

Photochromic Behavior of Naphthopyran in Styrene-Butadiene-Styrene Elastomer Thin Films: Effect of Stretching of Film and Linker

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ABSTRACT: Thermoplastic elastomers of styrene-butadiene-styrene (SBS) triblock copolymers containing grafts of naphthopyran as side-chain polymer were prepared by polymerization of naphthopyran acrylate monomer with a solution of SBS in tetrahydrofuran. Thin films of all grafted SBS polymers displayed photochromism, the decoloration kinetics of naphthopyran in the films was modeled by fitting biexponential equations to the photochromic decay curves after UV light irradiation. Stretching of the grafted SBS film at room temperature affected the fading rate constant k_1 of the naphthopyran. The length of linker between photochromic naphthopyran moiety and the acrylate unit in monomer also affected the fading rate constant k_1 of the naphthopyran in SBS elastomers. This study presents an example of tuning the photochromic properties of naphthopyran via two approaches, polymer structure, and stretching of films. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: naphthopyran; elastomer; photochromism; film stretching; kinetics; fading rate

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INTRODUCTION

Photochromism is a reversible photochemical reaction of a chemical species between two molecular structures accompanied with a color change under stimulation of light with different wavelengths.^{1,2} Photochromic materials have a wide variety of applications, such as, optical switches, optical filters, ophthalmic lenses, and memory devices.^{3–7} There are many organic molecular systems exhibiting photochromism, such as, spirooxazine,⁷ spiropyran,^{4,7} naphthopyran,³ diarylethene,^{4,5} and azo compounds.⁴ Among them, naphthopyran is well-known photochromic compound because of its small background color and good resistance to photochemical fatigue and also because of easy controllable fading kinetics. Compared with other photochromic compounds, the merocyanine form of naphthopyran is easy to decolorize thermally in the absence of light irradiation.^{8,9} Under UV light irradiation, the heterolytic cleavage of the C—O bond in the pyran unit takes place and results in different stereoisomers. There are two kinds of open forms, merocyanine and zwitterionic (Scheme 1), which are colored because of their extended conjugations and quasiplanar structures.^{10,11}

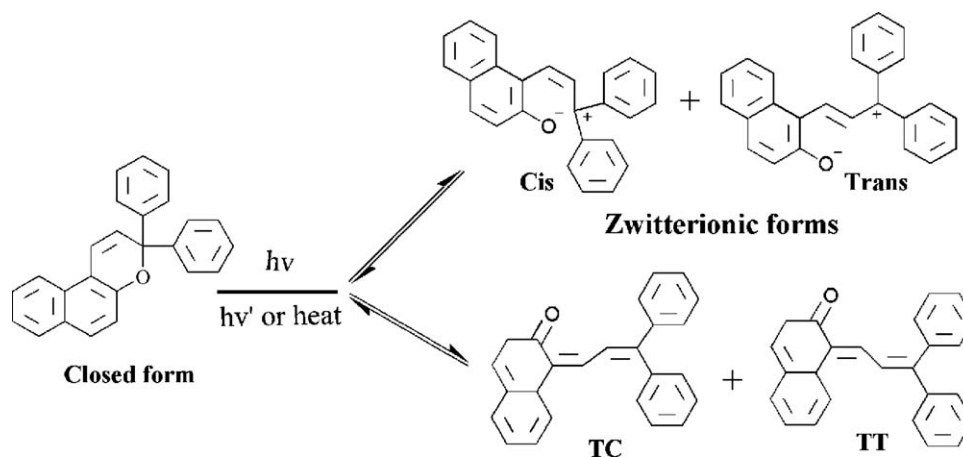
The photochromic behavior of the photochromic molecules is strongly influenced by the molecular structure and the medium in which they are incorporated. Many factors such as, rigidity, viscosity, polarity of the host environment, and free volume

around photochromic moiety affect the speed of the photochromic reaction.^{12–15} Photochromic transition involves substantial mechanical movement and requires a large intramolecular rotation during coloration and decoloration. Therefore, the speed of photochromic switching can be tuned by changing the host environment around the photochromic molecules.

