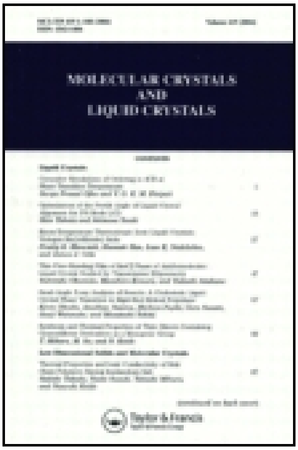

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Photoswitching of Diarylethene Polymers Synthesized by TEMPO Mediated Polymerization

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Optical and refractive index switching properties of diarylethene containing copolymers were studied. Polymers having different block distribution were synthesized from a controlled polymerization via living free radical method using ethyl α-2,2,6,6-tetramethylpiperidinyl-1-oxy-phenylacetate (ETEMPO) as an initiator. The diarylethene containing copolymers exhibited high thermal stability without loss of diarylethene unit up to 350°C. Photochromic films, having photochromic interconversion between colorless and red colored forms by UV and Vis laser sources, were prepared from the copolymers by solution coating method. The photochromic response of the copolymer was dependent on the distribution of diarylethene in the polymer and weight-average molecular weight (M_w) of the polymers. Thus films of copolymers having random distribution of diarylethene showed larger photochromic absorbance change (ΔA) and photo induced refractive index change (Δn) as compared to that of block copolymer. The photochromic response was larger in a film of a random copolymer with lower Mw. Large all optically controllable refractive index switching ($\Delta n \sim 0.01$) was achieved from the diarylethene copolymers, accompanied by photochromic interconversion between colorless and red colored forms.

Keywords: block; controlled polymerization; diarylethene copolymers; photochromic; random; refractive index switching

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INTRODUCTION

Photo induced swiching in photochromic polymer films are of great importance for opto-controlled devices such as in waveguides [1]. The important issues for the application of photochromic polymers in these devices are the optical properties, degree of refractive index change, response time, and processability. Large refractive index changes on the order of 10^{-3} can be induced by a light from photochromophores (photochromic dyes) dispersed polymer matrices [1(a)].

Photo induced refractive index change could be attained from a chromophore bound type diarylethene polymer. Particularly, such a modification of polymer network by a low molecular weight photochromophore is important for the development of stable photochromic polymers for practical applications. Chromophore bound system is expected to be more stable over time than the doped system, because of the motional hindrance introduced by chemical bonding [2]. Previously we reported radical polymerization of methacryl type diarylethene monomer to result in 5.3 mol% (22 wt%) of diarylethene incorporated polymer system [3]. Photo–induced refractive index change (Δn_{TE}) of the resultant polymer was 8×10^{-4}, monitored by light of 830 nm. Since Δn_{TE} is largely dependent on the chromophore content, it has been necessary to increase diarylethene content in the polymer. However, synthesis of chromophore bound polymers having a high degree of chromophore substitution is hampered by instability, unselectivity, or poor reactivity of monomers under conventional polymerization condition. Furthermore effect of photochromophore distribution in the polymer on the optical properties have been rarely explored. Therefore, we embarked on the synthesis of a diarylethene bound polymer system under stable free radical polymerization using nitroxide additives such as 2,2,6,6-tetramethyl-1-piperdinyloxy nitroxide (TEMPO). Compared to other controlled polymerization methods such as anionic [4], cationic [5], and group transfer polymerization [6], controlled radical polymerization using TEMPO derivatives does not require extraordinary conditions such as low temperature, inert atmosphere and has been an effective polymerization method in the sytreneic monomers [7].

We report here the optical and photo induced refractive index switching of diarylethene substituted polymers, synthesized by a controlled polymerization using 1-[6′-(4‴-vinylbenzoyl)-2′-methyl benzo[b]thiophene-3′-yl]-2-(2″-methylbenzo[b]-thiophene-3″-yl)hexafluorocyclopentene (**VBMBTF6**, **1**) as a diarylethene monomer and ETEMPO as a radical initiator.

