



Synthesis of photochromic diarylethene polymers for a write-by-light/erase-by-heat recording system

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ARTICLE INFO

Article history:

Received 30 April 2008

Accepted 18 May 2008

Available online 23 May 2008

Keywords:

Photochromism

Diarylethene

Photochromic polymer

Thermal bleaching reaction

ABSTRACT

A functionalized styrene monomer (**1a**) having a photochromic diarylethene chromophore with functional properties of photocoloration, photostability of the colored state, and thermal erasure by heating was synthesized, and the polymer and copolymers of **1a** were prepared by radical polymerization and copolymerization. Their polymers exhibited excellent photocoloration and rapid thermal bleaching above 150 °C in solution and in the solid state as well as the performance of the monomeric diarylethene chromophore. In addition, the colored state has a high photostability under visible room light. The diarylethene homopolymer had a glass transition temperature (T_g) as high as polystyrene. The copolymer of **1a** with *N*-1-adamantylmaleimide exhibited extremely high T_g above 200 °C with keeping the photofunctional performance. Such photochromic polymer and copolymers with high T_g can be potentially applied to rewritable display materials and image recordings by a write-by-light/erase-by-heat system.

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1. Introduction

Photochromic compounds undergo a photo-induced reversible isomerization process between two isomers with different absorption spectra upon irradiation with light of appropriate wavelength.^{1,2} They exhibit different chemical and physical property changes such as their absorption spectra, refractive indices, dielectric constants, oxidation–reduction potentials, and geometrical structures because of their molecular structural changes. They are classified into two types, P-type (thermally stable of the photogenerated isomer) and T-type (thermally unstable of the photogenerated isomer).¹ Among various photochromic compounds, diarylethenes with heterocyclic aryl rings have been developed as a P-type photochromic compound because of some excellent characteristics such as thermal stability of both isomers and fatigue-resistant property.^{3,4} Such materials can be potentially used for application to optical memory media,^{5,6} switching devices,^{7,8} display materials,^{9,10} and photo-mechanical actuators.^{11,12}

When the photochromic materials are applied to image recordings such as rewritable papers, the colored state should be stable under room light. The photogenerated colored isomer of a typical diarylethene derivative, 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene, is stable for more than 1900 years at 30 °C in the dark.^{13,14} However, the colored isomer returns to the initial colorless isomer under room light even at room temperature. For the recording

application, diarylethene molecules having very low photodecoloration quantum yields and thermal stability at room temperature have been developed.^{15,16} The photodecoloration quantum yield is strongly suppressed by the introduction of methoxy groups at the reactive 2- and 2'-positions of the thiophene rings.¹⁵ Furthermore, for the reusability of the materials, the colored isomers can return to the colorless isomers thermally at high temperature above 100 °C by the introduction of the cyclohexyloxy groups at the 2- and 2'-positions.¹⁶

From the viewpoint of the application in the thin film, we have designed and synthesized novel photochromic polymers, in which the photogenerated colored forms are stable under visible light and return to the initial forms at temperature above 100 °C though the colored isomers are stable even at room temperature (Scheme 1). In the present work, such polymer and copolymers including the diarylethene chromophores in a high content were synthesized by radical polymerization, and the chemical and physical properties of the polymers, such as photoreactivity, photostability, thermal bleaching reactivity, and thermal analysis, were examined in the neat film as well as in solution.

2. Results and discussion

2.1. Synthesis of diarylethene polymers and their characterization

Radical polymerization of **1a** was carried out using an azoinitiator (AIBN) at 60 °C under the condition shown in Table 1. After

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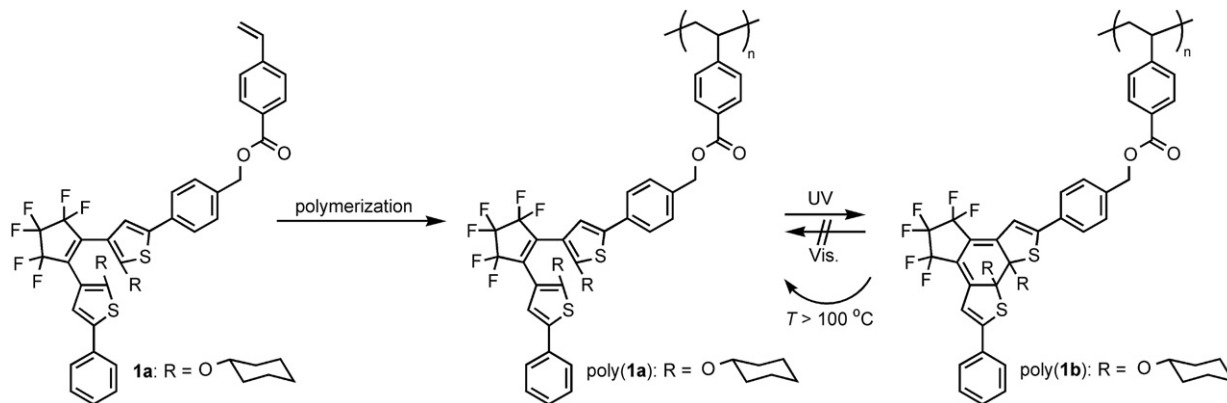
Scheme 1. Synthesis and photochromic reaction of poly(**1a**).

