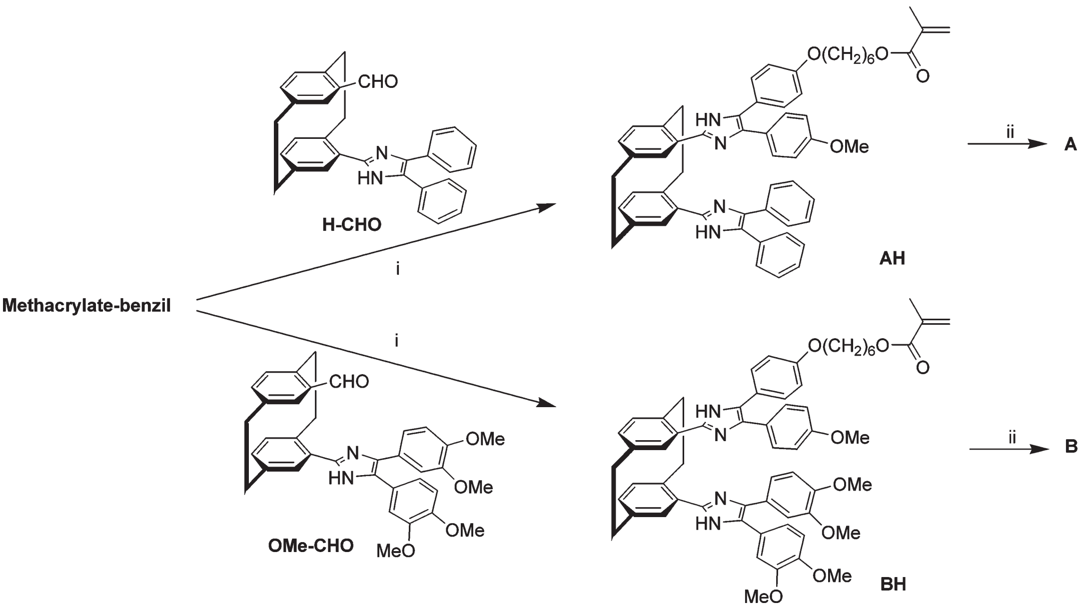
Synthesis of H−CHO or OMe−CHO. *Pseudogem*-bisformyl-[2.2]paracyclophane (1 equiv), benzil derivative (1 equiv), and ammonium acetate (15 equiv) were heated at 80 °C in acetic acid for 12 h. The reaction mixture was cooled to room temperature and was neutralized with aqueous NH_3. The resulting precipitate was filtered and washed with water. The crude mixture was purified with silica gel column chromatography using THF/hexane = 1/2 as eluent to give the target compound as yellow powders.

H−CHO. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 12.14 (s, 1H), 9.55 (s, 1H), 7.58 (d, J = 7.5 Hz, 2H), 7.51 (d, J = 7.0 Hz, 2H), 7.47 (dd, J = 7.5 Hz, 2H), 7.40 (t, J = 7.0 Hz, 1H), 7.31 (dd, J = 7.0 Hz, 2H), 7.16 (t, J = 7.0 Hz, 1H), 7.10 (s, 1H), 6.96 (s, 1H), 6.84 (d, J = 7.5 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 6.66 (d, J = 7.5 Hz, 2H), 4.49−4.45 (m, 1H), 3.95−3.92 (m, 1H), 3.15−2.97 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 190.45, 145.29, 140.38, 140.17, 138.52, 138.15, 138.10, 136.78, 136.57, 136.10, 135.37, 133.24, 132.84, 131.44, 131.10, 130.85, 129.20, 128.61, 128.30, 127.93, 127.14, 35.28, 35.24, 35.09, 31.82. FAB-MS: *m*/*z* 455 [M + H]$^+$.