Most of the practical applications require that the photochromic compounds should be incorporated into polymer matrices. The two methods, doping of the photochromic moiety and incorporating the photochromic moiety into the polymer matrices by chemical bonds, are often used to make photochromic materials.^{16–19} Until now, there are only few reports about naphthopyran-containing polymers, in which the authors reported the effects of different factors on the photochromic speed of naphthopyran with different molecular structures.^{9,20–22}

Thermoplastic elastomers have good processability character and a wide range of applications. They can be deformed freely in a large and reversible manner, and their thin films can easily be prepared and stretched.²³

In this article, we report the preparation of a system of naphthopyran elastomers in which naphthopyran side-chain polymer was grafted onto a styrene-butadiene-styrene (SBS) copolymer backbone. It was found that both the stretching of the films



Scheme 1. Chemical structure of the naphthopyran and its open-form isomers (merocyanines).

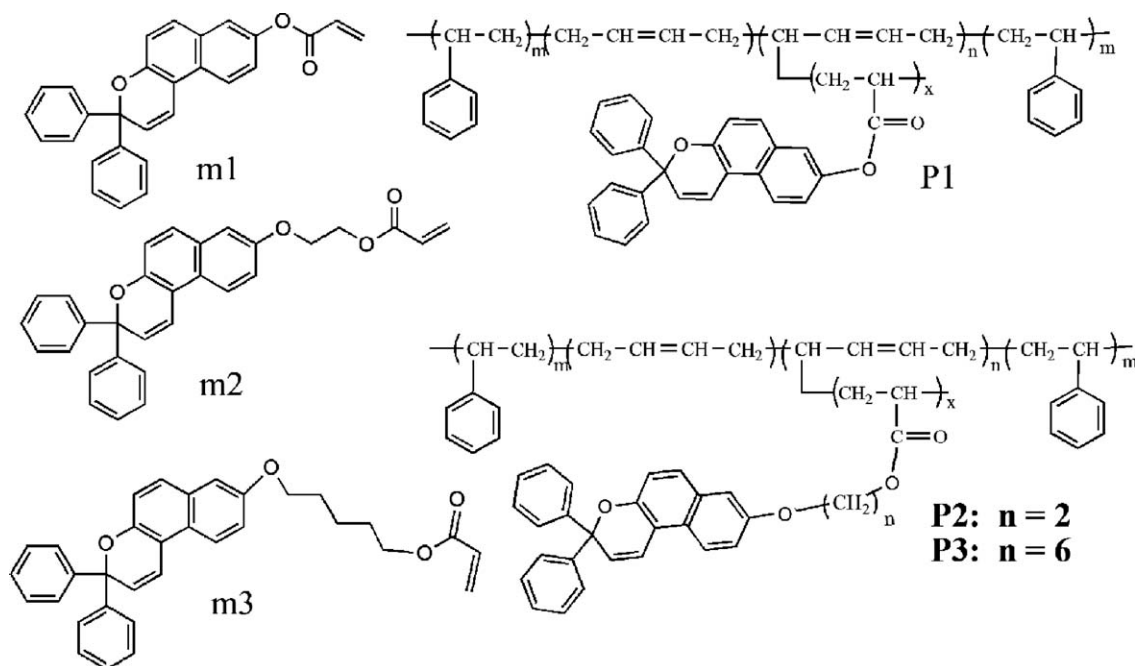
and the length of linker between acrylate unit and naphthopyran moiety in monomer affect the photochromic switch speed of naphthopyran. The motivation for our studies on photochromic naphthopyran elastomers was that we expected the stretching of the thin films can tune the photochromic switch speed of naphthopyran, which is beneficial for designing mechanically tunable optical devices. Conversely, it was expected that the different lengths of linker between the double bond of acrylate and naphthopyran moiety in monomer show different effects on the photochromic switch speed of naphthopyran. This phenomenon can change the distance of naphthopyran moieties with SBS main chain and further modulate the effect of SBS main chain on the photochromic process of naphthopyran. This study aimed to reveal the effect of mechanics and the length of linker on the photochromic speed of naphthopyran. To the best of our knowledge, no such studies have so

far been reported. Scheme 2 shows the structures of the naphthopyran monomers and the grafted SBS elastomers.

