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PAPER

Photochromic polymers bearing various diarylethene chromophores as the pendant: synthesis, optical properties, and multicolor photochromism†

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Photochromic polymers with various diarylethene derivatives were synthesized by a conventional radical polymerization of styrene derivatives having diarylethene chromophores as the pendant. All the polymers exhibited reversible photochromism in the film as well as in solution, while the photocyclization conversion in the film decreased in comparison with that in solution because of a restriction of the conformational structure in the solid state. Although the photocyclization and photocycloreversion quantum yields at the initial stage of the reactions in the film were comparable to those in solution, the apparent cycloreversion quantum yield decreased along with the reaction, which is derived from a distribution of the quantum yields in the solid state. Finally, the photochromic terpolymers consisting of three diarylethene monomers which show photochromism changing color to cyan, magenta, and yellow were synthesized. The terpolymers were demonstrated to show bright colors including black, green, red, and blue both in solution and in the solid state by selective bleaching processes. Such multicolor photochromic polymers composed of diarylethene derivatives have a potential for rewritable photochromic display devices.

Introduction

Rewritable media are of great benefit not only to our lives but also in terms of limited resources and environmental problems that we have been confronted with. Although plenty of rewritable data storage and display media have been developed with significant progress of personal computers, piles of paper media are still used in a variety of situations. One reason for the great use of the paper is that the medium has an advantage over electronic display media in terms of convenience and readability, and is useful for a temporary recording medium rather than for permanent data storage. Meanwhile, most of them are single-use and end up in the garbage. From this point of view, a lot of paper-like rewritable display devices such as electronic papers and thermosensitive rewritable papers have also been developed. Among them, a paper-like and full-color display medium using three photochromic fulgide derivatives changing color to yellow (Y), cyan (C), and magenta (M) has been reported.[1] Fulgide is one of the photochromic compounds whose color can be reversibly changed upon alternating irradiation with ultraviolet (UV) and visible light, and most of the fulgide derivatives never have bleached color at room temperature in the dark unlike azobenzene and spiropyran derivatives.[2] Thus, the photochromic medium can be reversibly written and erased by photoirradiation, and the written information does not disappear in the dark. In order to design and develop the photochromic full-color rewritable materials, it is necessary to examine more detailed information on the photochromic reactivities, thermal stability, color tones, and fatigue-resistance. In addition, it is also required to develop photochromic polymers.

Diarylethene is known as a thermally stable photochromic compound that undergoes back-and-forth photoisomerization between a colorless open-ring form and a colored closed-ring form upon alternating irradiation with UV and visible light.[3,4] The photochromic reaction of a diarylethene derivative can be repeated more than 10 000 cycles, and the color can be modulated by changing the structure or additional substituent.[3] These excellent properties are suitable for the rewritable display medium. Along these lines, there are several reports focusing on multicolor photochromic materials using the diarylethene derivatives. For instance, a fused diarylethene trimer consisting of three different diarylethene frameworks,[5] multicolor two- or three-component diarylethene mixed crystals,[6,7] diarylethene mixture on a silica plate,[8] and multicolor polymer materials[9] have been reported.

Diarylethene derivatives dispersed in a matrix,[8,10] incorporated into the main chain of a polymer,[11–14] or connected to the polymer chain[9,15–21] are useful in terms of application for the rewritable display devices because they can directly be coated on paper or any other solid surfaces. However, in most cases, the reactivity of the diarylethene derivatives in the polymer matrix is different from that in solution. Especially, the movement of the molecules

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depends on the glass transition temperature (T_g) and the free volume in the polymer matrix. Therefore, the photocyclization and cycloreversion quantum yields are affected by T_g of the polymer matrix.[21] A distribution of the quantum yields of diarylethenes in a polymer matrix has been evaluated by numerical calculation.[22,23] Namely, the photochromic reaction of the diarylethene derivatives in the polymer matrix is affected by the ambient surrounding such as stiffness of the matrix and the situation of the chromophores embedded in the matrix. An understanding of the photochromic reaction behavior in the solid state is still an important topic to develop the rewritable and paper-like display media.

Color-modulation is, of course, essential for the full-color photochromic display media. Multicomponent, multi-addressable polymers composed of diarylethenes showing blue (B), red (R), and yellow (Y) have already been synthesized by ring-opening metathesis polymerization.[9] Although the polymers showed a wide range of bright colors, they did not entirely demonstrate all the colors from a single polymer. A lot of diarylethene derivatives have been so far reported. However, there is no report on the completely full-color photochromism showing all the colors in the CMY system in a single component. If we can incorporate three diarylethene moieties showing C, M, and Y in the appropriate ratio, all the colors including black (K), green (G), and so forth can be demonstrated in the system.

We have previously synthesized a photochromic polymer with a diarylethene moiety as a pendant (poly(**2a**) in Scheme 1) by a conventional radical polymerization.[24] Such a pendant-type photochromic polymer has a large advantage to contain high density (76 wt% for poly(**2a**)) of the chromophores in the polymer, which can display vivid and high-contrast images. In addition, poly(**2a**) exhibited reversible photochromism with high cyclization conversion (92%) even in the film to change color to B. In order to develop the rewritable full-color display devices, we have to prepare the photochromic polymers showing all the colors in the CMY system.

In this study, we designed, synthesized, and characterized novel diarylethene homopolymers (poly(**1a**)–poly(**8a**)) as shown in Scheme 1. All the homopolymers exhibited reversible photochromism in the solid state as well as in solution with relatively high cyclization conversion. The cyclization and cycloreversion quantum yields of the polymers were examined both in solution and in the film. Finally, we chose three components from diarylethene monomers **1a–8a** to display all the colors in the CMY system and synthesized their diarylethene terpolymers to demonstrate the rewritable process on paper media by photoirradiation.