OMe−CHO. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.82 (s, 1H), 9.19 (s, 1H), 7.32−7.26 (m, 2H), 7.13−7.12 (m, 1H), 7.09−7.08 (m, 2H), 6.89−6.83 (m, 2H), 6.79−6.77 (m, 1H), 6.69−6.68 (m, 2H), 6.63−6.61 (m, 2H), 4.27−4.25 (m, 1H), 4.02−4.00 (m, 1H), 3.90 (s, 6H), 3.88 (s, 6H), 3.13−3.03 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 190.44, 149.24, 149.12, 148.96, 148.28, 144.73, 144.27, 140.38, 140.12, 138.23, 138.06, 137.87, 136.74, 136.47, 136.10, 132.86, 132.67, 131.23, 130.88, 128.45, 127.51, 124.19, 121.18, 120.24, 112.21, 111.63, 111.43, 111.33, 56.25, 56.22, 56.02, 35.33, 35.20, 35.06, 31.58. FAB-MS: *m*/*z* 575 [M + H]$^+$.

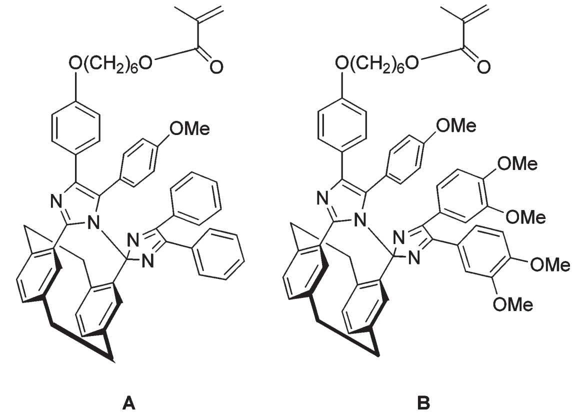
Synthesis of AH. Methacrylate-benzil (1.03 g, 2.4 mmol), H−CHO (1.11 g, 2.4 mmol), *p*-methoxyphenol (0.15 g), and ammonium acetate (2.82 g, 36 mmol) were heated at 80 °C in acetic acid (8 mL) for 4 days. The reaction mixture was cooled to room temperature and was neutralized with aqueous NH_3. The resulting precipitate was filtered and washed with water. The crude mixture was purified with silica gel column chromatography using THF/hexane = 1/2 as eluent to give AH as colorless powders (1.78 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.06 (br, 2H), 7.39−7.30 (br, 3H), 7.14−6.98 (m, 12H), 6.73−6.61 (m, 9H), 6.10 (s, 1H), 5.55 (s, 1H), 4.23−4.15 (m, 4H), 3.91−3.88 (m, 4H), 3.76 (s, 3H), 3.20−3.12 (m, 6H), 1.94 (s, 3H), 1.85−1.71 (m, 4H), 1.54−1.43 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.49, 146.21, 145.51, 139.66, 137.51, 136.65, 136.28, 133.27, 132.95, 130.46, 128.88, 128.08, 125.39, 67.81, 64.81, 55.29, 35.31, 35.13, 29.36, 28.72, 25.96, 18.48. FAB-MS: *m*/*z* 860 [M + H]$^+$.

Scheme 3. Synthesis of the Photochromic Monomers (A and B)[a]

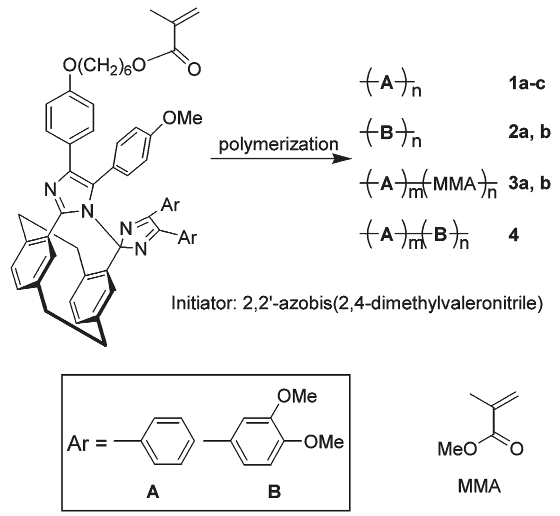


[a] Reagents and conditions: (i) NH_4OAc, AcOH, *p*-methoxyphenol, 80 °C, 4 days; (ii) $K_3Fe(CN)_6$, KOH, benzene, rt, 30 min.