Table 1

Polymerization and copolymerization of **1a** in toluene at 60 °C and physical properties of the resulting polymers

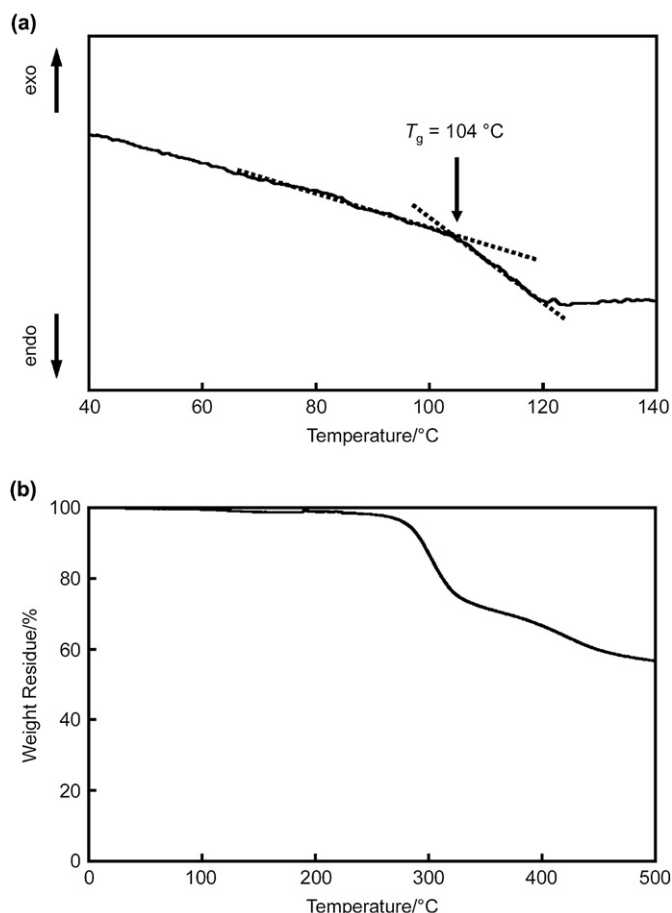
[1a] (mol dm ⁻³)	[3] (mol dm ⁻³)	[4] (mol dm ⁻³)	[AIBN] (mol dm ⁻³)	Time (h)	Yield (%)	Content of 1a in copolymer (mol %)	<i>M_n</i> (GPC)	<i>M_w</i> / <i>M_n</i> (GPC)	<i>T_g</i> ^a (°C)	<i>T_{init}</i> ^b (°C)
0.36	0	0	0.019	10	58	100	21,000	1.85	104	234
0.18	0.18	0	0.019	5	65	61	29,000	1.94	122	—
0.11	0.25	0	0.0050	9	57	49	67,000	2.20	125	—
0.24	0.36	0	0.019	4	56	42	24,000	2.04	130	—
0	0.41	0	0.019	4	59	0	15,000	2.26	>200 ^c	—
0.18	0	0.18	0.020	10	83	46	20,000	2.46	>230 ^c	240
0.18	0	0.18	0.010	10	74	49	36,000	2.39	>230 ^c	238

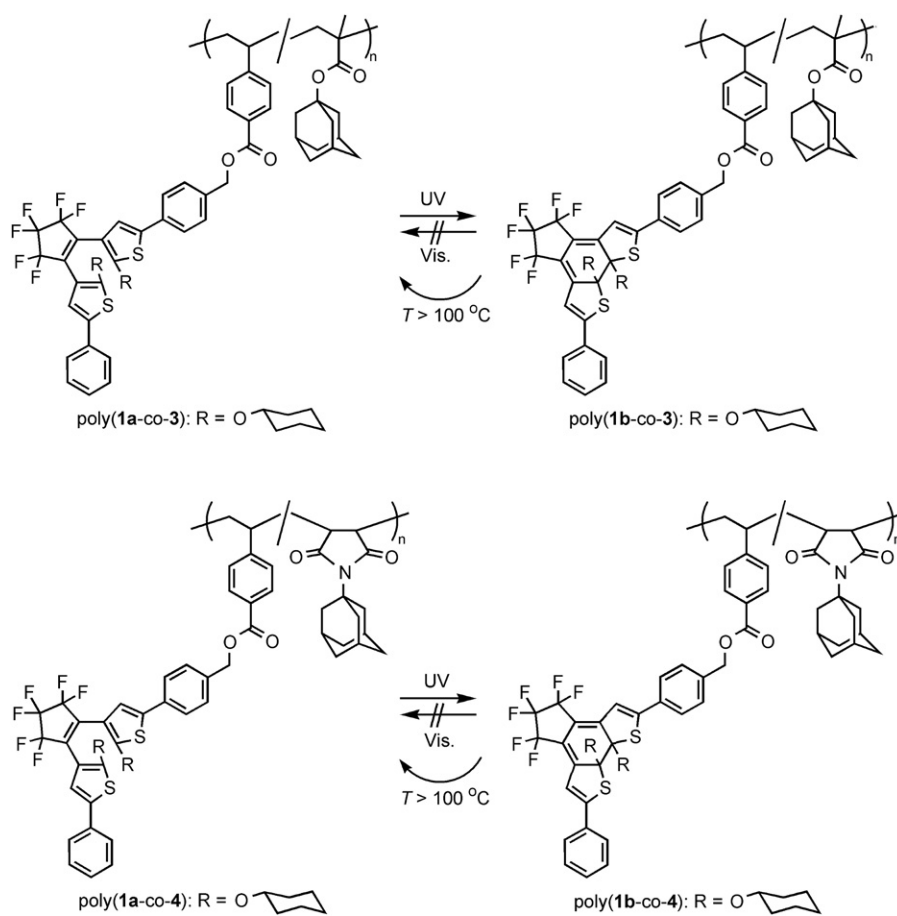
^a Glass transition temperature determined by DSC (10 °C min⁻¹).^b Initial decomposition temperature determined by TGA (10 °C min⁻¹).^c Not detected below decomposition temperature.

polymerization for 10 h, the diarylethene polymer was obtained in 58% yield. The resulting polymer had an *M_n* of 21,000 and an *M_w*/*M_n* of 1.85. The polydispersity of 1.5–2.0 indicates that the polymerization proceeded by a typical radical polymerization without any significant side reaction. The thermal properties of the polymer were evaluated using a differential scanning calorimetry (DSC) and a thermogravimetric analysis (TGA). Figure 1 shows DSC and TGA curves of the polymer. The polymer exhibited a *T_g* of 104 °C, a *T_{init}* of 234 °C, and a *T_{max}* of 300 °C. A diarylethene polymer with the methyl groups instead of the cyclohexyloxy groups has a *T_g* of 107 °C.¹⁷ Any significant decomposition of poly(**1a**) below 200 °C was not observed. The introduction of the cyclohexyl groups in the monomer and polymer was not affected to radical polymerization and the thermal properties, respectively.