Experimental

Measurements

^{1}H NMR spectra were recorded on a JEOL A-400 or a BRUKER AV-300N spectrometer. Mass spectra were taken with a JEOL JMS-700T mass spectrometer. Gel-permeation chromatography (GPC) was performed using a Tosoh 8000 series GPC system equipped with TSK-gel columns at 40 °C in tetrahydrofuran (THF) as the eluent. Standard polystyrenes were used as the calibration standard. Differential scanning calorimetry (DSC) was performed on a SEIKO Instruments EXSTAR 6000 DSC6200. Absorption spectra were measured using a UV/visible absorption spectrophotometer (JASCO V-560). Photoirradiation was conducted using a 200 W mercury–xenon lamp (MORITEX MUV-202) or a 300 W xenon lamp (Asahi Spectra MAX-301) as a light source. Monochromatic light was obtained by passing the light through a monochromator (Jobin Yvon H10 UV or JASCO CT-10) and glass filters. Photocyclization conversions of diarylethene chromophores were determined by ^{1}H NMR and absorption spectroscopies. Photocyclization and cycloreversion quantum yields were determined as relative quantum yields using diarylethene derivatives whose quantum yields have already been determined.[25] Molar absorption coefficients of the diarylethene polymer films are assumed to be the same as those in toluene.

Materials

2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Toluene was purified by distillation. All other reagents were commercially available and used without further purification.

Synthesis of diarylethene monomers

Diarylethene monomer **2a** was prepared by the method described in our previous paper.[24] **1a** and **3a–8a** were synthesized from the corresponding diarylethenes with a formyl group as well as **2a**. The synthetic scheme of all the diarylethene monomers is shown in Scheme S1 in the ESI†. The details are described in the ESI†.

Synthesis of diarylethene homo- and terpolymers

Diarylethene homo- and terpolymers were prepared by a conventional radical polymerization of the corresponding monomers using AIBN as the initiator in toluene at 60 °C. The polymers were obtained by precipitation in methanol for poly(**1a**)–poly(**7a**) or hexane for poly(**8a**) and terpolymers. The resulting polymers and terpolymers were purified by reprecipitation.

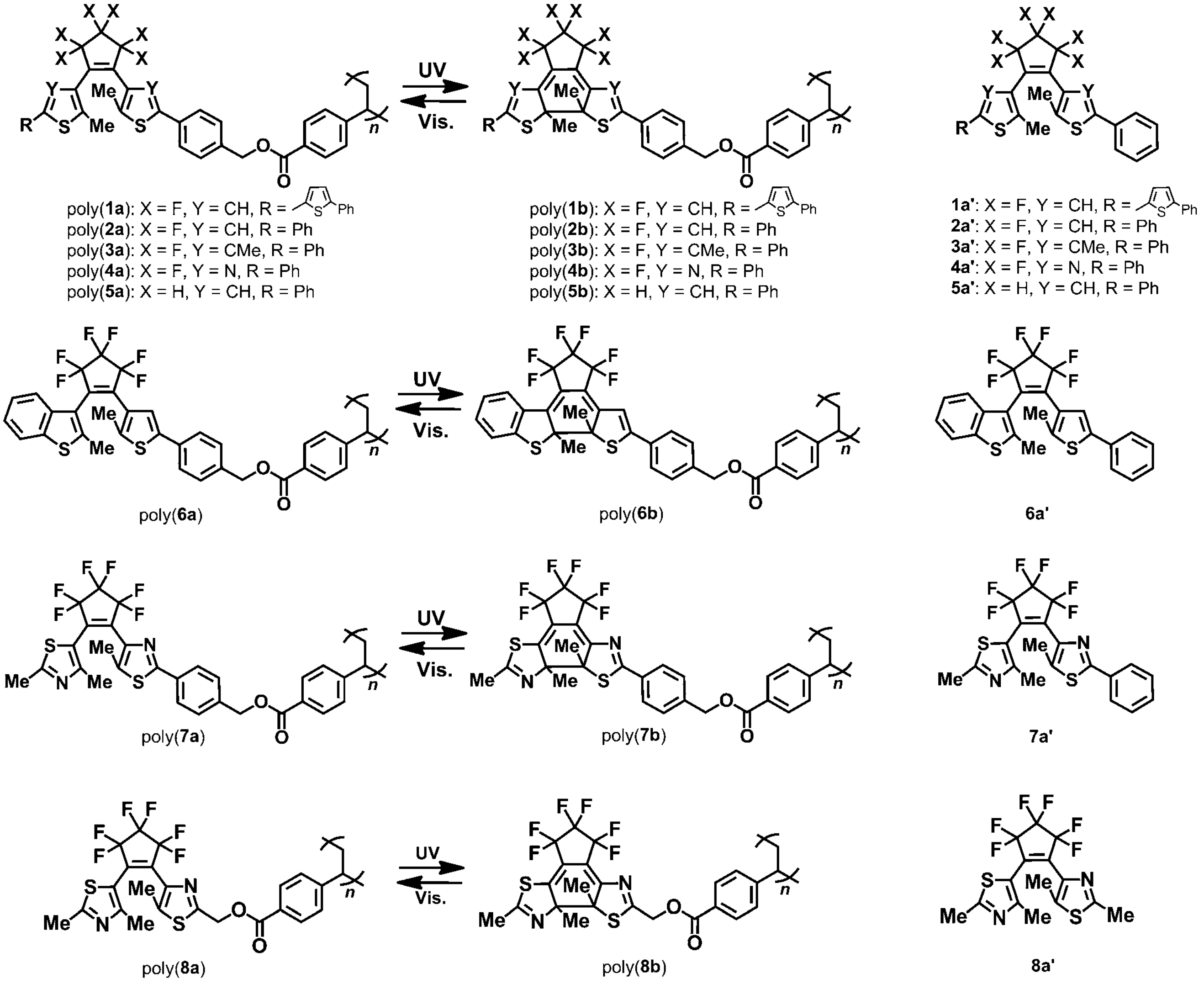
Synthesis of diarylethene derivatives

Diarylethene derivatives (**1a′–8a′**) as references were synthesized according to the methods similar to the diarylethene monomers. The details are described in the ESI†.