Chart 1. Structures of the Photochromic Monomers



Scheme 4. Polymerization of [2.2]Paracyclophane-Bridged Imidazole Dimer



Synthesis of BH. Methacrylate-benzil (0.216 g, 0.52 mmol), OMe−CHO (0.28 mg, 0.49 mmol), *p*-methoxyphenol (30 mg), and ammonium acetate (0.563 g, 7.3 mmol) were heated at 80 °C in acetic acid (4 mL) for 4 days. The reaction mixture was cooled to room temperature and was neutralized with aqueous NH_3. The resulting precipitate was filtered and washed with water. The crude mixture was purified with silica gel column chromatography using THF/hexane = 1/2 as eluent to give BH as pale yellow powders (0.249 g, 53%). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.47−11.42 (m, 2H), 7.13−7.08 (m, 4H), 7.01−6.98 (m, 1H), 6.92−6.86 (m, 3H), 6.78−6.76 (m, 3H), 6.69−6.51 (m, 9H), 6.02 (br, 1H), 5.66 (br, 1H), 4.61−4.45 (m, 2H), 4.11 (t, J = 6.0 Hz, 2H), 3.89−3.79 (m, 2H), 3.75−3.58 (m, 15H), 3.13−3.01 (m, 6H), 1.88 (s, 3H), 1.76−1.65 (m, 4H), 1.50−1.35 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.88, 148.91, 148.03, 145.93, 145.78, 139.94, 136.85, 136.63, 136.42, 133.54, 133.13, 130.71, 129.59, 128.67, 126.85, 125.86, 125.58, 123.91, 120.73, 120.34, 114.74, 114.19, 113.58, 111.72, 111.33, 111.17, 68.30, 68.02, 64.98, 56.10, 55.95, 55.45, 35.75, 35.58, 35.04, 34.57, 30.66, 29.55, 28.93, 26.19, 25.95, 18.68. FAB-MS: *m*/*z* 980 [M + H]$^+$.

Synthesis of the Monomer A. All manipulations were carried out with the exclusion of light. Under nitrogen, to a solution of AH (0.812 g, 0.95 mmol) in benzene (150 mL) was added the solution of potassium ferricyanide (15.57 g, 47 mmol) and KOH (5.31 g, 95 mmol) in water (105 mL), and the reaction mixture was vigorously stirred for 30 min. The organic layer was separated, exhaustively washed with water, and concentrated in vacuo. The crude mixture was purified with silica gel column chromatography using THF/hexane = 1/2 as eluent to give **A** as colorless powders (0.646 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47 (br, 1H), 7.31−7.03 (m, 15H), 6.92 (br, 1H), 6.82 (dd, J = 9.0 Hz, 2H), 6.71 (dd, J = 9.5 Hz, 2H), 6.64−6.61 (m, 2H), 6.48 (d, J = 7.5 Hz, 1H), 6.42 (d, J = 8.0 Hz, 1H), 6.09 (br, 1H), 5.54 (br, 1H), 4.54−4.51 (m, 1H), 4.18−4.15 (m, 2H), 4.00−3.93 (m, 2H), 3.84−3.80 (m, 3H), 3.33−2.94 (m, 7H), 1.94 (m, 3H), 1.83−1.70 (m, 4H), 1.55−1.42 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.95, 164.69, 147.42, 141.21, 138.34, 137.48, 136.84, 136.34, 134.98, 134.76, 133.78, 133.19, 132.82, 132.56, 132.05, 131.81, 128.52, 128.39, 128.29, 128.09, 127.19, 126.37, 125.57, 114.06, 113.71, 113.62, 113.26, 111.91, 68.17, 64.92, 55.68, 55.61, 35.65, 35.57, 34.78, 34.46, 29.42, 28.89, 26.14, 18.67. FAB-MS: *m*/*z* 858 [M + H]$^+$.