If such functionalized polymer materials are used for application to image recordings according to the write-by-light/erase-by-heat system, they are required to have a higher *T_g* than 160 °C and the performance should be maintained even at that temperature. Copolymers of styrene with 1-adamantyl methacrylate (**3**) exhibit characteristics of high *T_g*. *T_g* of the copolymer increases with increasing the content of **3**. For example, the copolymer in the composition ratio of 1:1 has a *T_g* of 166 °C.¹⁸ On the other hand, copolymers of styrene with *N*-1-adamantylmaleimide (**4**) gave the alternate copolymer.¹⁹ The alternate copolymer exhibits *T_g* above 200 °C. If the diarylethene monomer (**1a**) is copolymerized with **3** or **4**, the resulting polymers may exhibit a higher *T_g* value than that of the homopolymer of **1a**.

In order to obtain high *T_g* diarylethene polymers, the copolymerization of **1a** and **3** was done in the content of 50, 60, and 69 mol % in the feed of **3** (Scheme 2). The resulting copolymers had a higher *M_n* than that of homopolymer of **1a**. Table 1 shows a *T_g* of the copolymers of **1a** with **3**. The *T_g* value increased with increasing the content of **3** in the copolymer. However, *T_g* increased only up to 130 °C even including 69 mol % of **3**.

Figure 1. DSC trace (a) and TGA curve (b) of poly(**1a**).



Scheme 2. Photochromic reactions of poly(1a-co-3) and poly(1a-co-4).

The copolymerization of **1a** with **4** was done aiming at the improvement of high T_g polymer. No significant endothermic peak was observed below 200 °C, as shown in Figure 2. It means that poly(1a-co-4) exhibits much higher T_g value than 240 °C.

2.2. Photochromism of diarylethene polymer

Upon irradiation with ultraviolet (UV) light, the toluene solution of poly(1a) turned blue and the colored state was thermally and photochemically stable. Figure 3 shows UV–vis absorption spectral changes upon irradiation with 313-nm light. Upon irradiation with UV light the new absorption band of the closed-ring form appeared at 650 nm. The conversion to the closed-ring form was determined to be 92% by the ^1H NMR and UV–vis absorption spectroscopic analyses, as shown in Figure 4.

On the other hand, the photochromism in the film on a quartz glass reached to 60% conversion at a photostationary state. The photocyclization reaction rate at the early stage in the film was smaller than that in toluene. In order to evaluate the photo-reactivity, the photocyclization quantum yields were examined in toluene and in the film. The quantum yield in toluene was determined to be 0.40. It was similar to that of the low molecular weight diarylethene molecule, 1,2-bis(2-cyclohexyloxy-5-phenyl-3-thienyl)perfluorocyclopentene, 0.43.¹⁶ On the other hand, the quantum yield of the polymer in the film was determined to be 0.26, which was considerably smaller than that in toluene. Diarylethene molecules are fixed in some conformations in the solid-state film because of the presence of bulky substituents such as the cyclohexyloxy groups. Some of the conformations are photochemically inactive.^{20,21} Therefore, in the case of the solid-state

film, the decrease in the population of the photoactive conformations of diarylethene moieties may result in the smaller photocyclization quantum yield.²²

2.3. Photostability and thermal stability of the colored form

Poly(1b) was thermally stable at room temperature and also stable under visible light. The photostability is due to the introduction of alkoxy groups at the 2- and 2'-positions. A diarylethene polymer (poly(2a)) having the methyl groups instead of the cyclohexyloxy groups has photoreversibility between open- and closed-ring form (Scheme 3).¹⁷ The introduction of the cyclohexyloxy groups results in small photocycloreversion quantum yield by a factor of ca. 20. Figure 5 shows a photostability of the colored state. Poly(1b) and poly(1b-co-4) were very stable to visible light in toluene, whereas poly(2b) was bleached with a faster rate. Such photostability of the colored state can be maintained even in the polymer film as well as in solution.

When the colored state of poly(1b) is heated at high temperature above 100 °C, it is expected to return to the colorless state to give poly(1a). The thermal decoloration reaction in the film was followed by the absorbance changes of the closed-ring forms. Figure 6a shows decay curves of thermal bleaching reactions of the closed-ring forms in the film of poly(1b). The color disappeared completely within 10 min at 150 °C to reproduce poly(1a). The photocoloration and thermal decoloration cycles can be repeated. The thermal bleaching reaction was followed by a first-order kinetics as shown in Figure 6b. The slope of the first-order kinetic plots corresponds to the rate constant of the reaction. The rate constants were obtained as shown in Table 2. The thermal