Results and discussion

Polymerization

Table 1 shows polymerization conditions, yields, number-average molecular weight (M_n), polydispersity (M_w/M_n), and glass transition temperature (T_g) of the diarylethene homopolymers. The polymerization reactivities of **1a–8a** are similar to each other independent of the molecular structure of the diarylethene moieties in the side chain. T_g of the polymers was 77–120 °C depending on the molecular structure of the side chain. Fig. 1 shows the relationship between T_g and molar mass of the pendant group of the polymers. T_g increased with an increase in the molar mass of the pendant group. It is known that T_g values



Scheme 1 Diarylethene homopolymers and reference compounds used in this work.

Table 1 Polymerization conditions and characterization of poly(**1a**)–(**8a**)

Monomer	[Monomer]/M	[AIBN]/M	Time/h	Yield (%)	M_n	M_w/M_n	T_g/°C
1a	0.37	0.020	14.5	43	34 000	2.51	120
2a[a]	0.37	0.020	10	59	22 400	2.18	106
3a	0.37	0.020	10	70	24 000	2.26	104
4a	0.37	0.020	10	79	41 900	2.24	102
5a	0.37	0.020	10	83	25 900	2.21	93
6a	0.37	0.020	10	53	21 400	2.31	112
7a	0.37	0.020	10	73	28 600	1.99	82
8a	0.37	0.020	10	68	24 400	1.76	77

[a] Ref. 24

of polystyrene derivatives depend on the molecular weight of the polymer[26] and side chain structure.[27,28] Because there is no significant difference in M_n values of the polymers in the present work, it is considered that bulkiness of the diarylethene moieties in the side chain directly affects cooperative motion of the chain segments. The T_g values of the diarylethene polymers in the present work are much higher than room temperature as well as polystyrene. Therefore, they can be used as a film in the solid state at ambient temperature.

Photochromism of diarylethene homopolymers in solution

Fig. 2 shows absorption spectral changes of poly(**1a**) in toluene upon irradiation at 313 nm. The new absorption band appeared

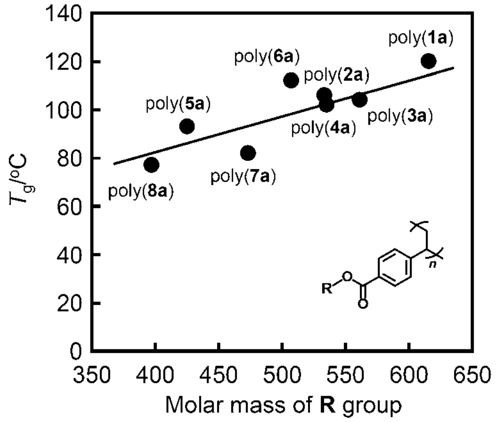


Fig. 1 Relationship between T_g and molar mass of the pendant group in poly(**1a**)–poly(**8a**).

in the visible region, which can be assignable to the generation of poly(**1b**). The spectrum reverted to the initial shape upon irradiation with visible light because of the photocycloreversion reaction to poly(**1a**). Such photochromic behavior was observed in all the diarylethene homopolymers. The absorption spectra of poly(**1a**)–poly(**8a**) in toluene in the photostationary state (PSS) upon irradiation at 313 nm are shown in Fig. 3a. The diarylethene polymers exhibited various colors depending on the structure of the diarylethene moiety in the side chain and ranging in the visible region from 400 nm to 750 nm. Therefore, we succeeded in preparing the photochromic polymer materials using the diarylethene derivatives with absorption spectra covering the entire visible region. Table 2 summarizes the absorption maximum (λ_{max}) in the visible region, molar absorption coefficient (ε) at λ_{max}, photocyclization conversions in the PSS, photocyclization quantum yields upon irradiation at 313 nm ($\Phi_{o\rightarrow c}$), and photocycloreversion quantum yields upon irradiation at λ_{max} ($\Phi_{c\rightarrow o}$) for poly(**1a**)–poly(**8a**) in toluene. Table 3 shows those for **1a′**–**8a′** as the reference compounds in hexane.[29,30] One can notice that the optical properties of the diarylethene polymers are almost the same as those of the corresponding reference compounds. This result indicates that the diarylethene moieties attached to the polymer chain can undergo the photochromic reaction in high photocyclization conversion in solution as well as polymer-free diarylethenes (**1a′**–**8a′**).

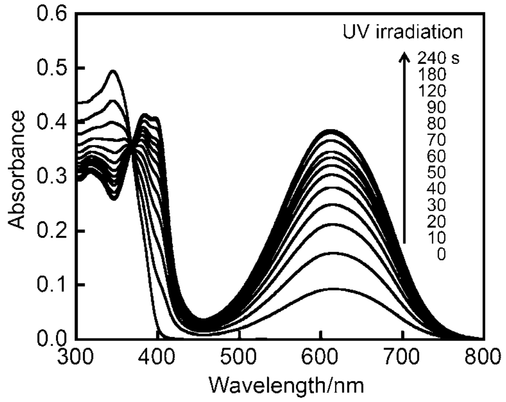


Fig. 2 Absorption spectral changes of poly(**1a**) in toluene upon irradiation at 313 nm: [poly(**1a**)] = 1.8×10^{-5} M.