Synthesis of the Monomer B. All manipulations were carried out with the exclusion of light. Under nitrogen, to a solution of BH (0.564 g, 0.64 mmol) in benzene (100 mL) was added the

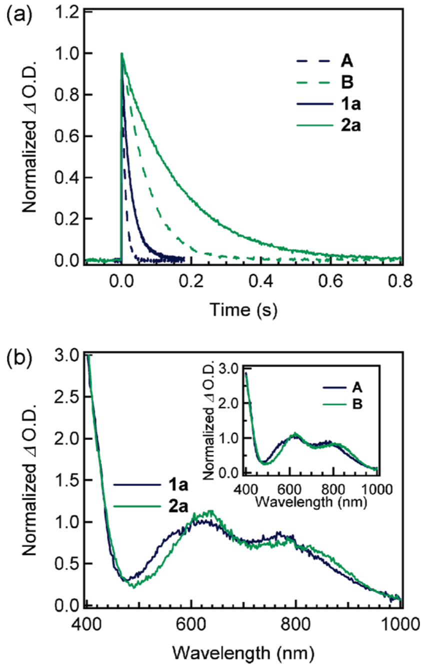


Figure 1. (a) Decay profiles of the colored species generated from **A**, **B**, **1a**, and **2a** monitored at 400 nm in degassed dichloromethane solution (**A** and **B**: 2.0×10^{-4} M; **1a** and **2a**: 50 μg/mL, 10 mm light path length) at 298 K with a nanosecond laser pulse (excitation wavelength, 355 nm; pulse width, 5 ns; power, 8 mJ/pulse). (b) Transient vis−NIR absorption spectra of **1a** and **2a** in degassed dichloromethane solution (50 μg/mL), normalized at 600 nm. Inset shows transient vis−NIR absorption spectra of **A** and **B** in dichloromethane (2.0×10^{-4} M, 10 mm light path length), normalized at 600 nm.

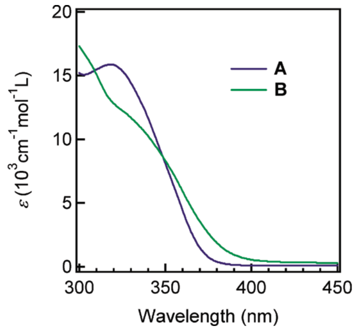


Figure 2. UV−vis absorption spectra of **A** and **B** in dichloromethane (2.0×10^{-4} M, 1 mm light path length) at 298 K.

solution of potassium ferricyanide (10.6 g, 32 mmol) and KOH (3.61 g, 64 mmol) in water (72 mL), and the reaction mixture was vigorously stirred for 30 min. The organic layer was separated, exhaustively washed with water, and concentrated in vacuo. The crude mixture was purified with silica gel column chromatography using THF/hexane = 1/3 to 1/1 as eluent to give **B** as pale yellow powders (0.469 g, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30−6.42 (m, 22H), 6.10 (br, 1H), 5.55 (br, 1H), 4.61−4.45 (m, 1H), 4.17−4.12 (m, 2H), 3.99−3.89 (m, 2H), 3.91−3.55 (m, 15H), 3.35−2.90 (m, 7H), 1.94 (m, 3H), 1.85−1.62 (m, 4H), 1.50−1.35 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.86, 151.85, 141.74, 136.83, 136.49, 136.36, 136.12, 132.44, 132.23, 131.07, 131.00, 130.90, 129.51, 129.16, 128.83, 128.59, 128.55, 126.92, 126.44, 125.93, 125.85, 125.59, 115.08, 114.98, 114.81, 114.66, 114.37, 64.95, 64.90, 55.63, 55.59, 54.51, 35.41, 35.03, 34.85, 34.56, 33.17, 31.92, 30.66, 29.45, 29.39, 28.91, 28.87, 26.17, 26.08, 26.06, 22.98, 21.52, 18.67, 14.45. FAB-MS: *m*/*z* 979 $[M + H]^+$.

Typical Procedure for Polymerization. The monomer **A** and 2,2′-azobis(2,4-dimethylvaleronitrile) (1.5 mol % of monomer) were dissolved in dry THF (0.35 mmol/L) and placed in a polymerization tube. After several freeze−pump−thaw cycles, the tube was sealed under vacuum. The mixture was stirred and heated in a sealed tube at 60 °C for 3 days. The cooled solution was poured into methanol with stirring. The precipitation was collected and dried under vacuum for 12 h to obtain the target polymer.