EXPERIMENTAL

Materials

Styrene (Aldrich) was distilled from CaH_2 under reduced pressure. 2,3-bis(2-methylbenzo[b]thiophene-3-yl)hexafluorocyclopentene (**BTF6**, **2**) and 1-[6′-(formyl)-2′-methylbenzo[b]thiophene-3′-yl]-2-(2″-methylbenzo[b]thiophene-3″-yl)hexafluorocyclopentene (**3**) were synthesized as described in the literature [8]. ETEMPO (**5**) was used as an initiator for TEMPO mediated polymerization. The initiator (**5**) was synthesized from phenylacetate and TEMPO radical according to the literature [9]. Other chemicals and solvents were purchased from either Aldrich or Tokyo Kasei and purified according to the literature. Styreneic monomer, VBMBTF6, and polymers were synthesized accoding to the method reproted before [10].

Poly(styrene-*ran*-VBMBTF6) (PSR1)

Yield 69%. Tg = 148°C. GPC: $M_p = 25700$, $M_w = 22100$ ($M_w/M_n = 1.50$).

Poly(styrene-*ran*-VBMBTF6) (PSR2)

Tg = 110°C. GPC: $M_p = 12500$, $M_w = 11000$ ($M_w/M_n = 1.30$).

Poly(styrene-*block*-VBMBTF6) (PSB)

$M_p = 24580$; $M_w = 22740$ ($M_w/M_n = 1.42$).

Preparation of Polymer Films

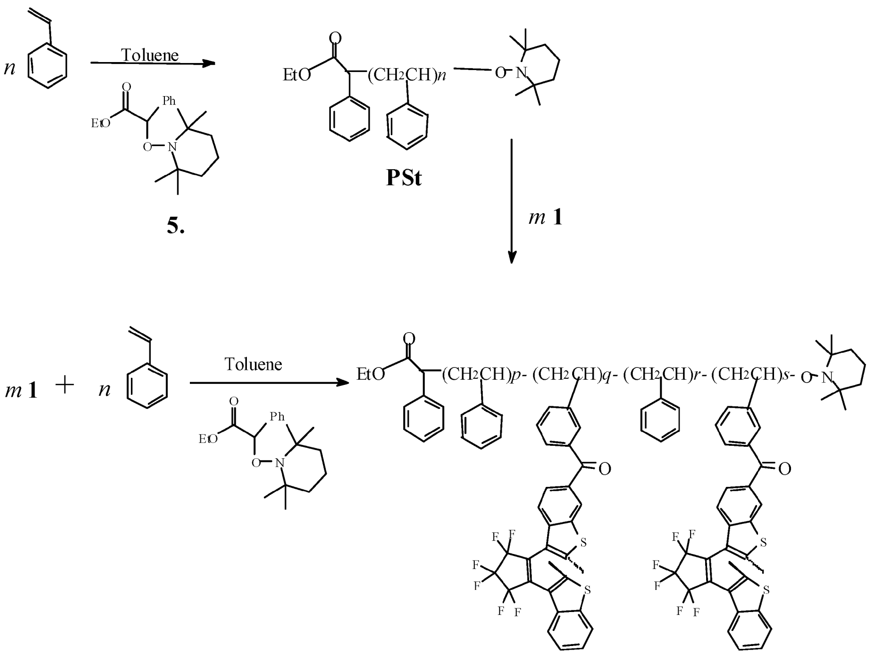
Diarylethene copolymers (0.1 g) were dissolved in 0.4 g of cyclohexanone and stirred at room temperature for 1 h. The solutions were filtered using membranes of 0.45 μm pore size attached to a Teflon syringe, and the solutions were coated on substrates (silicon wafer, quartz or slide glass) by a spin-coater with a spin rate of 500–2000 rpm. The coated films were dried at 80°C for 12 h in a vacuum oven to give transparent and homogeneous films. Diarylethene doped polystyrene (PSD) film was prepared from the solution of 0.056 g (25 mol%, 53 wt%) of 2 and 0.05 g of polystyrene (Aldrich, $M_w = 19300$, $M_w/M_n = 1.07$) in 0.4 g of cyclohexanone. The solution was coated by spin coating method, and dried at 80°C for 12 h in a vacuum oven.