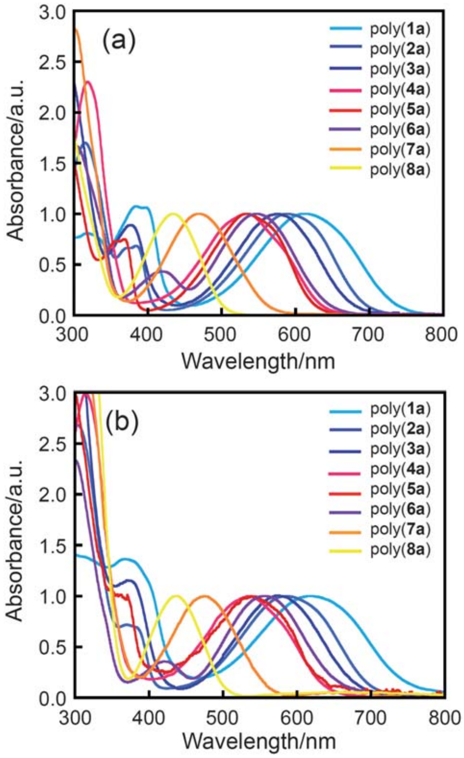


Fig. 3 Normalized absorption spectra of poly(**1a**)–poly(**8a**) (a) in toluene and (b) in the film in the PSS upon irradiation at 313 nm.

Photochromism of diarylethene homopolymers in the solid state

Fig. 4 shows photographs of poly(**1a**)–poly(**8a**) powders before and after UV light irradiation. All the polymer powders exhibited bright colors upon irradiation with UV light, and the color disappeared upon irradiation with visible light. These results indicate that poly(**1a**)–poly(**8a**) exhibited reversible photochromism in the solid state as well as in solution. Fig. 3b shows absorption spectra of poly(**1a**)–poly(**8a**) films cast on the quartz glass in the PSS upon irradiation at 313 nm. The cast films were fabricated by casting the toluene solution of the diarylethene polymers on the quartz glass. The absorption spectra in the cast films are similar to those in the solution, while the cyclization conversions decreased to 40–70% of those in the solution except for poly(**2a**) as can be seen from Table 2. The decrease of the cyclization conversion is considered to be mainly due to a structural restriction of the diarylethene moiety in the solid state. The open-ring form of diarylethene derivatives has two conformations: parallel conformation (P form) and antiparallel conformation (AP form) in which the aryl rings are in mirror symmetry and C_2 symmetry, respectively.[30] The cyclization reaction takes place only from the AP form. In solution, the ratio of the AP form to the P form is *ca.* 1 : 1 in most cases unless the diarylethene derivative is characteristically designed to form the AP form.[31,32] In addition, the diarylethene derivative can thermally transform to each conformation in solution at room temperature. This is the reason why the cyclization conversion in

Table 2 Absorption maximum in the visible region (λ_{max}), molar absorption coefficient at λ_{max} (ε), photocyclization conversions upon irradiation at 313 nm, photocyclization quantum yields upon irradiation at 313 nm ($\Phi_{o\rightarrow c}$), and photocycloreversion quantum yields upon irradiation at λ_{max} ($\Phi_{c\rightarrow o}$) of poly(**1a**)–poly(**8a**) in toluene and in the film

		Conversion (%)		$\Phi_{o\rightarrow c}$		$\Phi_{c\rightarrow o}$	
Diarylethene polymer	λ_{max}/nm (ε/M^{-1} cm^{-1}) in toluene	In toluene	In film	In toluene	In film[b]	In toluene	In film[c]
Poly(**1a**)	612 (22 700)	96	56	0.50	0.46	0.00033	0.00031
Poly(**2a**)[a]	592 (16 900)	97	92	0.54	0.53	0.0044	0.0034
Poly(**3a**)	576 (10 300)	79	40	0.57	0.34	0.013	0.0085
Poly(**4a**)	534 (14 200)	88	63	0.47	0.45	0.014	0.010
Poly(**5a**)	534 (14 300)	80	44	0.52	0.47	0.0045	0.0023
Poly(**6a**)	547 (12 800)	90	64	0.55	0.44	0.031	0.020
Poly(**7a**)	470 (10 300)	71	47	0.38	0.35	0.091	0.075
Poly(**8a**)	434 (5900)	69	28	0.43	0.39	0.57	0.49

[a] Ref. 24. [b] At the initial stage of photocyclization from the open-ring form. [c] At the initial stage of photocycloreversion from the PSS.

Table 3 Optical properties of **1a′**–**8a′** in hexane

Diarylethene	λ_{max}/nm (ε/M^{-1} cm^{-1})	Conversion (%)	$\Phi_{o\rightarrow c}$	$\Phi_{c\rightarrow o}$	Ref.
1a′	602 (24 900)	97	0.55	0.00038	This work
2a′	575 (15 600)	97	0.59	0.0083	29
3a′	562 (11 000)	79	0.46	0.015	30
4a′	524 (14 900)	87	0.48	0.018	This work
5a′	528 (17 200)	93	0.54	0.0083	This work
6a′	537 (15 500)	81	0.55	0.090	This work
7a′	459 (11 200)	77	0.40	0.11	This work
8a′	423 (6470)	77	0.45	0.57	This work

