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Preparation of diarylethene copolymers and their photoinduced refractive index change

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Abstract

Diarylethene copolymers were synthesized from 1-(6'-vinyl-2'-methylbenzo[*b*]thiophene-3'-yl)-2-(2''-methylbenzo[*b*]thiophene-3''-yl)hexafluorocyclopentene (VMBTF6) and 1-[6'-(4'''-vinylbenzoyl)-2'-methylbenzo[*b*]thiophene-3'-yl]-2-(2''-methylbenzo[*b*]thiophene-3''-yl)hexafluorocyclopentene (VMBMBTF6) via living free radical techniques using stable TEMPO derivatives. The diarylethene content was controlled by the feed ratio of diarylethene derivatives and styrene. Transparent photochromic polymer films were prepared from the diarylethene copolymers with narrow molecular weight dispersion (PD ~ 1.3) by spin coating method. Photoinduced refractive index changes (Δn_{TE}) of the polymer films, with 25 mol% of diarylethene content, accompanied by the photochromic change were determined as 0.0009 and 0.0030 for poly(styrene-*ran*-VMBTF6) and poly(styrene-*ran*-VMBMBTF6), respectively.

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1. Introduction

Photochromic dyes, dispersed in or bound to polymer matrices, are of significant interest for their potential application in optical memory, switches, and other optoelectronic devices [1]. Among those, diarylethene derivatives have attracted much interest for their high photochromic efficiency and thermal stability [2,3].

The photochromic properties of diarylethene molecules arise from photoinduced ring closure/

opening process. Photoinduced refractive index change could be attained from a photochromic polymer, in which photochromophores are dispersed in polymer matrices or attached to polymer chains by covalent bonding [4]. The diarylethenes dispersed polymer films, however, have problems of phase separation between the polymer and diarylethene, and aggregation of diarylethene molecules, which result in low cyclability and photochromic conversion of the film. One method to solve these problems is to develop a diarylethene bound polymeric system, which is important for its application in photochromic film processing.

In this work we report on the preparation and photochromic behavior of diarylethene copolymers.