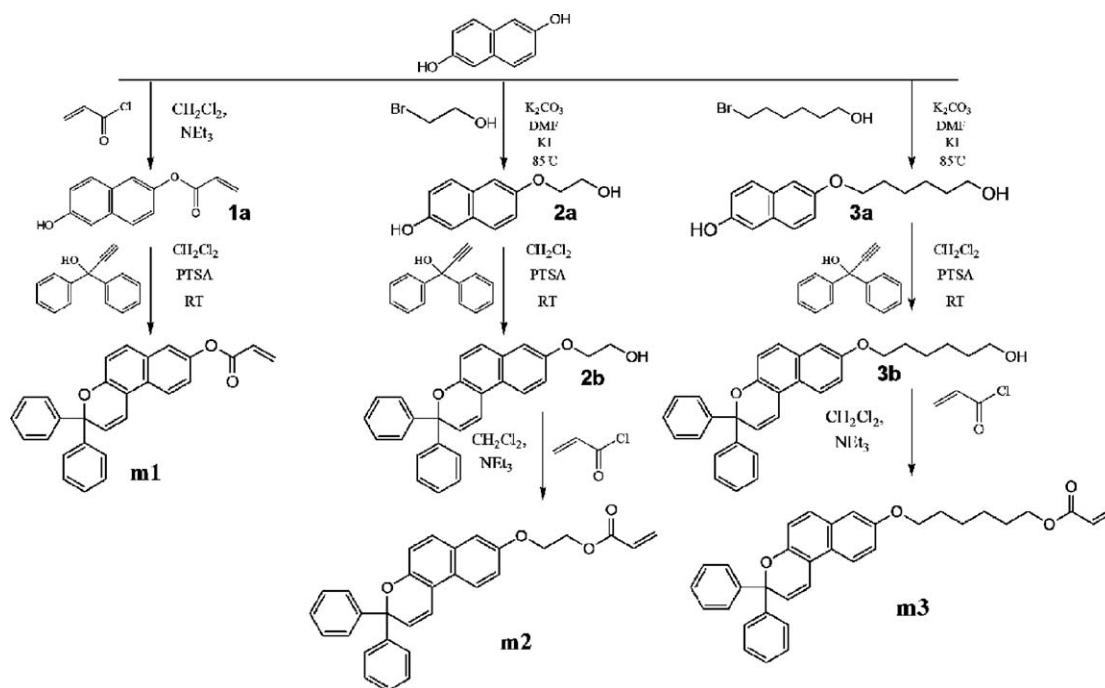
EXPERIMENTAL

Materials

All solvents and other reagents were of high purity and used as received unless stated. SBS elastomer containing 30 wt % of polystyrene (PS) was purchased from Aldrich (Shanghai, P.R.China). Acryloyl chloride (MA, 99%, Aldrich) was filtered before utilization through a basic alumina column to remove the radical inhibitor. Benzoyl peroxide (BPO, 99%) was recrystallized twice from solution in ethanol. 1,1-Diphenyl-2-propyn-1-ol, 2,6-dihydroxynaphthalene, *p*-toluene sulfonic acid (PTSA), 2-bromorthanol, and 6-bromo-1-hexanol were purchased from Aldrich. All chromatography examinations were performed using silica gel, and thin layer chromatography was performed on silica plates (made in China).



Scheme 2. Chemical structures of monomers and naphthopyran-grafted SBS elastomers.



Scheme 3. The synthetic route of naphthopyran monomers.

General Experimental Methods. Gel permeation chromatography (GPC) was performed by a Waters-410 system using tetrahydrofuran as the eluent and standard PS samples for calibration.

