Photochromism of Diarylethene-functionalized Polystyrene with High Conversion in a Solid-state Polymer Film

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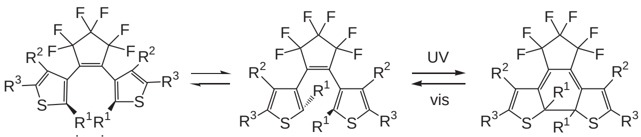
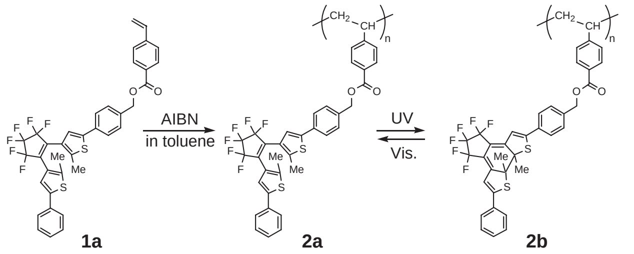
Photochromic polymers that exhibit thermally irreversible and photochemically reversible color changes were synthesized by radical polymerization of a styrene monomer having a photochromic diarylethene chromophore. The photocoloration reaction of the polymer proceeded with high conversion even in the solid-state polymer film.

Thermally irreversible photochromic compounds are potentially applicable for optical memory, display, and switching devices.[1,2] The use of photochromic compounds for such devices requires to respond in high sensitivity in a solid state. Diarylethenes can undergo thermally irreversible and fatigue resistant photochromic reactions even in a solid state.[3–5] Although various types of photochromic diarylethene polymers have been so far reported,[6–18] in most cases the photocoloration reaction in the solid film does not reach to high conversion. Diarylethenes have two stable conformations, antiparallel and parallel ones. They are in equilibrium each other in solution.[19] The photocyclization reaction can proceed only from the antiparallel conformation (Scheme 1). In the solid state, the maximum conversion depends on a content of the antiparallel conformations if the conformations are fixed. If the thienyl groups are rotated in the polymer film, a photocoloration reaction is expected to reach to high conversion even in solid-state polymer films. Some of diarylethene amorphous films had high photochromic conversions.[20,21] In this work, we examined photochromic reactions of polystyrene having a diarylethene chromophore (Scheme 2). The diarylethene chromophore in polymer **2a** was found to exchange between reactive antiparallel and nonreactive parallel conformations at room temperature in the polymer film even below glass-transition temperature (T_g). As a result, the photocyclization reaction proceeds with high conversion in a solid-state polymer film. Such polymers can exhibit high sensitivity for coloration even in thin films.

Styrene monomer having a diarylethene chromophore **1a** was synthesized and carefully purified by HPLC to give colorless crystals (see Supporting Information). The monomer was polymerized by a radical polymerization (see Supporting Information). The polymer had a high molecular weight (M_n = 40,400) and a polydispersity of 2.18. The polymer was soluble in $CHCl_3$, THF, and acetone, and it was insoluble in methanol.



Scheme 1.



Scheme 2.

T_g of the polymer was determined to be 106 °C, which is similar to those of polystyrene and poly(*p*-substituted styrene)s.[22]

Photochromic behavior of polymer **2a** was examined in toluene. Upon irradiation with ultraviolet (UV) light the solution turned to blue. The blue color is due to the formation of the closed-ring form. Figure 1a shows absorption spectral changes upon photoirradiation. Upon irradiation with 313-nm light, a new absorption band appeared at 592 nm. The absorption band increased in irradiation time showing an isosbestic point at 313 nm. After the irradiation for 10 min, the solution reached in a photostationary state. The blue-colored solution was bleached by visible light irradiation ($\lambda > 500$ nm).

To examine the conversion from the open- to closed-ring forms of the diarylethene chromophore, ^{1}H NMR spectroscopy was employed. The methyl protons in **2a** exist at 1.85 ppm. After irradiation with UV light for a few minutes, a new peak appeared at 2.08 ppm, which is assigned to the methyl protons in the

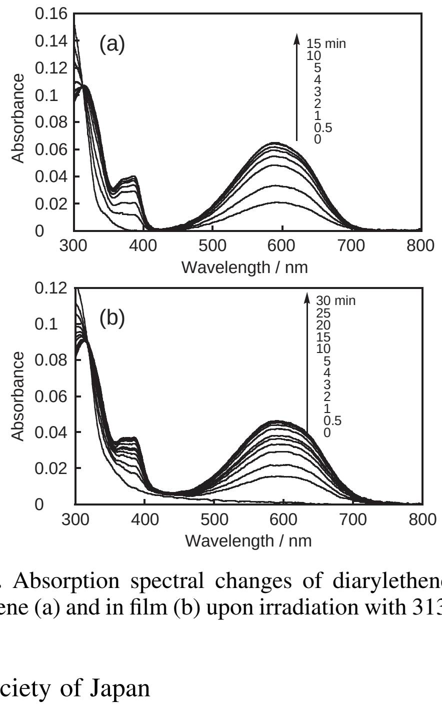


Figure 1. Absorption spectral changes of diarylethene polymer **2a** in toluene (a) and in film (b) upon irradiation with 313-nm light.