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2. Experimental

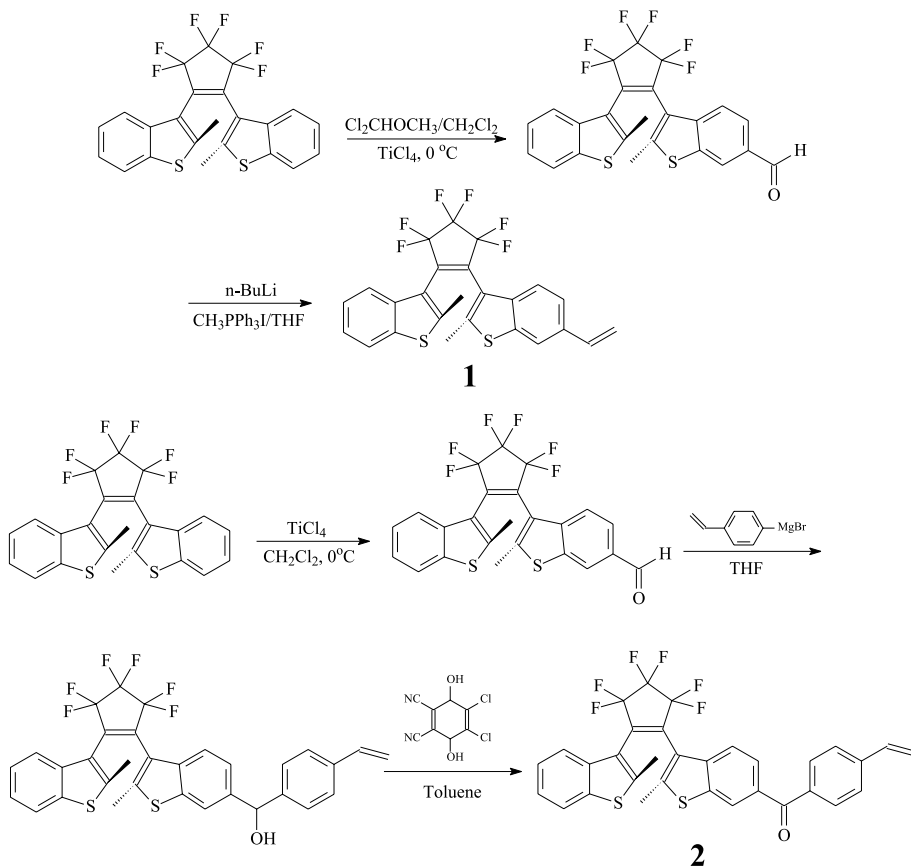
2.1. Materials

2,3-Bis(2-methylbenzo[*b*]thiophene-3-yl)hexafluorocyclopentene (BTF6) was synthesized from benzothiophene in three steps [4,5]. 1-(6'-vinyl-2'-methylbenzo[*b*]thiophene-3'-yl)-2-(2''-methylbenzo[*b*]thiophene-3''-yl)hexafluorocyclopentene (VMBTF6, **1**) and 1-[6'-(4''-vinyl-benzoyl)-2'-methylbenzo[*b*]thiophene-3'-yl]-2-(2''-methylbenzo[*b*]thiophene-3''-yl)hexafluorocyclopentene (VMBMBTF6, **2**) were synthesized from BTF6 in 2–3 steps as summarized in Scheme 1. Other chemicals and solvents were purchased from either Aldrich or Tokyo Kasei and purified according to the standard procedure in literature.

2.2. Synthesis of diarylethene copolymers

2.2.1. Poly(styrene-*ran*-VMBTF6) (*pstvm*, **3**)

To a mixture containing VMBTF6 (**1**) (0.95 g, 1.92 mmol) and styrene (0.60 g, 5.76 mmol) in 3 mL of toluene was slowly added 0.02 g of ethyl α -TEMPO-phenylacetate. The mixture was stirred at 150 °C under a nitrogen atmosphere for 48 h. After cooling to room temperature, the reaction mixture was precipitated into methanol. Further purification was carried out by repeated precipitation from THF into a mixture of *n*-hexane and ethyl acetate. The polymer was filtered and dried under vacuum to yield yellow powder. The diarylethene content was determined as 25 mol% by ¹H NMR. Yield 74%; $T_g = 98$ °C; $M_w = 16,000$ ($M_w/M_n = 1.37$).



Scheme 1.

2.2.2. Poly(styrene-ran-VMBTF6) (*pstvbm*, **4**)

Polymer **4** was produced from styrene and VMBTF6 (**2**) using the identical procedure described for polymer **3**. The diarylethene content was determined as 25 mol% by ^1H NMR. Yield 65%; $T_g = 128\text{ }^\circ\text{C}$; $M_w = 11,500$ ($M_w/M_n = 1.30$).

2.3. Preparation of polymer films

Diarylethene copolymers (0.1 g) were dissolved in cyclohexanone and stirred at room temperature for 1 h. The solutions were filtered using membranes of $0.45\text{ }\mu\text{m}$ pore size attached to a Teflon syringe, and the solutions were coated on the substrates (silicon wafer, quartz or slide glass) by a spin-coater with a spin rate of 500–2000 rpm. The coated films were dried at $80\text{ }^\circ\text{C}$ for 12 h in a vacuum oven to yield transparent and homogeneous films.

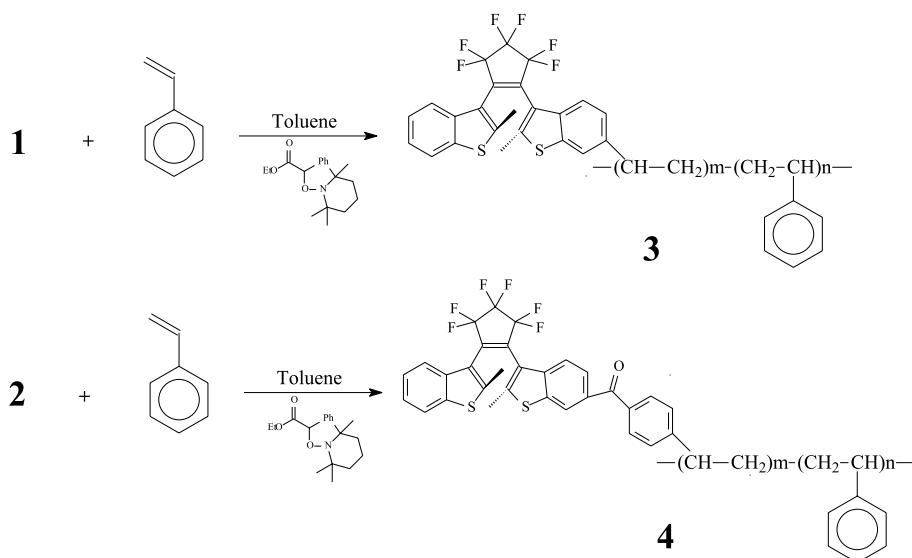
2.4. Instruments

^1H NMR spectra were determined on a Bruker ARX-300 spectrometer. The molecular weight average of the diarylethene copolymers was characterized by gel permeation chromatography (GPC) (model: Waters R-401 ALC/GPC) with THF as an