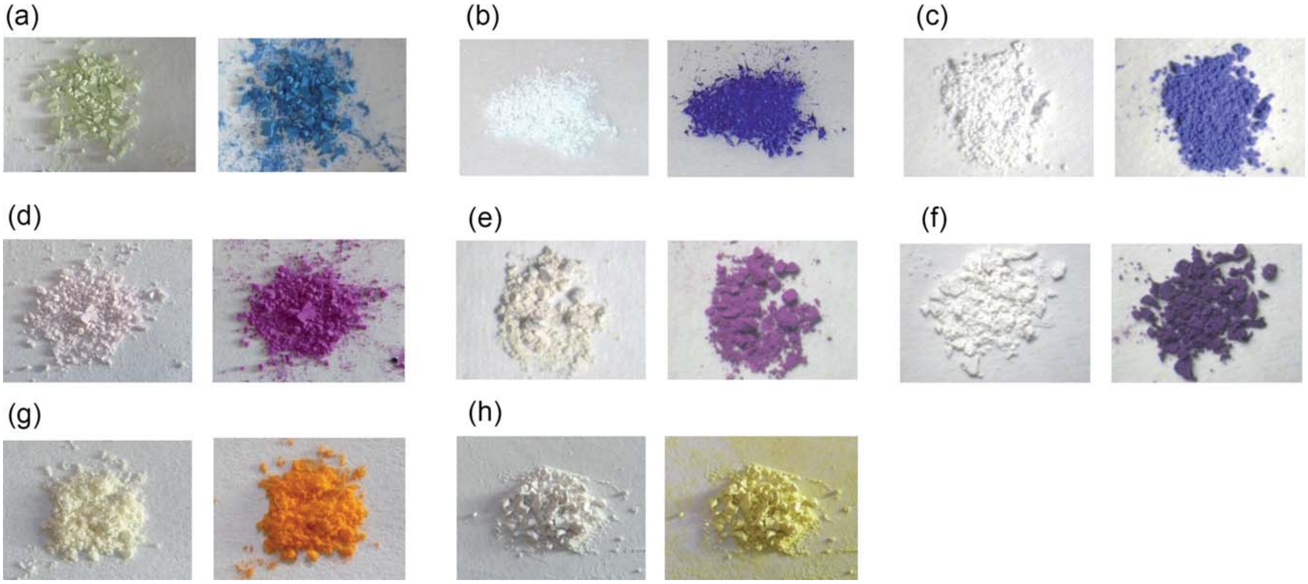


Fig. 4 Photographs of (a) poly(**1a**), (b) poly(**2a**), (c) poly(**3a**), (d) poly(**4a**), (e) poly(**5a**), (f) poly(**6a**), (g) poly(**7a**), and (h) poly(**8a**) powders before (left) and after (right) irradiation with UV light.

solution upon irradiation with UV light is relatively high (69–97%) while the photocyclization quantum yield is around 50%. In the film whose T_g is higher than room temperature, however, it is difficult for the diarylethene moiety to convert to each form during the two conformations because the chromophore is confined in the solid state. Thus, the photocyclization conversions of poly(**1a**)–poly(**8a**) in the film were lower than those in the solution. In fact, the cyclization quantum yields in the film at the initial stage of the reaction are comparable to those in the solution as shown in Table 2. These results indicate that the decrease of the cyclization conversion was ascribed not to the decrease of the quantum yield, but to the structural restriction of the chromophore in the solid state. It is noteworthy that the poly(**2a**) film exceptionally exhibited high cyclization conversion.[24] It is possible that each conformation (P and AP forms) of the diarylethene moiety in poly(**2a**) can easily transform into another form even in the film. This fact is considered to arise from a structural character of poly(**2a**). In the solid state, it is concluded that the cyclization conversions for poly(**1a**)–poly(**8a**) are high enough to exhibit brilliant colors.

Cycloreversion quantum yields of diarylethene homopolymers in the solid state

In order to discuss the photochromic reactivity of the diarylethene homopolymers in the solid state, the photocycloreversion quantum yields in the films of poly(**1a**)–poly(**8a**) were examined using the films in the PSS upon irradiation at 313 nm. The cycloreversion quantum yields ($\Phi_{c\rightarrow o}$) can be determined using the following equation:[25]

$$\log\left(10^{A(t)} - 1\right) = -\Phi_{c\rightarrow o}\varepsilon It + \log\left(10^{A(0)} - 1\right) \tag{1}$$

where $A(0)$ and $A(t)$ are absorbances at the irradiation wavelength before and after irradiation for time t, respectively. ε and I are the molar absorption coefficient and intensity of the incident light, respectively, at the wavelength. The plot of t against the left-hand side term in eqn (1) shows a linear relationship as far as the $\Phi_{c\rightarrow o}$ value is constant. The $\Phi_{c\rightarrow o}$ values for poly(**1a**)–poly(**8a**) and **1a′**–**8a′** in the solution can be unambiguously determined from the slope as shown in Table 2 because of the linear relationship. In the film, however, the plots between the left-hand side term in eqn (1) and irradiation time did not show the linear relationship. It means that the cycloreversion quantum yields change depending on the conversion. The relationship between the apparent $\Phi_{c\rightarrow o}$ determined from the slope of the tangential line to eqn (1) fitted to the experimental data and the content of the closed-ring form in the polymer is shown in Fig. 5. The $\Phi_{c\rightarrow o}$ value at the initial stage of the reaction in the film shown in Table 2 is comparable to that in the solution, while a significant decrease derived from the structural restriction of the chromophore in the solid state was observed as the reaction proceeds. These results are consistent with a system reported previously in which diarylethene derivatives are dispersed in polymer matrices.[22] As seen in Fig. 5, a trend of the decrease of the apparent $\Phi_{c\rightarrow o}$ along with the cycloreversion reaction is similar to each other. It is worth mentioning that the molecular structure and the optical property of the diarylethene moiety in the side chain have a significant effect on the apparent $\Phi_{c\rightarrow o}$ distribution. We could show that the photocycloreversion reactivities of the diarylethene derivatives tethered to polymer chain as the pendant are also affected by the structural restriction in the film as well as the diarylethene derivatives dispersed in the polymer matrix.