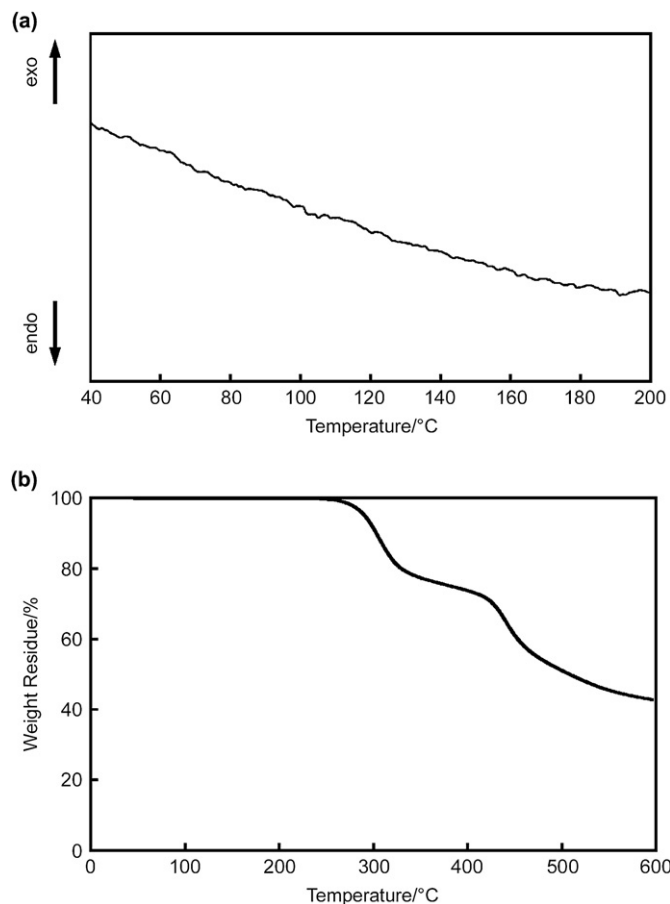


Figure 2. DSC trace (a) and TGA curve (b) of poly(**1a-co-4**).

decoloration reaction rates of poly(**1b**) were similar to that of the monomeric diarylethene.¹⁶ The activation energy (E_a) and the frequency factor (A) of the decoloration reaction were determined from the linear relation of the temperature dependence of the rate constants to be 125 kJ mol^{-1} and $2.0 \times 10^{13} \text{ s}^{-1}$, respectively, as shown in Figure 7. The values are identical with those of the monomeric diarylethene in solution: $E_a = 120 \text{ kJ mol}^{-1}$, $A = 4.4 \times 10^{12} \text{ s}^{-1}$.

The half-life times of the thermal cycloreversion reactions for the closed-ring form at 170 and 25 °C were estimated from the extrapolation of the linear relation to be 19 s and 8.7 years, respectively. The similar values to the monomeric diarylethene in decalin indicate that the introduction of the diarylethene chromophore to the polymer in the side chain functioned without any loss of the performance. The polymer has very rapid thermal cycloreversion rate at high temperature and high thermal stability at room temperature. The temperature dependence of the thermal cycloreversion reaction of poly(**1b-co-4**) is also shown in Figure 7. The performance of poly(**1b-co-4**) was maintained without any loss of the reactivity.

2.4. Application

The copolymer of **1a** with **4** satisfies requirements of photostability, thermally rapid reversibility at 170 °C, and higher T_g above 200 °C. The writing by UV light irradiation and erasing by heat in the poly(**1a-co-4**) film were accomplished below T_g of the polymer. Figure 8 shows image recordings of the poly(**1a-co-4**) by UV light irradiation in photowriting and erasing by heating at 140 °C. When the colorless film was irradiated with 365-nm light using a photo-mask, the colored pattern was observed. The pattern was stable for more than 1 day under visible light and was bleached by heating.

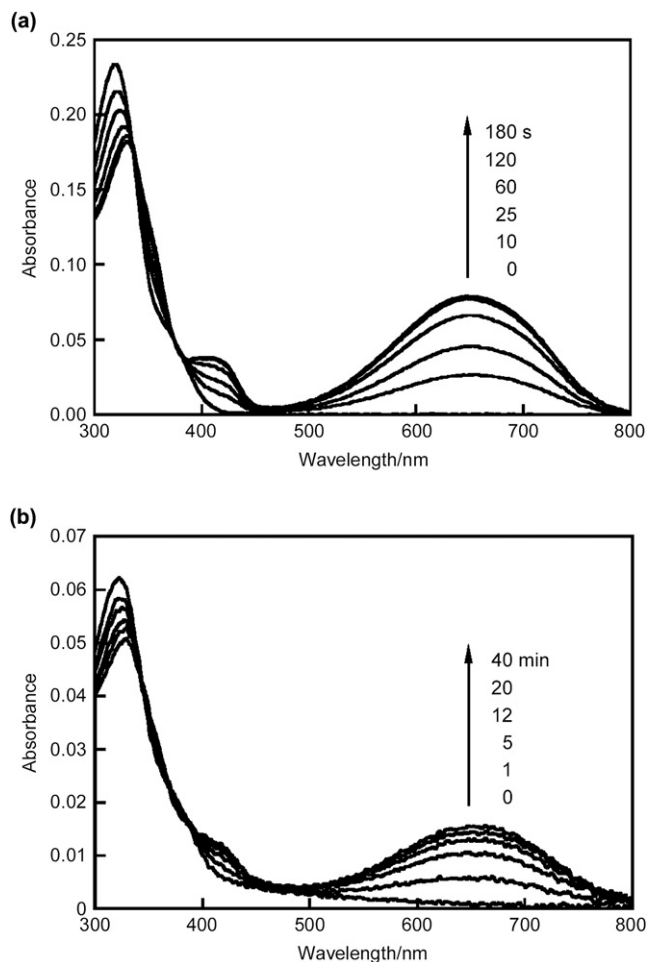


Figure 3. Absorption spectral changes of poly(**1a** in toluene (a) and in the film (b) upon irradiation with 313-nm light).