Instruments

^{1}H NMR spectra were obtained from 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. Thermo gravimetric analyses (TGA) were carried out with Du Pont 951 thermo gravimetric analyzer. The sample weight was 3 $\sim$ 10 mg. The work was performed from 30 to 700°C at a heating rate of 10°C/min in nitrogen atmosphere with a gas flow rate of 100 ml/min. The film thickness of polymer films was measured on an α step (TENCOR instrument, α step). UV spectra were obtained from Spectra View 2000 (K-MAC, Inc., Korea). The refractive index of the polymer films was determined using a prism coupler (Sae Ron, Korea) with 830 nm diode laser as a monitoring beam. The photodetector for the prism coupler was silicon type detector. The reported refractive index and its change were obtained after five times of measurement on each sample. The experimental error was within 0.0001. The light source for the characterization of the photochromic property of polymer films was a Xe lamp (Oriel) equipped with a monochromator. The light sources for the refractive index change were He-Cd 325 nm laser (output power = 10 mW) and 532 nm laser (output power = 20 mW).

RESULTS AND DISCUSSION

Photochromic polymers containing diarylethene molecules could be synthesized from a controlled polymerization of **VBMBTF6** (**1**) via living free radical techniques [7,10,11]. Using ETEMPO (**5**) as summarized in Scheme 1. Homopolymer of **1** (PSH) was obtained with M_w/M_n of 1.20 but the molecular weight of the diarylethene bound homo-polymer was low. Thus we attempted to synthesize a copolymer using styrene as a co-monomer. The diarylethene content in the copolymer was controlled by the feed ratio of **1** and styrene. Interestingly, polymerization proceeded to yield polymers of a reasonably high molecular weight ($M_w > 10{,}000$) in the presence of styrene. Furthermore high concentration of diarylethene molecules could be introduced into polymer chain up to 25 mol%(65 wt%) by the TEMPO mediated living free radical polymerization, as determined by ^{1}H NMR. Integration of peaks showed that all the feed amount of **1** was incorporated in the polymer. Since M_w and distribution of diarylethene could be controlled by the living free radical polymerization, by controlling reaction condition and the sequence of monomer addition, we synthesized random



SCHEME 1 **PSR1**: Mw = 22100 ($p+r=0.25$), **PSR2**: Mw = 11000 ($p+r=0.25$), **PSB**: Mw = 22740 ($pr=0.25$, $r=s=0$), **PSH**: Mw = 6900 ($p+r=1$), **PSt**: Mw = 8970 ($q+s=1$ or n = 1).

copolymers having two different M_w (**PSR1** and **PSR2**) and a block copolymer (**PSB**).

The polydispersities (M_w/M_n) of the polymers were 1.2~1.5 and much lower as compared with traditional free radical systems (ca. 2.0). Figure 1 shows GPC of the polymers prepared from this study. Diarylethene bound copolymers were stable up to ~350°C as determined by TGA (Fig. 2). The block coplymer (**PSB**) showed higher Td (5 wt% loss) than random (**PSR1**), possibly due to the blocking of the inner DA units in the block copolymer. On the other hands, diarylethene (BTF6, 53 wt%) doped polystyrene(**PSD**) showed significant weight loss beginning from 100°C and about 53% weight loss was observed at 310°C. Such weight loss in the doped system is possibly due to the evaporation of BTF6 molecules and the weight loss of 53% was corresponded to the doped quantity of **2**. Thus by attaching diarylethene unit chemically into a polymer chain, the diarylethene molecules could be remained intact even at 350°C, to result in a stable photochromic polymers. A slight weight loss at around 130°C (~3 wt%) for diarylethene bound copolymer is thought to arise from the carbon