Design of multicolor diarylethene terpolymer

In order to express multicolor photochromism based on the CMY system, we should prepare at least three diarylethene components showing C, M, and Y. As described above, we prepared various types of diarylethene polymers and examined their optical properties. According to their properties, poly(**1a**), poly(**4a**), and poly(**8a**) were chosen as the C, M, and Y components, respectively. Although the multicolor photochromism can be achieved by a polymer blend consisting of poly(**1a**), poly(**4a**), and poly(**8a**), we aimed to create more sophisticated photochromic materials, terpolymers composed of three diarylethene monomers, **1a**, **4a**, and **8a**. Using such terpolymers we can demonstrate all the colors from only a single polymer component, which leads to no concern with phase separation of the chromophores or homopolymers, ease of the coating process to fabricate the full-color devices, and writing more microscopic images. If the terpolymers can exhibit K upon irradiation with UV light, various colors and images will be expressed by selective bleaching to apply to multicolor displays, inks, and barcodes. In order to demonstrate K, the three diarylethene chromophores in the terpolymer should show similar extent of color (absorbance)

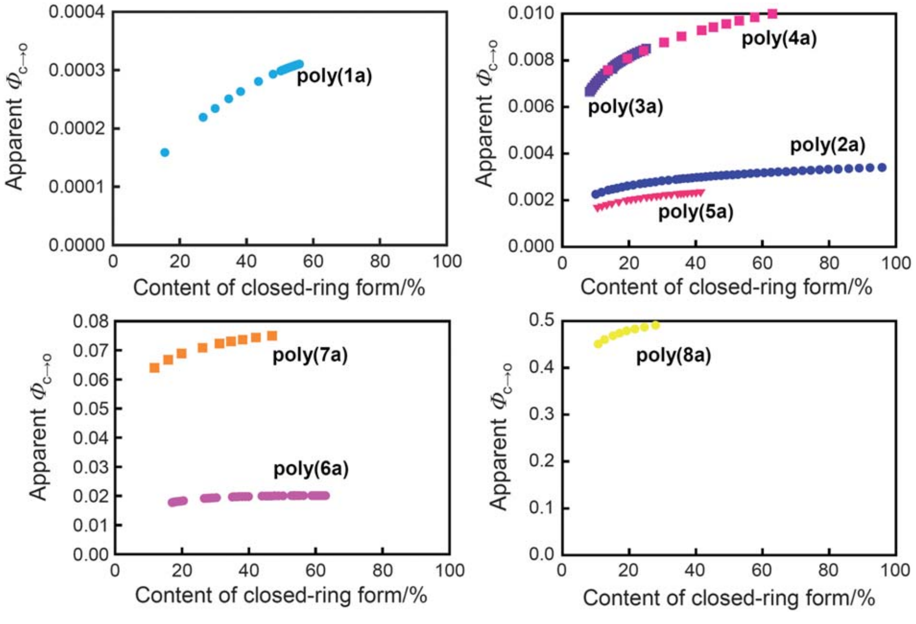


Fig. 5 Relationship between the apparent cycloreversion quantum yield and the content of the closed-ring form for poly(**1a**)–poly(**8a**).

in the polymer after UV light irradiation, as shown in Fig. 6. The ideal molar ratio of three components in the terpolymer ([**1a**] : [**4a**] : [**8a**] = 10 : 14: 76) can be calculated by considering the cyclization conversion in the film and the molar absorption coefficient shown in Table 2: (0.56 × 22 700 × [**1a**]) : (0.63 × 14 200 × [**4a**]) : (0.28 × 5900 × [**8a**]) = 1 : 1 : 1.

The polymerization conditions including the ideal one discussed above, yields, M_n, M_w/M_n, and T_g of the terpolymers are shown in Table 4. The molar ratio of [**1a**] : [**4a**] : [**8a**] in the terpolymer was determined by ^{1}H NMR spectroscopy, and was almost the same as that in the feed. In addition, yield, M_n, and M_w/M_n of the terpolymers were similar to each other. These results also indicate that the diarylethene monomers have similar polymerization reactivities independent of the side-chain structure and we can prepare photochromic terpolymers consisting of the desirable diarylethene monomers in an arbitrary ratio. T_g of the terpolymers were 85–88 °C, which is well reproduced by Fox and Pochan equations[33] using weight fractions of **1a**, **4a**, and **8a** in the terpolymer and T_g of the homopolymers. Thus, the molar ratio and the weight fraction of the chromophores in the polymer chain, T_g, solubility, and so on can be controlled by copolymerization in the presence of the various diarylethene monomers and other versatile monomers.

Photochromism of diarylethene terpolymer in solution

Fig. 7a and b show absorption spectral changes of terpolymer **1** in toluene upon irradiation with UV and visible light. A new absorption band ranging from 400 to 750 nm appeared upon irradiation at 313 nm. The absorption band assigned to poly(**1b**) segment disappeared upon irradiation at >680 nm because of the cycloreversion reaction to poly(**1a**). In the same manner, absorption bands derived from poly(**4b**) and poly(**8b**) segments also disappeared upon irradiation at >580 nm and >450 nm, respectively, and the absorption spectrum reverted to the original position as shown in Fig. 7b. The absorption spectra corresponding to poly(**1b**), poly(**4b**), and poly(**8b**) are summarized in Fig. 7c. The spectral components have almost the same shape as those of homopolymers. It means that the diarylethene chromophores exhibited their original color even in the terpolymer. The coloration and decoloration of the terpolymer upon alternating irradiation at 313 nm and >480 nm could be repeated at least more than 50 times in toluene without being degassed, keeping the photochromic performance in more than 80%.[3]

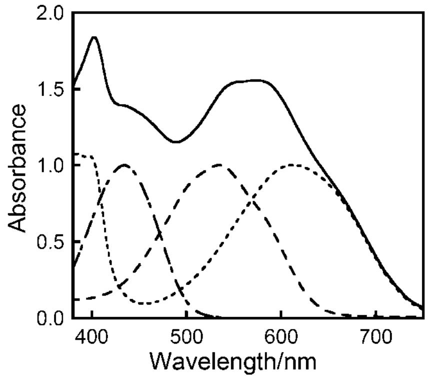


Fig. 6 Normalized absorption spectra of poly(**1a**) (---), poly(**4a**) (– – –), and poly(**8a**) (- - - - -) in toluene in the PSS upon irradiation at 313 nm and the sum of these spectra (solid line).