Thermal analysis of the photochromic block copolymers was conducted using a Perkin-Elmer DSC-7 differential scanning calorimetry (DSC) in a nitrogen atmosphere. For measurement of the glass transition temperature (T_g), about 3–5 mg samples in an aluminum holder were heated from 20 to 200°C, then they were cooled to 20°C and reheated to 200°C. The heating and cooling rate was set at 10°C/min. The DSC traces presented in this article are the second heating curves.

The photochromic properties of the polymeric films were examined using a Varian Cary 500 UV–vis spectrophotometer. Samples were placed on the sample holder in the spectrophotometer at a slope of about 45° and their absorbances were measured. The samples were then irradiated to a constant intensity with UV light (365 nm) to ensure the sample has reached steady coloration state. A CHF-XM35 parallel light system with a 500-W xenon lamp was used as the UV source of irradiation. The absorbance decay was then measured continuously in the dark within 5 min. The wavelength of the maximum absorption (λ_{\max}) of the ring-opened form (colored) of naphthopyran was obtained by plotting the UV spectrum of the sample. All of the experiments were performed at room temperature.

¹H-NMR spectroscopy spectra were recorded on a Varian Unity Inova Spectrometer (500 MHz) at room temperature and d-chloroform was used as solvent.

Films preparation and stretching experiment. All polymer films for stretching and irradiation were prepared on the 35 T flat stream of machine (made in China) at 80°C, the thicknesses

of the films were carefully controlled to be about 0.1–0.2 mm and were measured using DEKTAK 6M Stylus profiler. A simple device designed in our laboratory was used to do the stretching experiments. After the polymer films were prepared, they were cut in strips with a 1.5 cm width, one end was fixed to the device and the other end could be shifted.

Synthesis of Naphthopyran Acrylate Monomers

The monomers were synthesized as shown in Scheme 3. 2-Hydroxy-6-acyloyloxy-naphthalene **1a**: 2,6-dihydroxynaphthalene (20 g, 124.9 mmol) and triethylamine (6.54 mL, 187.35 mmol) were dissolved in dry CH₂Cl₂ (50 mL) under nitrogen atmosphere and stirred well in ice/water bath. A solution of acryloyl chloride (2.1 mL, 20.0 mmol) in 5 mL CH₂Cl₂ was added dropwise under stirring, the reaction solution was stirred overnight at room temperature. The precipitated amine hydrochloride was filtered off; the organic solution was washed with brine two times and then was dried with anhydrous magnesium sulfate. The purified product was obtained by column chromatography on silica gel (eluent: ethyl acetate : petroleum ether = 1 : 6), white solid 7.12 g, 50% yield. ¹H-NMR (CDCl₃, 500 MHz) δ : 7.63 (d, 1H, $J = 7.5$ Hz), 7.60 (d, 1H, $J = 7.5$ Hz), 7.19 (s, 1H), 7.07 (s, 1H), 7.16 (d, 1H, $J = 2.0$ Hz), 7.14 (d, 1H, $J = 2.5$ Hz), 6.34–6.28 (m, 1H), 6.60 (d, 1H, $J = 7.5$ Hz), 5.99 (d, 1H, $J = 10.0$ Hz).

8-Acyloyloxy-[3,3-diphenyl]-3H-naphtho[2,1-b]pyran **m1**: A mixture of **1a** (1 g, 4.67 mmol), 1,1-diphenyl-2-propyn-1-ol (1.07 g, 5.137 mmol), and PTSA (0.0934 g) in 15 mL of dry CH₂Cl₂ solution were stirred at room temperature under nitrogen atmosphere for 48 h. The reaction mixture was washed with water (3 × 100 mL) and was dried with anhydrous sodium sulfate. The crude product was further purified by column

chromatography on silica gel (petroleum ether : $\text{CH}_2\text{Cl}_2 = 4 : 1$), orange solid (0.6 g, 35% yield). $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 7.97 (d, 1H, $J = 14.0$ Hz), 7.61 (d, 1H, $J = 9.5$ Hz), 7.48 (d, 4H, $J = 7.0$ Hz), 7.34–7.30 (m, 4H), 7.27 (s, 2H), 7.26 (d, 1H, $J = 3.0$ Hz), 7.22 (d, 1H, $J = 9.0$ Hz), 7.24 (d, 1H, $J = 4.0$ Hz), 7.22 (d, 1H, $J = 9.0$ Hz), 6.65 (d, 1H, $J = 16.5$ Hz), 6.39–6.33 (m, 1H), 6.30 (d, 1H, $J = 10.0$ Hz), 6.04 (d, 1H, $J = 9.5$ Hz).