3. Conclusion

We synthesized functionalized polymer and copolymers having photochromic diarylethene chromophores with functional properties of photocoloration, photostability of the colored state, and

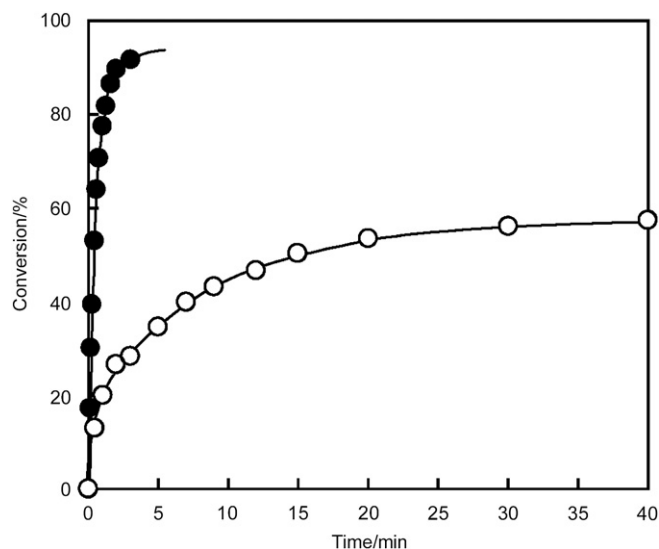
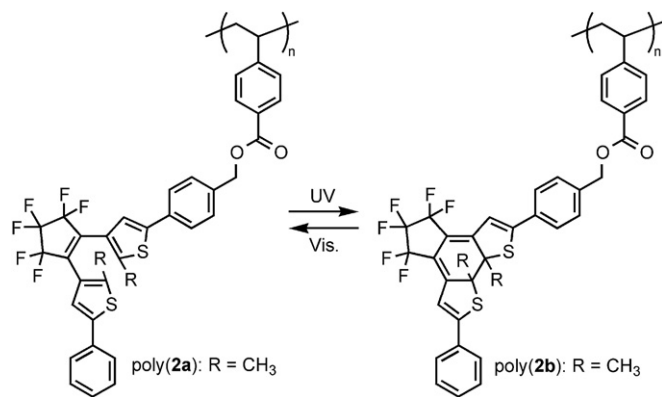


Figure 4. Time-conversion curves for the photocyclization reactions of poly(**1a**) in toluene (●) and in the film (○) upon irradiation with 313-nm light.



Scheme 3. Photochromic reaction of poly(2a).

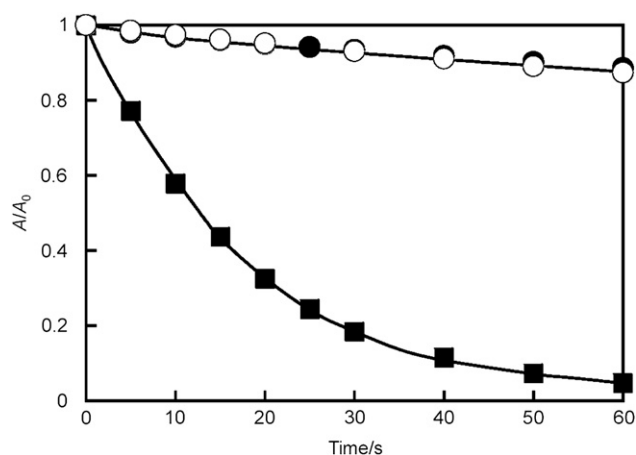


Figure 5. Photostability of poly(1b) (●), poly(1b-co-4) (○), and poly(2b) (■) in toluene upon irradiation with visible light.

thermal erasure by heating. Their polymers exhibited excellent photocoloration and rapid thermal bleaching above 150 °C. The colored state has a high photostability under visible room light. The copolymer with *N*-1-adamantylmaleimide exhibited extremely high T_g above 200 °C with keeping the photofunctional performance. Such photochromic polymer and copolymers with high T_g can be potentially applied to rewritable display materials and image recordings by a write-by-light/erase-by-heat system.

4. Experimental section

4.1. General

Solvents used were spectroscopic grade and purified by distillation. ¹H NMR spectra were recorded on a Jeol A-400 NMR spectrometer at 400 MHz. Initial temperature of degradation (T_{init}) and maximum degradation rate temperature (T_{max}) of the polymers were determined by a thermogravimetric analysis (TGA). TGA was carried out using a Seiko TG/DTA-6200 and a polymer sample was heated in a nitrogen stream at a heating rate of 10 °C min⁻¹. Glass transition temperature (T_g) was determined from an initial inflection point of temperature dependence on a differential scanning calorimetry (DSC). DSC was run using a Seiko DSC-6200 at a heating rate of 10 °C min⁻¹. Absorption spectra in a solution were performed with a JASCO V-560 spectrophotometer. A high-temperature chamber was used to maintain constant temperature of an absorption quartz cell in a solution. Absorption spectra of the

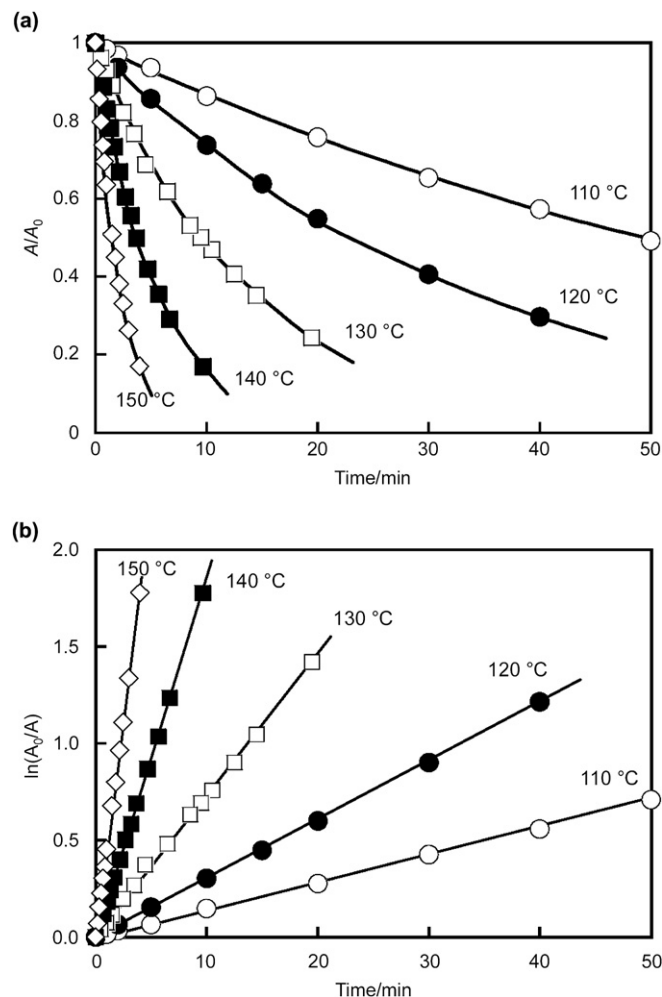


Figure 6. Decay curves (a) and first-order kinetic plots (b) for thermal cycloreversion reactions of poly(1b) in the neat film.