The appearance of the multicolor photochromism of terpolymer **1** in toluene by selective bleaching is shown in Fig. 8. The colorless solution turned to K upon irradiation at 313 nm. The K solution changed into vivid R, G, and B solutions upon irradiation at >680, 550, and 434 nm, which is due to the disappearance of C, M, and Y, respectively. Then, Y, C, and M solutions were obtained by exposure of >580, 434, and >680 nm light to the R, G, and B solutions, respectively. We successfully prepared a multicolor photochromic terpolymer showing all the colors in the CMY system. To the best of our knowledge, such multicolor photochromism including K using only a single polymer component have not been so far reported.

Photochromism of diarylethene terpolymer in solid state

To apply the photochromic polymer as the full-color display medium, the photochromic polymer should be used in the solid state such as film, paper, and glass. Thus, in this section, the photochromic reaction of terpolymer **1** was investigated in the film and was demonstrated for the multicolor photochromism on a paper medium. Fig. 9a and b show the changes in difference spectra of terpolymer **1** in the film upon irradiation with UV and visible light. A new absorption band appeared upon irradiation at 313 nm and the C, M, and Y components were selectively bleached upon irradiation at >680, >580, and >450 nm, respectively as well as in the solution. The absorption spectra of poly (**1b**), poly(**4b**), and poly(**8b**) segments in the PSS are summarized in Fig. 9c. The three spectral components show almost the same absorption intensity as designed in the previous section. In addition, the spectral shape of the terpolymer in the PSS is similar to the simulated one expected in Fig. 6. These results indicate that we succeeded in designing and preparing the photochromic terpolymer with an ideal ratio of diarylethene chromophores.

Finally, we fabricated a rewritable photochromic display medium using a filter paper to demonstrate multicolor photochromism in the solid state. The filter paper (55 mm in diameter) was impregnated with terpolymer **1** in $CHCl_3$ and dried under air. Fig. 10 shows the demonstration of the multicolor photochromism on the filter paper upon photoirradiation. Upon irradiation with UV light, the filter paper turned to complete K, and the color G appeared as a spot by partial irradiation with G light (550 nm). In the same manner, a partial exposure of R and B light (>680 and 434 nm, respectively) generated R and B spots on the paper. The image could be selectively or completely removed upon irradiation with visible light (>480 nm), and a new image could be rewritten on the filter paper. The photochromic terpolymer consisting of **1a**, **4a**, and **8a** exhibited vivid colors in the CMY system even in the solid state. Furthermore, the image has never been bleached even at 100 °C for a week. Our photochromic terpolymer has appropriate properties such as thermal stability, fatigue-resistance, high content of the chromophore in the polymer chain (*ca.* 72 wt% for terpolymer **1**), and brilliant colors based on the CMY system to be used as the rewritable display device. This work will contribute to fabricate the full-color rewritable display device.

Table 4 Polymerization conditions and characterization of the resultant diarylethene terpolymers[a]

Entry	[**1a**] : [**4a**] : [**8a**] in feed	Yield (%)	M_n	M_w/M_n	[**1a**] : [**4a**] : [**8a**] in terpolymer	T_g/°C (Fox)[b]	T_g/°C (Pochan)[c]	T_g/°C (Observed)
1	10 : 14 : 76	64	24 200	1.98	8 : 14 : 78	84	84	85
2	6 : 16 : 78	71	23 900	2.05	7 : 18 : 75	84	85	88
3	3 : 10 : 86	61	23 400	1.98	4 : 11 : 85	81	82	85

[a] [Monomers] = 0.37 M, [AIBN] = 0.020 M, in toluene, 60 °C, 10 h. [b] Calculated by the Fox equation. [c] Calculated by the Pochan equation.

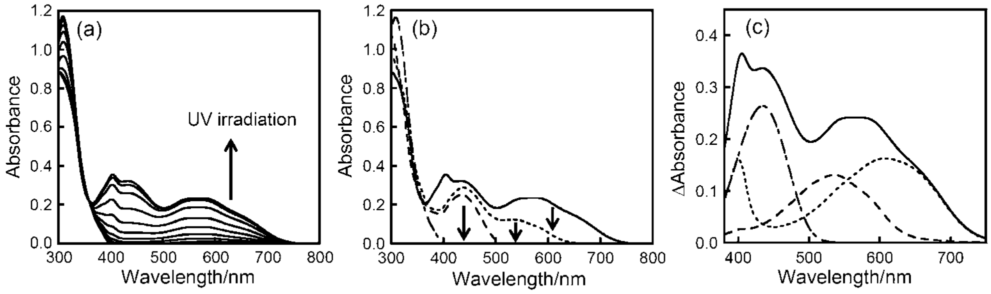


Fig. 7 Absorption spectral changes of terpolymer **1** in toluene (a) upon irradiation at 313 nm, (b) upon subsequent irradiation at >680 nm (---), >580 nm (– – –), and >480 nm (– - – - –), and (c) difference spectrum before and after irradiation at 313 nm (solid line) and spectral decrease upon the subsequent irradiation at >680 nm (---), >580 nm (– – –), and >480 nm (– - – - –).

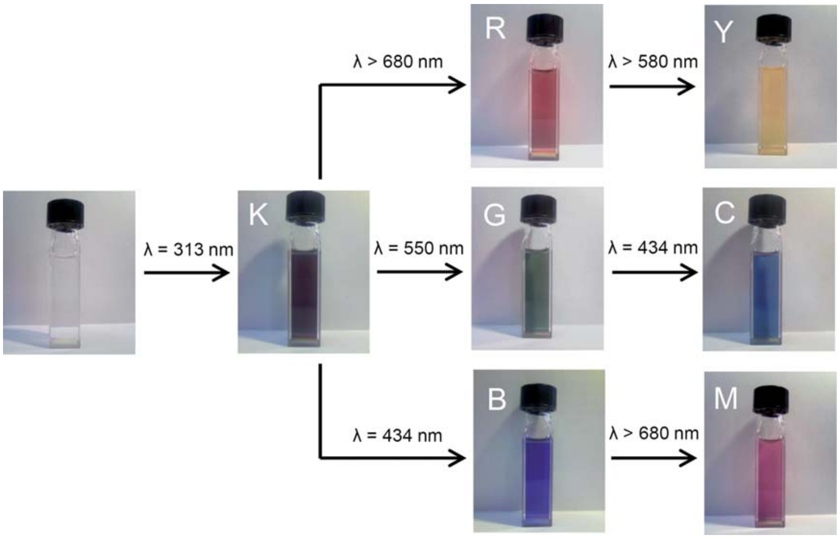


Fig. 8 Multicolor photochromism of terpolymer **1** in toluene.