2-Hydroxy-6-(2-hydroxy)ethoxy-naphthalene **2a**: A mixture of 2,6-dihydroxynaphthalene (20 g, 124.9 mmol), anhydrous K_2CO_3 (24.3 g, 174.8 mmol), 2-bromo-1-ethanol (15.6 g, 124.9 mmol), and a pinch of KI in 200 mL DMF were stirred at 85°C for 48 h. After cooling to room temperature, the mixture was poured into water and filtered. The precipitate was dissolved into ethyl acetate (3×100 mL) and the organic solution was dried over anhydrous sodium sulfate. The purified product was obtained by column chromatography on silica gel (ethyl acetate : petroleum ether = $5 : 8$), white solid (10 g, 39% yield). $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 7.64 (d, 1H, $J = 9.0$ Hz), 7.61 (d, 1H, $J = 9.0$ Hz), 7.16 (d, 1H, $J = 10.0$ Hz), 7.08 (d, 1H, $J = 10.0$ Hz), 7.26 (s, 1H), 7.11 (s, 1H), 4.20–4.17 (m, 2H), 4.03–4.02 (m, 2H).

8-(2-Hydroxy)ethoxy-[3,3-diphenyl]-3*H*-naphtho[2,1-*b*]pyran **2b**: A mixture of **2a** (10 g, 48.9 mmol), 1,1-diphenyl-2-propyn-1-ol (11.2 g, 53.8 mmol), and PTSA (0.1958 g) in 60 mL of dry CH_2Cl_2 solution were stirred at room temperature under nitrogen atmosphere for 48 h. The reaction mixture was washed with water (3×100 mL) and dried with anhydrous sodium sulfate. The crude product was further purified by column chromatography on silica gel (ether : $\text{CH}_2\text{Cl}_2 = 1 : 55$), orange solid 6.0 g, 35% yield. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 7.80 (d, 1H, $J = 9.0$ Hz), 7.46 (d, 1H, $J = 7.5$ Hz), 7.41 (d, 4H, $J = 7.5$ Hz), 7.25–7.22 (m, 4H), 7.20–7.15 (m, 2H), 6.20 (d, 1H, $J = 10.0$ Hz), 6.98 (d, 1H, $J = 2.5$ Hz), 7.08 (s, 1H), 7.10 (d, 1H, $J = 2.5$ Hz), 7.11 (d, 1H, $J = 7.5$ Hz), 4.10–4.07 (m, 2H), 3.95–3.92 (m, 2H).

8-(2-Acyloyloxy)ethoxy-[3,3-diphenyl]-3*H*-naphtho[2,1-*b*]pyran **m2**: The compound **2a** (0.5 g, 1.27 mmol) and triethylamine (0.27 mL, 1.91 mmol) were dissolved in dry CH_2Cl_2 under nitrogen atmosphere and stirred well in ice/water bath. A solution of acryloyl chloride (0.14 mL, 1.4 mmol) in dry CH_2Cl_2 was added dropwise into the above mixture, and the mixture was warmed gradually to room temperature and stirred for 48 h. The precipitated amine hydrochloride was filtered off, the filtrate was washed with water (3×100 mL) and then dried with anhydrous sodium sulfate. The purified product was obtained by column chromatography on silica gel (ether : $\text{CH}_2\text{Cl}_2 = 1 : 55$), white solid 0.4g, 75% yield. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 7.88 (d, 1H, $J = 9.5$ Hz), 7.54 (d, 1H, $J = 7.5$ Hz), 7.48 (d, 4H, $J = 7.5$ Hz), 7.42–7.26 (m, 4H), 7.25–17 (m, 2H), 7.16 (d, 1H, $J = 2.5$ Hz), 7.17 (m, 1H), 7.15 (d, 1H, $J = 3.0$ Hz), 7.05 (d, 1H, $J = 3.0$ Hz), 6.47 (d, 1H, $J = 15.0$ Hz), 6.28 (d, 1H, $J = 9.5$ Hz), 6.21–6.16 (m, 1H), 5.88 (d, 1H, $J = 7.5$ Hz), 4.60–4.54 (m, 2H), 4.32–4.27 (m, 2H).

