Polymerization of a Photochromic Diarylethene by Friedel−Crafts Alkylation

Yong-Chul Jeong,[†] **Dae Gyu Park,**[†] **Eunkyoung Kim,***[‡,§]
Sung Ik Yang,*[†,⊥] **and Kwang-Hyun Ahn***[†,||]

*College of Environment and Applied Chemistry, and
Institute of Natural Science, Kyung Hee University,
Yongin, 449−701, Republic of Korea, and Department of
Chemical Engineering, Yonsei University, 134 Sinchon-dong,
Seodaemun-gu, Seoul, 120-749, Republic of Korea*

Received January 28, 2006
Revised Manuscript Received March 15, 2006

Introduction. Photochromic materials have been received great attention recently because of their potentials in various applications such as optical memory, switching, and display devices.[1,2] Diarylethenes which undergo reversible photocyclization and ring opening reaction between their open- and closed-ring isomers with a good fatigue resistance and thermal stability are regarded as the best candidates for such purposes.[2−3]

For practical applications of these materials, the photochromic compounds have to be fabricated in the form of films, sheets, or beads, which requires the incorporation of the photochromophores into a polymer media. Several methods including the dispersion of the photochromophores into the polymer matrix as an additive or covalently grafting them onto the polymer main chain as a pendant group have been developed recently.[4] However, the content of diarylethene unit in these polymeric media are generally low. As the photochromism and the resultant switching are highly dependent on the content of photochromophores in polymer media, diarylethene polymers containing a high effective concentration of the photochromic component is desirable, especially in applications such as optical information processing.[5−9] To increase the content of the photochromic diarylethene in the polymer, homopolymers where the diarylthene resides in the main polymer backbone were prepared by Zerbi,[9a] Branda,[9b] and Irie[9c] groups. Although, the main-chain homopolymers showed good photochromic properties in film state as well as in solution, each has drawbacks in molecular weight, fatigue resistance and polymerization yield, respectively.

In our previous studies, we reported the syntheses and the phothochromic properties of diarylethene copolymers.[6a,b,7c] On a continuing study, cationic polymerization of diarylethene have been investigated for its fast polymerization rate and efficiency.[10] Conventionally, the Friedel−Crafts alkylation could be carried out by using acid catalysts such as $TiCl_4$ or various Brönsted acids. Surprisingly, we found that BTF6 could be easily polymerized to produce poly-BTF6 in a reaction with $TiCl_4$ and chloromethyl methyl ether. The density of photochromic unit incorporated into the polymer is expected to be very high (98 wt %) as shown in the structure. Thus, we report here the first time synthesis of main-chain diarylethene homopolymer (poly-BTF6) using new convenient polymerization method based on Friedel−Crafts alkylation and its photochromic properties.

Results and Discussion.

Synthesis and Characterization. BTF6 was prepared according to the procedure described in the literature.[2e,6b] BTF6 (1.1 mmol) in CH_2Cl_2 was readily reacted with chloromethyl methyl ether (1.3 mmol)[11] and $TiCl_4$ (0.9 mmol) at 0 °C. After 1 h of stirring of the solution at room temperature under N_2 condition, the reaction mixture was quenched with H_2O, extracted, washed, and then dried to afford poly-BTF6. The polymer was soluble in common organic solvents such as tetrahydrofuran, dichloromethane, chloroform and ethyl acetate. The glass transition temperature (T_g = 110 °C) and melting temperature (T_m = 227 °C) of the polymer were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) indicates that the polymer is stable at high temperature (up to 330 °C). The weight-average molecular weights (M_w) and dispersity of M_w of the resultant polymer were 40 000 and 2.6, respectively. However, the M_w and dispersity of the polymer were varied depending on the reaction condition and the content of the reagent. Thus, M_w of the polymer was reduced to 7970 with the same dispersity (2.6) when the content of $TiCl_4$ and CME were reduced to 0.9 equiv.

The polymerization is expected to proceed through initial chloromethylation[12a,b] and following Friedel−Crafts alkylation[12c] as shown in Scheme 1. To confirm the structure of the poly-BTF6, a model study using benzothiophene derivatives was performed. When 2,3-dimethylbenzothiophene (**7**) prepared from 3-bromo-2-methylbenzothiophene was reacted with chloromethyl methyl ether in the presence of $TiCl_4$, a mixture of two inseparable compounds whose structures could be assigned as **3** and **4**, based on ^{1}H NMR analysis, was obtained (Scheme 2).