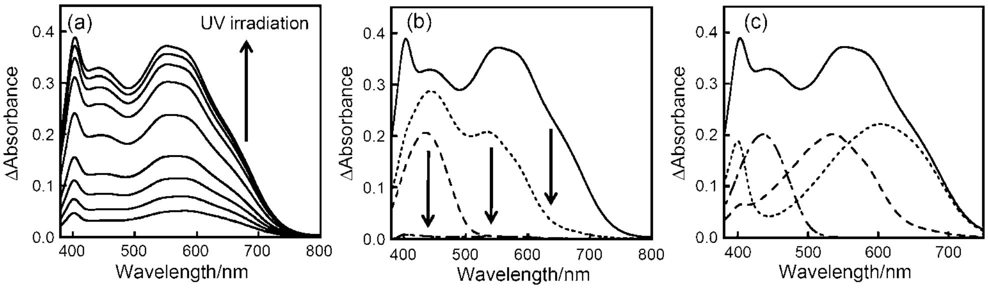


Fig. 9 Changes in difference spectra of terpolymer **1** in the film (a) upon irradiation at 313 nm, (b) upon subsequent irradiation at >680 nm (---), >580 nm (– – –), and >480 nm (– - – - –), and (c) difference spectra before and after irradiation at 313 nm (solid line) and spectral decrease upon the subsequent irradiation at >680 nm (---), >580 nm (– – –), and >480 nm (– - – - –).

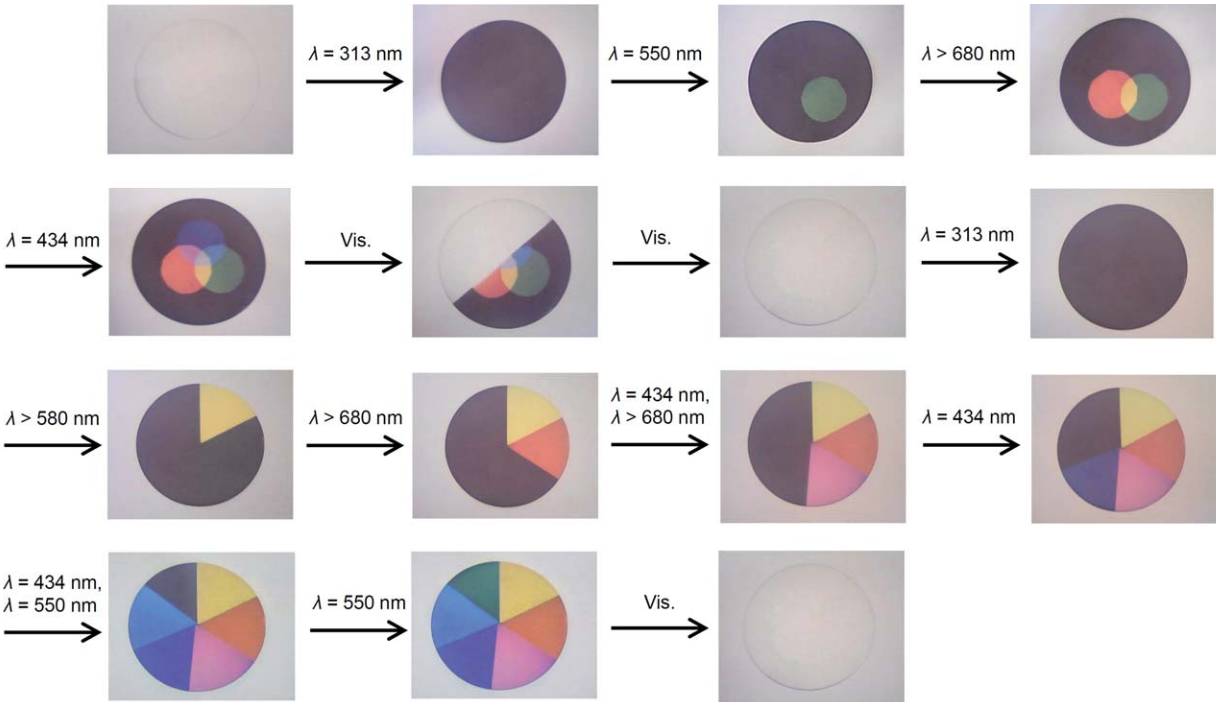


Fig. 10 Multicolor photochromism of filter paper impregnated with terpolymer **1** upon irradiation at 313 nm and selective irradiation with visible light.

Conclusions

We synthesized various types of diarylethene homopolymers and terpolymers by a conventional radical polymerization. The photochromic polymers exhibited reversible photochromism in the film as well as in solution. In the film, however, the photocyclization quantum yield of diarylethene moieties in the polymer decreased in comparison with that in solution due to the structural restriction in the polymer matrix whose T_g is higher than room temperature. The distribution of the photocycloreversion quantum yields in the film was observed for all the diarylethene homopolymers. It is ascribed to the difference in the environment around the molecule. The photochromic terpolymer consisting of three types of diarylethene chromophores showing C, M, and Y exhibited multicolor photochromism including K, R, G, B, C, M, and Y on the paper media as well as in solution by only a single polymer component. The terpolymer has thermal stability, fatigue-resistance, high content of the chromophores, and the brilliant color in the solid state. Such polymers show the potential of the diarylethene derivatives for a rewritable display device.

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