eluent and polystyrene standard for calibration. The thickness of polymer films was measured on an α step. UV spectra were obtained from a Spectra View 2000. The refractive index of the polymer film was determined using a prism coupler with 633 nm He–Ne laser and 830 nm diode laser as a monitoring beam. The photodetector for the prism coupler was silicon type or IR detector. The light source for the characterization of the photochromic property of polymer films was a Xe lamp (Oriel) equipped with a monochromator. The light source for the refractive index change and photochromic recording was a UV lamp (365 nm) and a He–Cd laser (325 nm).

3. Results and discussion

Diarylethene copolymers could be synthesized from VMBTF6 and VMBTF6 via living free radical techniques using stable nitroxide free radicals (Scheme 2) 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) derivatives as described in Scheme 2. The polymerization proceeded in a living fashion to yield narrow polydispersity polymers and control macromolecular structure of polymers. The diarylethene content was controlled by the feed ratio of diarylethene derivatives and styrene.



Scheme 2.

The content of diarylethene chromophore for both polymer **3** and **4** was determined as 25 mol% by ^1H NMR.

Diarylethene copolymers were soluble in organic solvent including cyclohexanone. The polymer solutions were spin-coated to make transparent and homogeneous films. The photochromic spectral changes in the UV–VIS absorption spectrum for polymer films are shown in Fig. 1. Within 2 min of irradiation, the film changed its color to red, which bleached completely to an original colorless state upon irradiation with a light of 500–650 nm.

Quantum yields of the photochromic ring-cyclization (Φ_{pc}) could be determined from the above absorption changes upon excitation with a UV light. The conversion and the number of absorbed photons at a given radiation power and absorbance of the sample were determined from the linear range in a plot of exposure time vs absorbance at λ_{max} [6]. Fig. 2 shows the linear range of absorption changes at λ_{max} for each polymer film. Table 1 summarizes the photochromic quantum yields of diarylethene polymer films, indicating that photochromic efficiency of the polymer **3** is slightly but obviously higher than that of polymer **4**. The higher quantum yield of polymer film of **3** as compared to that of **4** reflects the effect of

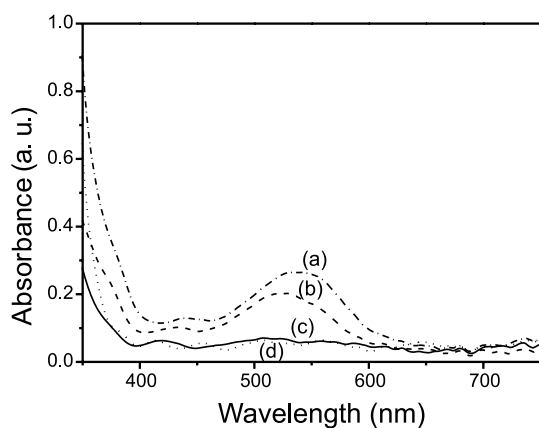


Fig. 1. UV spectral changes of diarylethene copolymer films by light of 365 nm: (a) polymer **4** after irradiation, (b) polymer **3** after irradiation, (c) polymer **3** before irradiation, and (d) polymer **4** before irradiation.

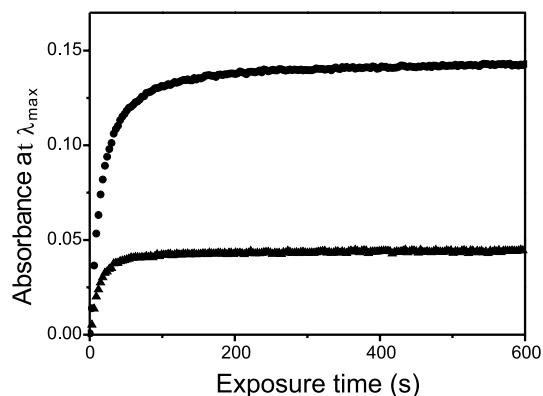


Fig. 2. Change of the absorbance at λ_{max} with irradiation time for polymer film of **3** (\blacktriangle); and **4** (\bullet).