Table 2

Rate constant (k) and half-life time ($t_{1/2}$) of thermal cycloreversion reaction of poly(1b) and poly(1b-co-4) in the film

Temperature (°C)	Poly(1b)		Poly(1b-co-4)	
	k (s ⁻¹)	$t_{1/2}$ (min)	k (s ⁻¹)	$t_{1/2}$ (min)
90	2.2×10^{-5}	530	—	—
100	7.0×10^{-5}	170	—	—
110	1.9×10^{-4}	61	—	—
120	5.0×10^{-4}	23	3.8×10^{-4}	30
130	1.2×10^{-3}	9.6	1.0×10^{-3}	12
140	3.1×10^{-3}	3.7	2.7×10^{-3}	4.3
150	7.4×10^{-3}	1.6	6.7×10^{-3}	1.7
160	1.9×10^{-2}	0.61	1.8×10^{-2}	0.64

polymer film were measured using a microscope connected with a Hamamatsu PMA-11 photodetector. A hot stage (Mettler-Toledo FP90/FP82) was used to maintain constant temperature of the polymer film. Photoirradiation was carried out using a 200 W mercury-xenon lamp (Moritex MUV-202) as the light source. Monochromatic light was obtained by passing the light through a monochromator and a UV filter. The relative quantum yields were determined by comparing the reaction yield with a reference sample. The films were prepared by casting the toluene solution of the polymers on the quartz glass substrate.

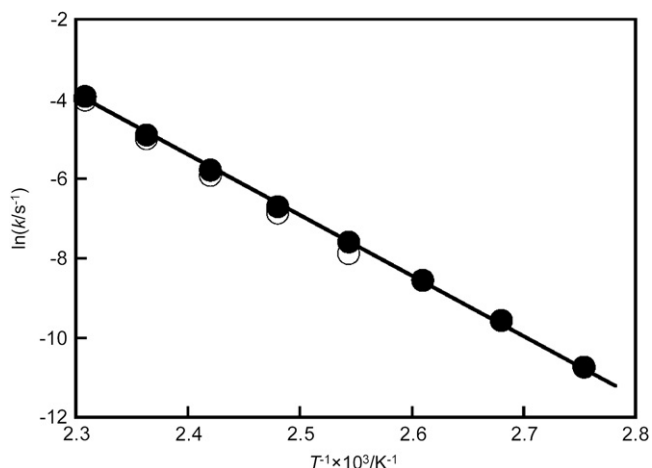


Figure 7. Temperature dependence of thermal cycloreversion reaction rate constants of poly(**1b**) in the film (●) and poly(**1b-co-4**) in the film (○).

4.2. Diarylethene monomer (**1a**)

Compound **1a** was prepared according to the synthetic routes as shown in Scheme 4.

4.2.1. 4-(4-Bromo-5-cyclohexyloxythiophen-2-yl)benzaldehyde (**6**)

To 45 mL of dry THF containing 3,5-dibromo-2-cyclohexyloxythiophene (**5**) (2.4 g, 7.0 mmol) was added 1.6 M *n*-BuLi solution in hexane (4.5 mL, 7.5 mmol) at -78°C under argon atmosphere, and the solution was stirred for 1 h at the low temperature. Tri-*n*-butyl borate (2.7 mL, 10 mmol) was slowly added to the reaction mixture at -78°C , and the mixture was stirred for 1.5 h at that temperature. After warming the solution up to room temperature, 20 wt% Na_2CO_3 (aq) (16 mL), 4-bromobenzaldehyde (1.3 g, 7.0 mmol), and tetrakis(triphenylphosphine) palladium(0) (0.34 g, 0.29 mmol) were added to the reaction mixture. The mixture was refluxed for 7.5 h at 70°C . The product was extracted with ether. The organic layer was dried over MgSO_4 , filtered, and concentrated. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (9:1) as the eluent to give 1.5 g of **6** in 59% yield. ^1H NMR (400 MHz, CDCl_3): δ =1.3–2.1 (m, 10H), 4.2 (sep, J =4 Hz, 1H), 7.15 (s, 1H), 7.6–7.9 (m, 4H), 10.0 (s, 1H).

4.2.2. 2-[4-(4-Bromo-5-cyclohexyloxythiophen-2-yl)-phenyl]-[1,3]dioxolane (**7**)

A toluene solution (46 mL) of **6** (0.46 g, 1.3 mmol) and ethylene glycol (0.85 g, 14 mmol) in the presence of a small amount of

p-toluenesulfonic acid was refluxed using a Dean–Stark condenser for 2.5 h by heating an oil bath at 150°C . The reaction mixture was neutralized by a sodium hydrogen carbonate solution. The product was extracted with ether. The organic layer was dried over MgSO_4 , filtered, and concentrated. The residue was purified by recrystallization from hexane to give 0.40 g of **7** in 78% yield. ^1H NMR (400 MHz, CDCl_3): δ =1.3–2.1 (m, 10H), 4.0–4.2 (m, 5H), 5.81 (s, 1H), 6.98 (s, 1H), 7.45–7.47 (m, 4H).