Since the alkylation can readily occur at 5- and 6-positions of benzothiophene, we prepared 2,3,5-trimethylbenzothiophene (**11**) from 4-methylbenzene thiol (**8**) in two step[13] to block the 5-position from the dimerization. In the reaction of **11** under the same reaction condition, dimer **5** was obtained in 70% yield. From these model studies, the bridged methylene unit of poly-BTF6 is expected to connect between either the 5- or 6-position of the benzothiophene moiety.

Although cationic polymerization methods from vinyl units or olefinic group are known, there is no report on the polymerization of aromatic compounds, such as benzothiophene, directly by Lewis acid catalysts.[10] Thus, the polymerization method reported here using Friedel−Crafts alkylation could be applied conveniently in the polymerization of many functional aromatic compounds.

Photochromic Properties. The progress of the photoisomerization of poly-BTF6 (M_w = 40 000) in a $CDCl_3$ solution (5.0×10^{-3} M) was followed by ^{1}H NMR spectroscopy. Figure 1 shows the ^{1}H NMR spectra of open ring isomer (B) and at the photostationary state of poly-BTF6 (C) along with open ring isomer of monomeric BTF6 (A). The ^{1}H NMR spectrum of the polymer shows broad peaks similar to those of BTF6. Additional two broadened peaks at 4.66 and 4.11 ppm for the polymer (B) verified the presence of the bridged methylene proton of antiparallel (a−p) and parallel (p) conformations. After UV irradiation (313 nm), a new broad peak corresponding to the methyl proton of closed-ring isomer subunit, appeared at 2.0 ppm. The cyclization conversion at the photostationary state

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* Corresponding author.

[†] College of Environment and Applied Chemistry and Institute of Natural Science, Kyung Hee University.

[‡] Department of Chemical Engineering, Yonsei University.

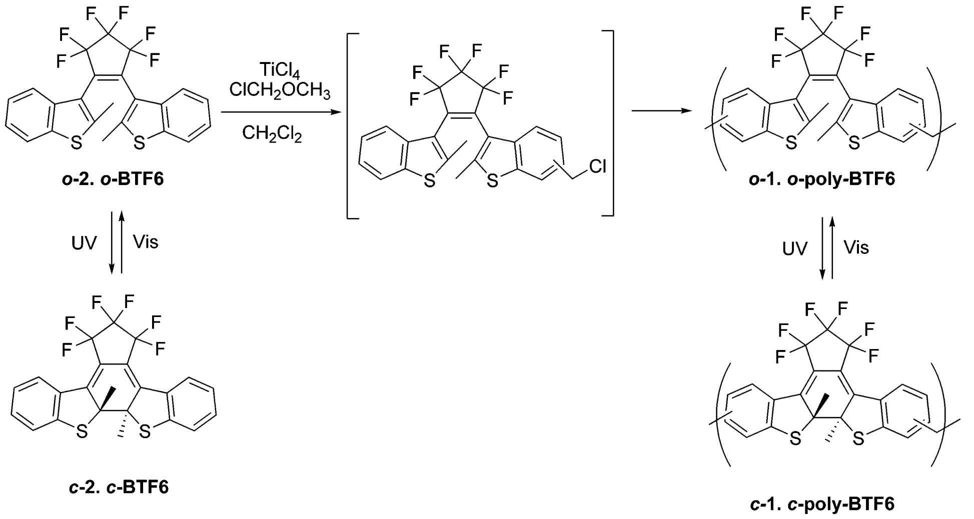
[§] Fax: 82-2-312-6401. Tel: 82-2-2123-5752; eunkim@yonsei.ac.kr.

[⊥] Fax: 82-31-202-7337. Telephone: 82-31-201-3735. E-mail: siyang@khu.ac.kr.