Results and Discussion

Two photochromic monomers with [2.2]paracyclophane-bridged imidazole dimer (**A** and **B**, Chart 1) possessing a methacrylate moiety at their terminus were designed in this study. The methacrylate-terminated benzil (Methacrylate-benzil) was prepared by the etherification between 4-hydroxy-4′-methoxybenzil[23] and 6-chloro-1-hexanol in the presence of potassium carbonate, followed by reaction with methacryloyl chloride to give Methacrylate-benzil (Scheme 2). The benzil was reacted with the corresponding [2.2]paracyclophane aldehyde (H−CHO or OMe−CHO) to form the monomer precursor (AH and BH), which was allowed to be oxidized to yield the photochromic monomer (**A** and **B**) (Scheme 3). The structural feature of these monomers is that polymerization unit and photochromic controlling unit is separately introduced into a different imidazole ring. Irradiating UV light to dichloromethane solution of the monomers, rapid photochromism from colorless to blue (**A**) or green (**B**) is observed. Under continuous irradiation, the dichloromethane solution of the methacrylate monomers reaches the photostationary equilibrium, and the absorption decays rapidly following first-order thermal-bleaching kinetics after ceasing the illumination. While the half-life of the colored species is 7.2 ms (**A**) at 298 K in dichloromethane, the half-life of the colored species is 52 ms (**B**), which has 3,4-dimethoxyphenyl moiety, with ∼8 times longer than that of the unsubstituted monomer, **A** (Figure 1a). The transient vis−NIR absorption spectra of the monomers in degassed dichloromethane solution at 298 K are shown in the inset of Figure 1b. A characteristic absorption around 400 nm and a broad absorption from 500 to 1000 nm can be attributed to the colored species. Compared with monomer **A**, a spectral red shift can be observed for **B** (Figures 1b and 2). These substituent effects on decoloration rate and coloring suggest that this monomer design approach is useful to control the photochromic property of methacrylate monomers.

The homopolymers were prepared by radical polymerization using a low-temperature initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (Scheme 4). **1a**−**1c** and **2a**−**2b** have been prepared starting from the monomer **A** and **B**, respectively. The polymerization was performed at 60 °C for 3 days to yield the polymers (Table 1). Photochromic properties of the polymers in solution were investigated in order to study the influence of the polymerization. The polymers readily show fast photochromism, which implies that no decomposition of the imidazole dimer unit occurred under the radical polymerization conditions. In dichloromethane at 298 K, the half-life of the colored species is 17 ms (**1a**) and 108 ms (**2a**), and the decoloration of **1a** finishes within 200 ms, whereas that of **2a** within 800 ms, indicating that the substituent effect by methoxy moieties is maintained even after the polymerization (Figure 1a). We should note that the thermal-bleaching reaction is independent from molecular weight of the polymers (see Supporting Information Figures S2 and S3) and obeys first-order kinetics after ceasing the illumination (see Supporting Information Figure S4). This observed kinetics for decoloration of the homopolymers is attributed to the overall first-order recombination reaction for each chromophore with various local environments. The recombination reaction of the homopolymers, **1a** and **2a**, is slower than that of each monomer,

Table 1. Polymerization Characteristics of Poly([2.2]paracyclophane-bridged imidazole dimer)s and Their Copolymers

sample	initiator[a] (mol %)	concentration (mmol/L)	reaction time (days)	feed ratio (mol/mol)	yield (%)	M_w[b]	M_w/M_n
1a	1.5	0.35	3		55	28 400	2.15
1b	3.0	0.35	3		42	19 800	1.93
1c	5.0	0.35	3		55	19 100	1.76
2a	1.5	0.35	3		37	9 500	1.60
2b	3.0	0.35	3		50	7 800	1.41
3a	3.0	0.35	3	**A**/MMA = 1/1	70	11 200	1.65
3b	3.0	0.35	3	**A**/MMA = 1/4	62	9 600	1.59
4	3.0	0.70	6	**A**/**B** = 1/1	37	11 400	1.79

[a] 2,2′-Azobis(2,4-dimethylvaleronitrile) was used as an initiator. [b] Determined by GPC analysis (polystyrene calibration standard) using THF as eluent.