4.2.3. 1-(2-Cyclohexyloxy-5-phenyl-3-thienyl)-heptafluorocyclopentene (**8**)

To 25 mL of dry THF solution containing 3-bromo-2-cyclohexyloxy-5-phenylthiophene¹⁶ (0.39 g, 1.2 mmol) was added 1.6 M *n*-BuLi solution in hexane (0.87 mL, 1.4 mmol) at -78°C under argon atmosphere, and the solution was stirred for 1.5 h at that low temperature. Octafluorocyclopentene (0.27 mL, 1.9 mmol, Nippon Zeon) was added to the reaction mixture at -78°C , and the mixture was stirred for 1.5 h at that temperature. The reaction was stopped by the addition of water. The product was extracted with ether. The organic layer was dried over MgSO_4 , filtered, and concentrated. The residue was purified by silica gel column chromatography using hexane as the eluent to give 0.42 g of **8** in 81% yield. ^1H NMR (400 MHz, CDCl_3): δ =1.3–2.1 (m, 10H), 4.28 (sep, J =4 Hz, 1H), 7.15 (s, 1H), 7.25–7.50 (m, 5H); MS (FAB) m/z (M^+) 450.

4.2.4. 1-(2-Cyclohexyloxy-5-phenyl-3-thienyl)-2-[2-cyclohexyloxy-5-[4-([1,3]-dioxolanyl)-phenyl]-3-thienyl]perfluorocyclopentene (**9**)

To 5 mL of dry THF solution containing **7** (1.5 g, 3.7 mmol) was added 1.6 M *n*-BuLi solution in hexane (2.5 mL, 4.0 mmol) at -78°C under argon atmosphere, and the solution was stirred for 1.5 h at that low temperature. Compound **8** (1.0 g; 2.2 mmol) in dry THF (5 mL) was slowly added to the reaction mixture at -78°C , and the mixture was stirred for 6.5 h at that temperature. The reaction was stopped by the addition of water. The product was extracted with ether. The organic layer was dried over MgSO_4 , filtered, and concentrated. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (8:2) as the eluent to give 0.84 g of **9** in 50% yield. ^1H NMR (400 MHz, CDCl_3): δ =1.0–2.1 (m, 20H), 4.0–4.2 (m, 6H), 5.81 (s, 1H), 7.1–7.5 (m, 11H).

4.2.5. 1-[2-Cyclohexyloxy-5-(4-formylphenyl)-3-thienyl]-2-(2-cyclohexyloxy-5-phenyl-3-thienyl)perfluorocyclopentene (**10**)

Compound **10** was prepared from **9** by refluxing in the presence of pyridinium *p*-toluenesulfonate (0.18 g, 0.70 mmol) in acetone (5 mL) for 2 h. The product was extracted with ether. The organic layer was dried over MgSO_4 , filtered, and concentrated. The residue was checked by ^1H NMR and used for the following reaction without further purification. Yield: 0.15 g (100%). Compound **10**: ^1H

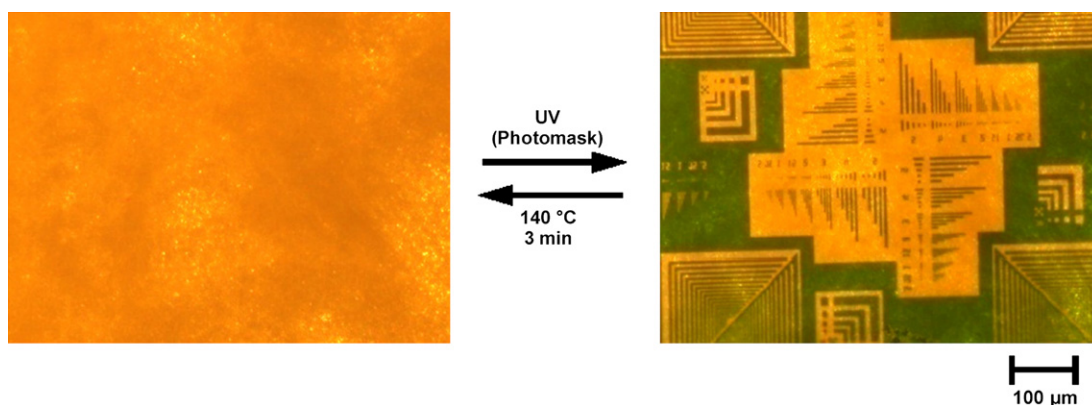
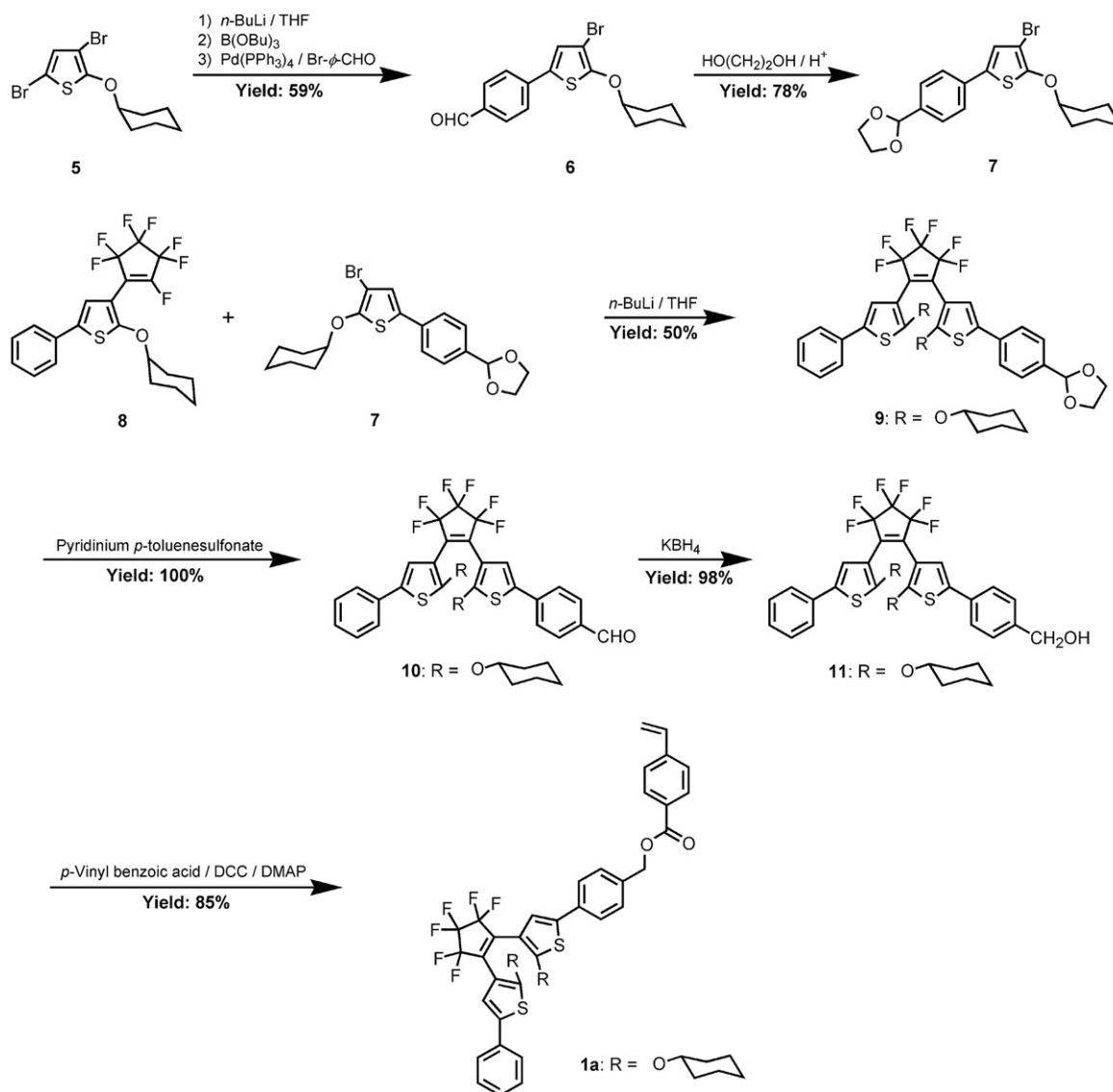