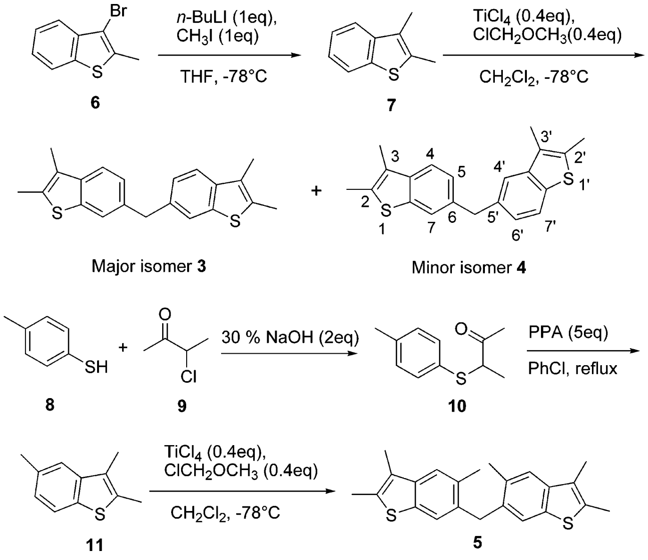
[||] Fax: 82-31-202-7337. Telephone: 82-31-201-2447. E-mail: khahn@khu.ac.kr.

10.1021/ma0602167 CCC: $33.50

Scheme 1. Synthesis and Photochromic Reactions of Poly-BTF6



Scheme 2. Synthesis of Dimers



was higher than 30% as determined from the integration of the methyl peaks. The new peak corresponding to a closed isomer was disappeared upon exposure to a visible light and the initial ^{1}H NMR was recovered.

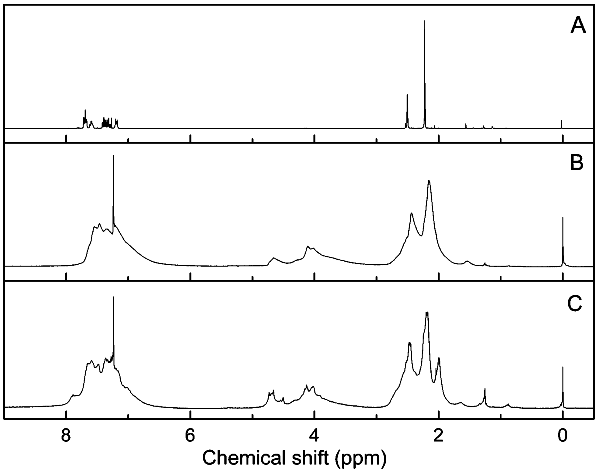


Figure 1. ^{1}H NMR spectra of open ring isomer of BTF6 (A), open ring isomer (B) and the photostationary state (C) of poly-BTF6 in $CDCl_3$ (5×10^{-3} M).

Spectral change of poly-BTF6 ($M_w = 40\,000$) in ethyl acetate upon irradiation with 313 nm light at room temperature is shown in Figure 2. New absorption band (534 nm), characteristic of the closed-ring isomer of the polymer, was observed, resulting from the photoinduced cyclization reaction. The maximum absorption of poly-BTF6 was red-shifted about 10 nm when compared to BTF6 (524 nm). The absorbance growth of the visible band for the polymer was dependent on the M_w of the polymer. Thus, the absorption increase for the solution of poly-BTF6 ($M_w = 7970$) by UV light over exposure time (B) was comparable to that of BTF6 (A), indicating that the photochromic conversion in the polymer is also efficient. On the otherhands, the growth for the solution of the polymer having high M_w ($M_w = 40\,000$) was smaller than that of low M_w poly-BTF6 as compared in Figure 2 under the similar condition. The photochromic ring cyclization efficiency was determined as 60%, 60%, and 43% in A, B, and C, respectively. Such a result may arise from the reduced rotational freedom by the linker between photochromic diarylethene subunit in the polymer. When the ring-closed sample was irradiated with visible light, the original spectrum was obtained immediately, confirming the reversibility of the electrocyclic reaction even in the polymer.