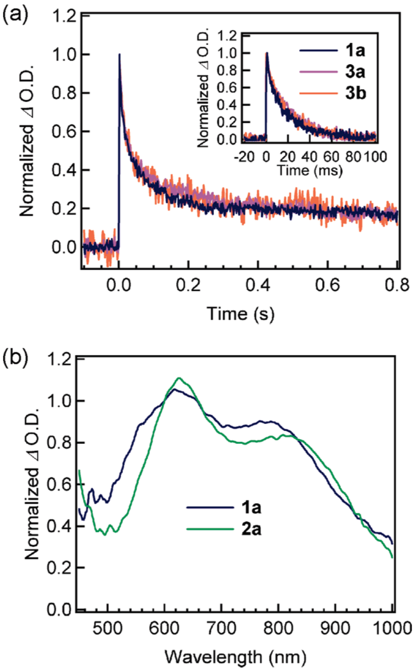


Figure 3. (a) Decay profiles of the colored species generated from the cast film of **1a**, **3a**, and **3b** monitored at 400 nm. Inset shows decay profiles of the colored species generated from **1a**, **3a**, and **3b** monitored at 400 nm in degassed dichloromethane solution (50 μg/mL). (b) Vis−NIR absorption spectra of the cast film of **1a** and **2a** after UV irradiation at 253 K, normalized at 600 nm.

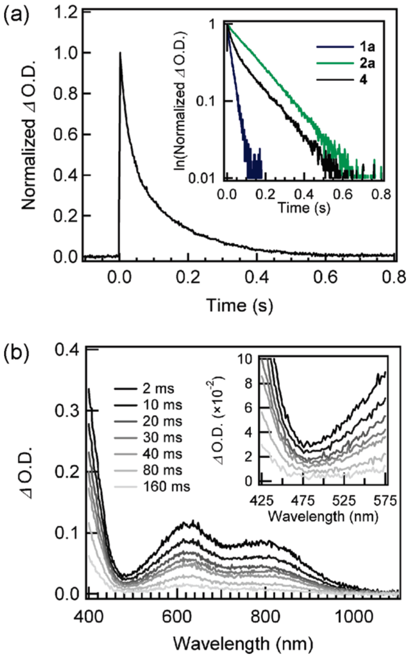


Figure 4. (a) Decay profile of the colored species generated from **4** monitored at 400 nm in degassed dichloromethane solution (50 μg/mL, 10 mm light path length) at 298 K with a nanosecond laser pulse (excitation wavelength, 355 nm; pulse width, 5 ns; power, 8 mJ/pulse). Inset shows the first-order kinetic plots for **1a**, **2a**, and **4**. (b) Transient vis−NIR absorption spectra of **4** in degassed dichloromethane solution (50 μg/mL, 10 mm light path length). Inset shows magnified view of the region from 425 to 575 nm.

A and **B**, respectively. This deceleration of thermal bleaching for [2.2]paracyclophane-bridged imidazole dimer as a pendant of the polymer is supported by the idea that larger structural change during the photochromic reaction of the polymer is required than that of the monomer. Absorption spectra of the colored species of the polymers, **1a** and **2a**, are quite similar to those of the monomers, **A** and **B**, respectively (Figure 1b). The transient spectrum of the colored species depends on the electronic state of the chromophores. In solution, there is no specific change on the transient spectrum after the polymerization because the photochromic unit is apart from the polymer main chain with small electronic effects.