Figure 8. Photopatterning of poly(**1a-co-4**) film using a photomask by UV light irradiation and thermal bleaching by heating for 3 min at 140°C .

Scheme 4. Synthetic route of photochromic diarylethene monomer **1a**.

NMR (400 MHz, CDCl₃): δ =1.0–2.1 (m, 20H), 4.05 (sep, *J*=4 Hz, 2H), 7.1–7.9 (m, 11H), 10.0 (s, 1H).

4.2.6. 1-[2-Cyclohexyloxy-5-[4-(hydroxymethyl)phenyl]-3-thienyl]-2-(2-cyclohexyloxy-5-phenyl-3-thienyl)-perfluorocyclopentene (**11**)

To a solution of **10** (0.15 g, 0.22 mmol) in ethanol (7 mL) was added slowly a solution of potassium borohydride (12 mg, 0.22 mmol) in ethanol (1 mL) and water (1 mL). After stirring for 1 h at room temperature, the reaction mixture was extracted with ether and the organic layer was dried over MgSO₄. Removal of the solvent gave alcohol **11**. It was used for the following reaction without any further purification. Yield: 0.15 g (98%). Compound **11**: ¹H NMR (400 MHz, CDCl₃): δ =1.0–2.1 (m, 21H), 4.03 (sep, *J*=4 Hz, 2H), 4.7 (s, 2H), 7.1–7.5 (m, 11H).

4.2.7. Monomer **1a**

A solution of **11** (0.15 g, 0.21 mmol), *p*-vinylbenzoic acid (0.062 g, 0.42 mmol), dicyclohexylcarbodiimide (DCC) (0.094 g, 0.46 mmol), and 4-dimethylaminopyridine (DMAP) (0.028 g, 0.23 mmol) in dry THF (4.6 mL) was stirred under argon for 24 h at room temperature. To the reaction mixture was added an

aqueous sodium hydrogen carbonate solution, and the mixture was extracted with ether. The organic layer was dried over MgSO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel using hexane/ethyl acetate (8:2) as the eluent. Pure **1a** was obtained by a further purification with HPLC. Yield: 0.15 g (85%). Compound **1a**: ¹H NMR (400 MHz, CDCl₃): δ =1.0–2.1 (m, 20H), 4.03 (sep, *J*=4 Hz, 2H), 5.36 (s, 2H), 5.39 (d, *J*=11 Hz, 1H), 5.86 (d, *J*=18 Hz, 1H), 6.74 (dd, *J*=11 and 18 Hz, 1H), 7.1–7.5 (m, 13H), 8.0–8.1 (m, 2H). HRMS (FAB) *m/z*=848.2438; calcd for C₄₇H₄₂F₆O₄S₂ *m/z*=848.2429 (M⁺).

4.3. Polymerization

Polymerizations were run in glass tubes sealed off under vacuum. Monomer **1a** was polymerized by a radical polymerization using 2,2'-azobisisobutyronitrile (AIBN) as an initiator in toluene at 60 °C. After the polymerization, the polymer was obtained by precipitation in methanol. Number- and weight-average molecular weight (*M_n* and *M_w*) of the polymers was determined by gel-permeation chromatography (GPC) at 40 °C in THF as the eluent. GPC

was performed with a Tosoh 8000 series GPC system equipped with TSK-gel columns.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research (C) (No. 19550142) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and PRESTO, Japan Science and Technology Agency.

References and notes

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