Table 1
Photochromic quantum yields for ring-cyclization reaction

Polymer	$\lambda_{\text{max}}^{\text{a}}$ (nm)	Φ_{pc}	$\lambda_{\text{irr}}^{\text{b}}$ (nm)
3	529	0.1623	365
4	542	0.1520	365

^a Maximum wavelength of new absorption after irradiation of UV light.

^b Irradiation wavelength.

long conjugation and large molecular size in VMBTf6 monomer. The result correlates well with the previous studies that quantum yields are low in the system with extended conjugation [7].

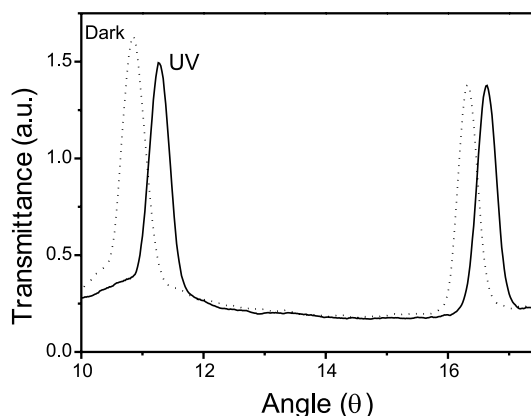


Fig. 3. Photoinduced peak shift in the angle spectra for polymer film of **4**.

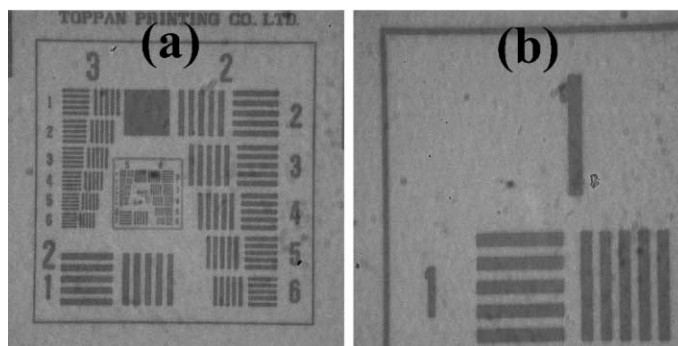


Fig. 4. Photochromic recorded image obtained from diarylethene copolymer film of **4** by excitation with UV light (film thickness of 1.2 μm). The full size line width is of (a) 8 μm and (b) 25 μm .

The refractive index of an optical waveguide coated with diarylethene polymer film could be evaluated by the prism coupling method [8]. The incident angle dependence of measured reflectance is shown in Fig. 3 for the polymer film prepared from polymer **4**. Upon irradiation of the polymer film with a light of 365 nm for 10 min, the peak in the coupling angle was shifted to a higher value.

The refractive indices (n_{TE}) of the UV irradiated polymer films were determined as 1.5769, 1.5877, resulting in a photoinduced refractive index change (Δn) of 0.0009, 0.0030 for polymer film of **3** and **4**, respectively. In the diarylethene doped system, Δn increases in proportion to the absorbance changes [9]. However, Δn for a system that photochromophores are attached to polymer chains by covalent bonding is rather complicated and the relationship between Δn and Φ has to be carefully examined. It is noticeable that the refractive index change for polymer **4** by UV/VIS light was largest among the diarylethene bound polymer systems, as compared to the results in the previous work [5].

Photochromic recording was possible with He–Cd laser (325 nm) and the image was completely erased with a 532 nm laser. Photochromic cyclability was determined by analyzing optical contrast using UV and visible (532 nm laser) light sources. The initial optical contrast was not decreased even after 1000 cycles, from which we assume that the cyclability of diarylethene bound polymer film is over 10,000 cycles. The recorded image with a resolution of 8 and 25 μm was analyzed using a

near IR light (>700 nm) without destroying the original image as shown in Fig. 4.

4. Conclusions

Diarylethene copolymers were synthesized from vinylic diarylethene derivatives, such as VMBTF6 and VMBMTF6 in the presence of 2,2,6,6-tetramethylpiperidiny-1-oxy radical as an initiator. Photochromic efficiencies (Φ_{pc}) of the polymer films were determined as 0.1623 and 0.1520 and photoinduced refractive index changes as 0.0009 and 0.0030 for polymer **3** and polymer **4**, respectively. The large value of the refractive index change from diarylethene copolymer films brings up possibility of near IR imaging with non-destructive reading system.

Acknowledgement

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