We prepared copolymers of **A** and MMA (methyl methacrylate) with a different copolymerization ratio (**3a** and **3b**) in order to study the influence on the photochromism by copolymerization with another monomer. The copolymerization ratio (**3a**: $m/n = 1/1.3$ and **3b**: $m/n = 1/4.6$) was estimated from the ^{1}H NMR measurement. In dichloromethane solution, the thermal-bleaching behavior of the copolymers, **3a** and **3b**, is almost the same as that of the homopolymer, **1a**, even though MMA unit is incorporated (Figure 3a, inset). The decoloration completes within 200 ms, and the half-life is 16 ms (**3a**) and 13 ms (**3b**) at 298 K. The photochromic behaviors of the cast film of **1a**, **3a**, and **3b** are also analogous to those observed in solution (Figure 3a). Considering that the reaction rate of photochromism is generally influenced by the environment around the photochrome,[24−29] the photochromic properties of the film cannot be predicted from those in solutions. On the other hand, the similarity of the photochromic properties between the homopolymers and copolymers of [2.2]paracyclophane-bridged imidazole dimer allows further versatile functionalization by copolymerization with various monomers, which does not affect the fast photochromism in solution. In the cast film, although the absorption decays do not follow first-order thermal-bleaching kinetics, the bleaching behavior of the fast component seems to be similar to that in solution. The half-life for the film is defined as the time with 50% of the normalized ΔOD (optical density) and estimated to be ~30 ms. The slow bleaching component also exists during the thermal bleaching, which is commonly generated in other polymeric photochromic systems. Also, the absorption spectra of the colored species are quite similar to those in dichloromethane and characteristic absorption bands around 600 and 800 nm are observed (Figures 1b and 3b). In other words, the fast photochromism of [2.2]paracyclophane-bridged imidazole dimer remains intact even in the film state.

In order to ensure the advantage of functionalization via the copolymerization approach, we preliminarily prepared the copolymer of **A** and **B** (**4**, $m/n = 1/0.44$) and investigated its photochromic behavior (Figure 4 and Figure S5). In dichloromethane solution, the thermal bleaching finishes within 800 ms, which is identical to that of the slower photochromic unit, **2a** (Figure 4a). The thermal back-reaction reveals the existence of two components of the first-order reaction, and there is an inflection point around 50 ms. Notably, the slope of the decay of **4** over the time range from 200 ms, where the recombination of **A** has completed, is identical to that of **2a** (Figure 4a, inset). As proceeding the recombination reaction, the absorption spectrum of the photogenerated colored species eventually varies (Figure 4b). This result suggests that even introduction of the other photochromic unit maintains the photochromic properties, and no reactions between the chromophores occur, which is similar to the photochromic behavior of homopolymers. The structural difference between the homopolymers, **1a** and **2a**, and the copolymer, **4**, is composition of the photochromic units on the polymer main chain. All the photochromic polymers in this study are classified into pendant-type photochromic polymers; the photochromic behavior of **4** is essentially the same as that of the homopolymers. Considering the decay profile of the colored species of the homopolymers obeys the first-order plot (Figure 4a, inset), the recombination reaction between the imidazolyl radicals of the individual chromophore in these pendant-type photochromic polymers takes place without cross-recombination between neighboring chromophores; the decay profile of the copolymer (**4**) is the sum of recombination reaction in the individual chromophores with the first-order kinetics.

Conclusion

In conclusion, the synthesis of the fast photochromic polymers carrying [2.2]paracyclophane-bridged imidazole dimer is demonstrated. We can modify the photochromic properties such as coloration/decoloration rate, coloring, and photosensitivity via the stepwise synthetic approach of the imidazole dimer system. Notably, the photochromic behavior is not affected by the environment around the photochromes and copolymerization with other monomers both in solution and film, which cannot be realized in any other conventional photochromic systems. The comparable photochromic behavior of the homopolymers and copolymers in solution and film indicates that the photochromic unit is independent from the local environment, which allows effective molecular design of the photochromic monomer unit to accomplish desired photochromic properties of the polymer. Generally, advantage of polymeric materials is comprised of their good film-forming property with assembled and concentrated functions in polymer chain, which cannot be realized by simple doping into the host polymer matrices because phase separation and precipitation of the dopant takes place at higher doping level. When developing functional polymers into electronic applications, the cooperativity between functional units derived from "polymer effect" is favored. On the other hand, in the photochromic polymer system, interaction with other components or host polymer matrices deteriorates the photochromic property as usually seen in common photochromic polymer systems. Hence, the independent photochromic behavior in polymeric [2.2]paracyclophane-bridged imidazole dimers is expected as a quite reasonable system for various applications, especially in bulk phase. This photochromic system is proved to be a powerful candidate for applying various phototriggered modules into photo-oriented systems. By copolymerizing with various functional monomers, we can open up possibilities of this fast photochromic system.