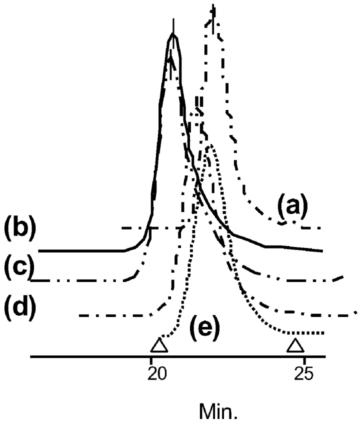


FIGURE 1 GPC of the polymers prepared from **1**: (a) PSH (Mw = 6900), (b) PSB (Mw = 22700), (c) PSR1 (Mw = 22100), (d) PSR2 (Mw = 11000) and (e) polystyrene (PSt) macromer.

oxygen group(C—ON) at the terminal TEMPO group, since it has been reported that the cleavage of C—ON bond of similar alkoxy amine derivatives occurs at 125°C [11].

Diarylethene bound styrene copolymers (**PSR1, PSR2** and **PSB**) were soluble in organic solvent such as cyclohexanone. The polymer solutions were spin-coated to give transparent and homogeneous films. The photochromic changes in absorption spectra of polymer films before and after irradiation are shown in Fig. 3. Within one

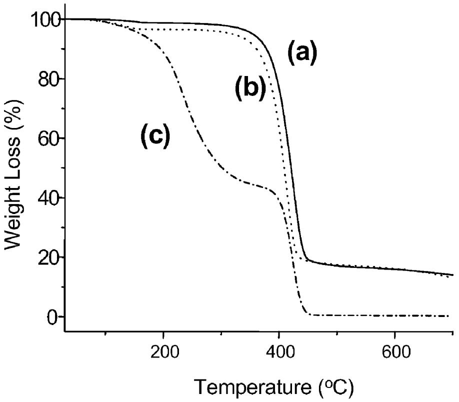


FIGURE 2 TGA thermograms of (a) **PSB**, (b) PSR1 and (c) diarylethene doped PS (PSD). Diarylethene content is 25 mol% (60 wt%) in all samples.

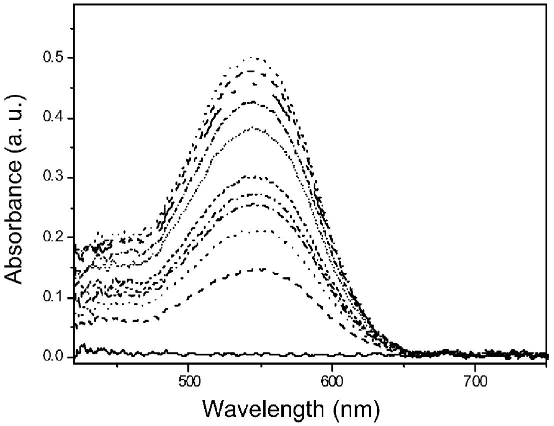


FIGURE 3 Temporal evolution of absorption band in the film of **PSR1** upon excitation with a light of 325 nm for 0, 2, 4, 6, 8, 10, 20, 30, 40, 50, and 60 s (from bottom to top). (b) UV spectra of the polymer film (**PSR1** and **PSD**) irradiated with a 325 nm laser for 1 min. (Film thickness of **PSR1** = 1.8 μm, **PSD** = 1.5 μm).

minute of irradiation, the film changed its color to red, which bleached completely to an original colorless state upon irradiation with a visible light (500 ~ 650 nm). The ring open form of diarylethene polymer has intense absorption peaks at UV region (300 nm), and after UV irradiation new absorption peaks was observed at 544 nm. The absorption peaks at visible region for the copolymers (**PSR1, PSR2** and **PSB)** were same (544 nm). This result indicates that the difference in average molecular weight of polymer (**PSR1** *vs* **PSR2**), and the difference in diarylethene distribution (**PSR1** *vs* **PSB**) do not affect the first excited state structure of diarylethene.