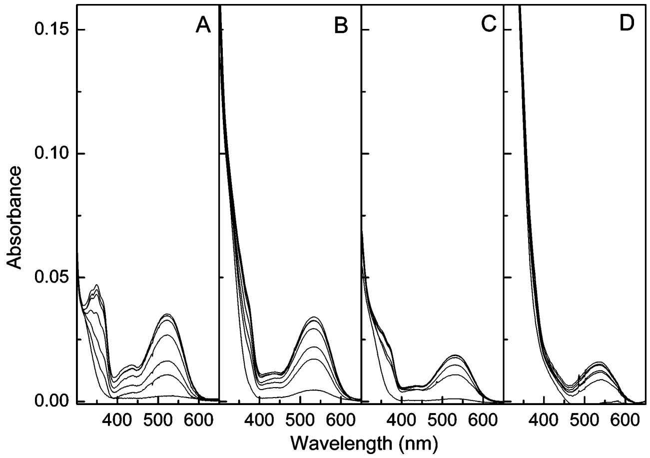


Figure 2. Absorption spectra change of (A) BTF6 in ethyl acetate (1×10^{-5} M), (B) poly-BTF6 ($M_w = 7970$), (C) poly-BTF6 ($M_w = 40\,000$) in ethyl acetate (1×10^{-5} M based on the photochromic unit), and (D) poly-BTF6 film ($M_w = 40\,000$) upon irradiation with a UV light (313 nm). Irradiation time 0, 10, 20, 50, 100, 200, and 500 s for solution and 0, 10, 30, 60, 300, 600, and 1200 s for film (bottom to top).

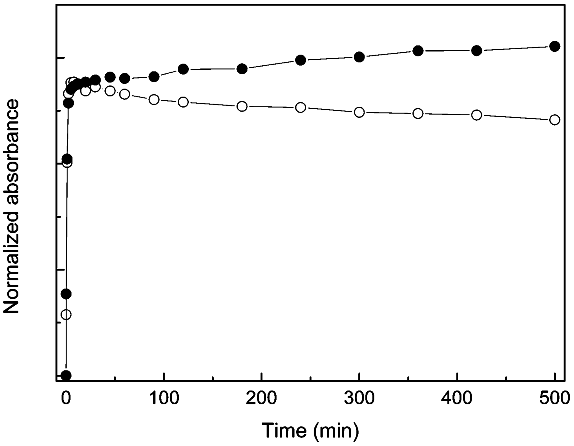


Figure 3. Absorbance changes of BTF6 (open circle) and poly-BTF6 (closed circle, M_w 40 000) at absorption maximum of closed-ring isomer as a function of UV illumination time.

Poly-BTF6 retains its photochromic behavior in the solid film (140 nm thickness) prepared from spin-coating of the polymer solution in $CHCl_3$ (20 mg/mL) onto quartz substrate (Figure 2D). Irradiation of the film with UV light results in immediate color change, indicating that the photochromic property of the polymer is conserved in the processed state. The film was bleached back upon irradiation of visible light. The absorbance growth of the visible band for the polymer film over exposure time (D) was smaller than that in solution (C) under the same exposure condition, due to the reduced rotational freedom in the solid film media.

The fatigue resistance of poly-BTF6 was investigated to examine the synergetic effect of the polymerization. In particular, fatigue resistance to UV light is important for the practical application of organic functional materials in outdoor products. Figure 3 shows the absorbance changes of BTF6 (open circle) and poly-BTF6 (closed circle) in ethyl acetate (1.0×10^{-5} M) at room temperature, monitored at λ_{max} of the closed-ring isomers as a function of UV illumination time for 500 min. After initial increase of the absorbance which is related to the photocyclization from open- to closed-ring isomer of both BTF6 and the polymer, the absorbance of BTF6 was started to decrease. However, the absorbance of poly-BTF6 was slowly increased for 500 min. When visible light was irradiated to both samples after 500 min, closed-ring isomer of poly-BTF6 was returned to the open-ring isomer giving the original absorption spectrum, whereas the absorption spectrum of BTF6 did not match with its open-ring isomer spectrum due to the formation of byproduct under UV light as reported by Irie,[14] Branda,[15] and our groups.[16] This result indicates that the polymerization of BTF6 leads to a significant improvement in the fatigue resistance to UV light as compared with monomeric BTF6.

Conclusions. In summary, we have synthesized and characterized a high-density diarylethene main-chain homopolymer, poly-BTF6, from the reaction of BTF6 with $TiCl_4$ and chloromethyl methyl ether. The new polymerization method is very efficient to produce the polymers of various molecular weights in high yield. The polymer exhibits the characteristic photochromic property as the corresponding monomeric unit in solution and also in solid film. The fatigue resistance of the polymer to UV light was significantly improved compared with its monomer unit. This novel polymerization of a photochromic diarylethene using Friedel−Crafts alkylation could be widely applied in the polymerization of many functional aromatic compound as evidently shown by the dimerization of a benzothiopene derivative (Scheme 2).

Acknowledgment. This research was supported by the Korea Research Foundation (KRF-2005-005-J00801) (K.-H.A, S.I.Y.), and the Ministry of Science and Technology, Korea, through the Nanotechnology Development Program (E.K.).

Supporting Information Available: Text giving the experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0602167