Acknowledgment. This work was supported by a Grant-in-Aid for Science Research in a Priority Area "New Frontiers in Photochromism (No. 471)" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan and by a High-Tech Research Center project for private universities with the matching fund subsidy from MEXT.

Supporting Information Available: Typical ^{1}H NMR spectrum of the photochromic polymer and photochromic properties for each polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Crano, J. C.; Guglielmetti, R. J. *Organic Photochromic and Thermochromic Compounds*; Plenum Press: New York, 1999.
(2) Dürr, H.; Bouas-Laurent, H. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, 2003.
(3) Yu, Y.; Nakano, M.; Ikeda, T. *Nature* **2003**, *425*, 145.
(4) Yamada, M.; Kondo, M.; Mamiya, J.; Yu, Y.; Kinoshita, M.; Barrett, C.; Ikeda, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 4986.
(5) Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M. *Nature* **2007**, *446*, 778.
(6) Kawai, T.; Nakashima, Y.; Irie, M. *Adv. Mater.* **2005**, *17*, 309.
(7) Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. *Nature* **2002**, *420*, 759.
(8) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 7195.
(9) Sangeetha, N. M.; Maitra, U. *Chem. Soc. Rev.* **2005**, *34*, 821.
(10) Kato, T.; Hirai, Y.; Nakaso, S.; Moriyama, M. *Chem. Soc. Rev.* **2007**, *36*, 1857.
(11) Sagara, Y.; Kato, T. *Nat. Chem.* **2009**, *1*, 605.
(12) Iwahori, F.; Hatano, S.; Abe, J. *J. Phys. Org. Chem.* **2007**, *20*, 857.
(13) Fujita, K.; Hatano, S.; Kato, D.; Abe, J. *Org. Lett.* **2008**, *10*, 3105.
(14) Kishimoto, Y.; Abe, J. *J. Am. Chem. Soc.* **2009**, *131*, 4227.
(15) Harada, Y.; Hatano, S.; Kimoto, A.; Abe, J. *J. Phys. Chem. Lett.* **2010**, *1*, 1112.
(16) Caspar, J. V.; Khudyakov, I. V.; Turro, N. J.; Weed, G. C. *Macromolecules* **1995**, *28*, 636.
(17) Kawano, M.; Sano, T.; Abe, J.; Ohashi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 8106.
(18) Abe, J.; Sano, T.; Kawano, M.; Ohashi, Y.; Matsushita, M. M.; Iyoda, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 580.
(19) Fukushima, K.; Vandenbos, A. J.; Fujiwara, T. *Chem. Mater.* **2007**, *19*, 644.
(20) Zhu, L.; Wu, W.; Zhu, M.-Q.; Han, J. J.; Hurst, J. K.; Li, A. D. Q. *J. Am. Chem. Soc.* **2007**, *129*, 3524.
(21) Lee, H.-i.; Wu, W.; Oh, J. K.; Mueller, L.; Sherwood, G.; Peteanu, L.; Kowaleski, T.; Matyjaszewski, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 2453.
(22) Iwamura, T.; Sakaguchi, M. *Macromolecules* **2008**, *41*, 8995.
(23) Simbürger, H.; Kerna, W.; Hummel, K.; Hagg, C. *Polymer* **2000**, *41*, 7883.
(24) Evans, R. A.; Hanley, T. L.; Skidmore, M. A.; Davis, T. P.; Such, G. K.; Yee, L. H.; Ball, G. E.; Lewis, D. A. *Nat. Mater.* **2005**, *4*, 249.
(25) Such, G. K.; Evans, R. A.; Davis, T. P. *Macromolecules* **2006**, *39*, 1391.
(26) Sriprom, W.; Néel, M.; Gabbutt, C. D.; Heron, B. M.; Perrier, S. *J. Mater. Chem.* **2007**, *17*, 1885.
(27) Ercole, F.; Malic, N.; Davis, T. P.; Evans, R. A. *J. Mater. Chem.* **2009**, *19*, 5612.
(28) Norikane, Y.; Davis, R.; Tamaoki, N. *New J. Chem.* **2009**, *33*, 1327.
(29) Ercole, F.; Davis, T. P.; Evans, R. A. *Macromolecules* **2009**, *42*, 1500.