Such photochromism arises from the photocyclization of inner hexatriene in diarylethene (ring open form) to result a cyclohexadiene type (ring closed form) [12]. Since the ring closure results in a change in electron delocalization, optical density of molecules in visible region could be changed. Furthermore the structure of the polymer chain can be altered as a result of ring cyclization in diarylethene molecules. Figure 4 shows absorbance changes (ΔA) at λ_{max} of closed form by a UV light (350 nm, 1 mW) at different irradiation time. Interestingly, ΔA was affected by the diarylethene block sequence, and thus ΔA was larger in the random copolymer (**PSR1**) than that in the block copolymer (**PSB**).

Quantum yields of the photochromic ring-cyclization (Φpc) of the polymer in solution could be determined from the absorption changes

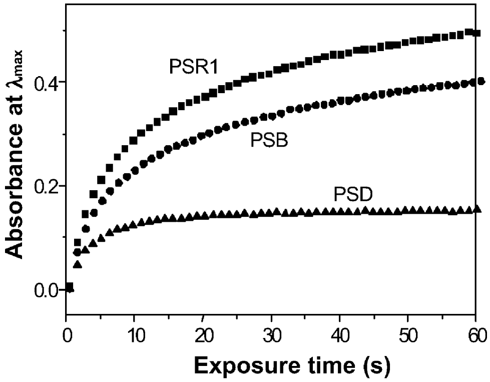


FIGURE 4 Absorbance changes of photochromic polymer films at 540 nm (**PSR1**) film in a prism coupler upon by UV light of 350 nm.

at early time scale, by determining the conversion and the number of absorbed photons at a given radiation power and absorbance of the sample [13]. Φpc was determined as 0.34 and 0.30 for the solution of **PSB** and **PSR1**, respectively, indicating that the one-photon photochromic efficiency of the copolymers are quite high and are not much affected by the block distribution.

It is noteworthy, though, ΔA of the films at longer exposure showed ovious difference bewteen **PSB** and **PSR**. This indicates that photochromic conversion in polymeric media are multistep: one in a fast transion at early time scale (one-photon conversion) and the others in slow transitions affected by the block distribution in polymer chain and other factors such as free volume around the chromophore. Such difference between block and random was also observed in the refractive index chagne as described below.

Accompanied by the increase in absorption at visible region, the refractive indices of polymer films was increased upon excitation with a UV light, as monitored by a light of 830 nm. The refractive indices of **PSR1** at stationary state were determined as 1.5744 and 1.5836 for the colorless (ring opened form) and red colored (UV excited, ring closed form) polymer film, respectively. The photo-induced refractive index change, within 20 s of irradiation with a 325 nm laser was determined as 0.0092, which was greatly enhanced as compared to BTF6 doped PMMA polymer film or diarylethene bound acrylic copolymer film [12]. The increase of refractive index change (Δn_{TE}) in this study is largely attributed to the high content of diarylethene in the polymer. Another reason for large Δn_{TE} may be due to the homogeneity of diarylethene distribution in the copolymer. Figure 5 shows

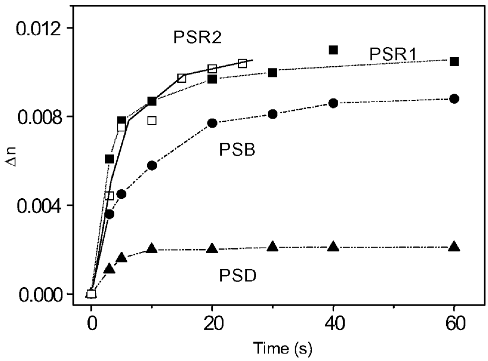


FIGURE 5 Photo-induced refractive index changes (Δn) for photochromic polymer films prepared from **PSR2**, **PSR1**, **PSB** and **PSD** at different irradiation time.