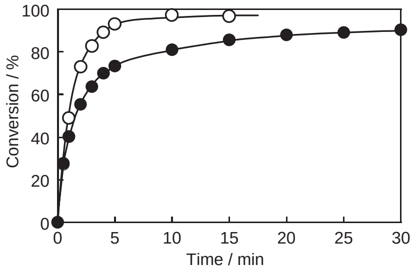


Figure 2. Time-conversion curves for the photocyclization reaction of **2a** in toluene (○) and in film (●).

closed-ring form.[23] The ratio of the peak intensity at 1.85 and 2.08 ppm was estimated to be 36:64. The solution was concentrated in dark and the residue was dissolved in toluene. The absorption spectrum of **2b** was obtained by calculation from those of the toluene solutions of **2a** and **2a**/**2b** (36:64) considering the isosbestic point at 313 nm. The absorption coefficiency of the diarylethene chromophore in **2b** at λ_{max}, 592 nm, was determined to be 16900 $\text{M}^{-1}\,\text{cm}^{-1}$, which is similar to that of a monomeric diarylethene, 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3a**).[23]

Figure 2 shows the time-coversion curve for photocyclization upon photoirradiation. Upon irradiation with 313-nm light for 15 min in toluene, the conversion reached to 97%. This was similar to that of **3a** in hexane.[23] This indicates that the diarylethene chromophores in the polymer underwent an efficient photocyclization reaction in toluene.

Photochromism of the diarylethene polymer was examined in the solid-state neat film, which was prepared on a quartz glass plate by the casting method of the toluene solution. Figure 1b shows absorption spectral change in the polymer film upon photoirradiation. Reversible color changes were observed even in the solid-state neat polymer film. Upon irradiation with 313-nm light for 15 min, the conversion reached to 85%, as shown in Figure 2. In contrast to photocyclization in toluene, upon further prolonged photoirradiation the conversion increased gradually in irradiation time. Photocyclization reaction was found to proceed with high conversion of more than 90% in the solid-state film as well as in toluene.

In most cases, the photocyclization in the solid polymer film does not proceed with high conversion. There are two possibilities for a reason why the reaction proceeded with 90% conversion in the film: One is a high content of the antiparallel conformation in the film as well as in toluene, and the other is equilibrium between two conformations even in the film. Diarylethene **3a**, which has the same structure as the diarylethene chromophore of **2a**, undergoes photochromism even in the single-crystalline phase.[23] In crystal, all of the diarylethene molecules are fixed in the antiparallel conformation. In addition, the crystal undergoes very efficient photocyclization reaction with a photocyclization quantum yield of unity.[4] This indicates that the photocyclization quantum yield of **3a** is comparable to the content of the antiparallel conformation. To clarify the above two possibility, the photocyclization quantum yield in the neat polymer film was examined.

The photocyclization quantum yield of polymer **2a** at the early stage of the photocyclization reaction was measured in toluene and in the film. The photocyclization reaction rates in both cases upon irradiation with 313-nm light were almost the same.

Table 1. Photocyclization/cycloreversion quantum yields and conversion

	$\Phi_{\text{o}\rightarrow\text{c}}$	$\Phi_{\text{c}\rightarrow\text{o}}$	Conversion/%[a]
2a/**2b** in toluene	0.54	0.0044	97
2a/**2b** in film	0.53	0.0034	92
3a/**3b** in hexane[b]	0.59	0.013	97

[a]Upon irradiation with 313-nm light. [b]Ref. 23.

The cyclization quantum yields were determined to be 0.54 in toluene and 0.53 in the film, as shown in Table 1. The value is almost the same as that of the monomeric diarylethene **3a**. If two conformers cannot be exchanged in the film, the maximum conversion in the film should be below 53% conversion. High conversion with 90% and the cyclization quantum yield of 0.53 indicate that the equilibrium between two conformations takes place even in the film though T_g is much higher than room temperature. This is attributed to the structure of diarylethenes. The diarylethene-functionalized polymer which exhibited high photoreactivity with high conversion (more than 90%) in the neat polymer film and contained high content of the diarylethene chromophore can be potentially used for display materials.

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