Δn_{TE} for diarylethene bound copolymer systems as compared to the doped system (**PSD**).

Interestingly films prepared from the diarylethene bound copolymer showed larger Δn_{TE} as compared to the doped system with similar content of diarylethene. We expect that much aggregation between chromophores could occur in diarylethene doped polystyrene film due to high loading of diarylethene (53 wt%). This result strongly suggests that Δn_{TE} is indeed affected by the molecular dispersion of photochromophores.

Another interesting point is that slightly but larger Δn_{TE} was observed from the film of low Mw copolymer (**PSR2**). Figure 6 shows the result of differential scanning calorimetry (DSC), indicating

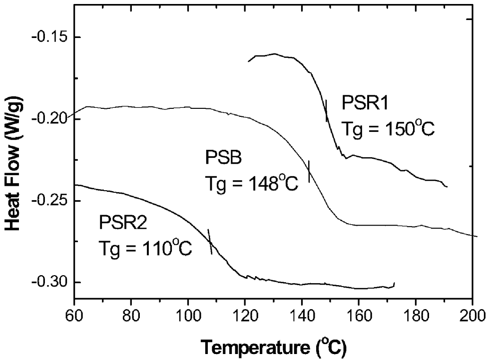
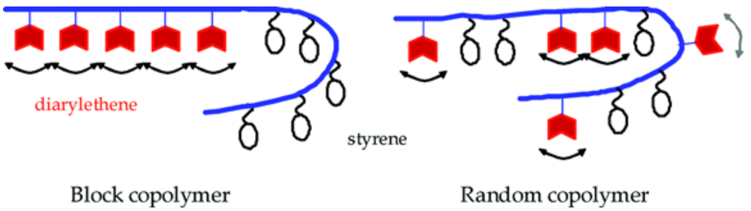


FIGURE 6 DSC thermograms of diarylethene bound copolymers.

higher glass transition temperature (Tg) for the high M_w copolymer (**PSR1**). This result indicates that free volume around the chromophores and segmental motion of polymer chain are important for refractive index change. On the other hands, **PSR1**showed larger ΔA (Fig. 4) and Δn (Fig. 5) as compared to **PSB**, of which Tg (148°C) is similar to that of **PSR1**(150°C). Since M_w and content of diarylethene in **PSB** and **PSR1** are comparable, the difference in photochromic response(ΔA, Δn) could be attributed to the difference in chromophore distribution in the polymer chain, as pictorially drawn below:



STRUCTURE 1

The photochromic response is a result of ring cyclization in each diarylethene molecule. Such ring cyclization would be more difficult in the block copolymer (**PSB**), in which most diarylethenes are sequentially connected one after the other, than in the random copolymer (**PSR1**). Particularly inner part of diarylethenes in **PSB** would require additional energy to undergo ring cyclization. In **PSR1** diarylethene molecules are randomly connected to styrene unit that could facilitate segmental motion of polymer chain required for the ring cyclization. A limited photochromism in directly linked diarylethenes was reproted for a dimeric 1,2-dithienylethenes (DTE), in which only one of DTE undergoes photoinduced cyclization reaction while the other DTE is intact but decomposed under prolonged irradiation condition [14]. Since the difference between PSR and PSB are not large, the inactivation by the covalently DA molecules in the block copolymers may not be large.

CONCLUSION

By virtue of TEMPO mediated controlled polymerization, it was possible to synthesize a block and random copolymers of diarylethene with narrow Mw/Mn and finely tuned block struture. High content of diarylethene could be introduced in the polymer up to 65-wt%. Large photo-induced refractive index change(Δn_{TE}) of 0.01(at 830 nm) by UV/V is switching was obtained from the diarylethene bound copolymers. Although λ_{max} of the closed form was not much dependent on the polymer structure and molecular weights, ΔA and Δn_{TE} was highly affected by them. Thus ΔA and Δn_{TE} was larger in low Mw random copolymer.

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