2-Hydroxy-6-(6-hydroxy)hexoxy-naphthalene **3a** and 8-(6-hydroxy)hexoxy-[3,3-diphenyl]-3*H*-naphtho[2,1-*b*]pyran **3b** were synthesized using the same procedure as **2a** and **2b**.

8-(6-Acyloyloxy)hexoxy-[3,3-diphenyl]-3*H*-naphtho[2,1-*b*]pyran **m3**: This product was synthesized from **3b** and acryloyl chloride using the same general synthesis procedure as **m2** and was isolated as a white solid (yield 70.4%) after purification by column chromatography on silica gel (ether : $\text{CH}_2\text{Cl}_2 = 1 : 55$). $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 7.85 (d, 1H, $J = 9.0$ Hz), 7.52 (d, 1H, $J = 8.0$ Hz), 7.48 (d, 4H, $J = 3.5$ Hz), 7.47–7.30 (m, 4H), 7.29–7.22 (m, 2H), 5.81 (d, 1H, $J = 10.0$ Hz), 6.15–6.08 (m, 1H), 6.40 (d, 1H, $J = 2.0$ Hz), 6.37 (d, 1H, $J = 2.0$ Hz), 7.02 (d, 1H, $J = 2.5$ Hz), 7.12 (s, 1H), 7.14 (d, 1H, $J = 2.5$ Hz), 7.16 (d, 1H, $J = 7.5$ Hz), 4.04–4.02 (m, 2H), 3.68–3.65 (m, 2H), 1.85–1.82 (m, 2H), 1.74–1.69 (m, 2H), 1.56–1.51 (m, 2H), 1.49–1.46 (m, 2H).

Synthesis of Naphthopyran-Grafted SBS Elastomers (P1, P2, and P3)

The three naphthopyran monomers, denoted as **m1**, **m2**, and **m3** (Scheme 2), were used to prepare photochromic SBS elastomers, denoted as **P1**, **P2**, and **P3** hereafter (Scheme 2). The three polymers were prepared through radical polymerization of the monomers using BPO as initiator. Unless otherwise stated, the following procedure was used to prepare photochromic SBS elastomers with naphthopyran grafted onto the central polybutadiene (PB) block.

The mixture of SBS (1 g), **m1** (0.08 g), BPO (2 mg), and toluene (15 mL) in 50 mL flask was stirred to be transparent. Then, the mixture was frozen in liquid nitrogen and a vacuum was applied. Then, the three freeze–pump–thaw cycles were performed, the flask was sealed and put in an oil bath at 80°C for 16 h. The **P1** was obtained by precipitated in methanol three times, $M_w = 12,2011$ and $M_w/M_n = 1.49$.

All grafted SBS samples were purified through multiple precipitations in methanol, ensuring the removal of unreacted monomer as well as the naphthopyran polymer that was not chemically linked to SBS. The grafting sites could not be confirmed by $^1\text{H-NMR}$ spectra. Suggesting the structures of naphthopyran-grafted SBS elastomers as shown in Scheme 2, it was assumed that a radical transfer to the methylene group of the PB block initiated the graft polymerization.^{23–25} In $^1\text{H-NMR}$ spectra of grafted elastomers, the hydrogen peak at about 6.2, attributed to the double bond of pyran ring were observed, which also indicates that the naphthopyran monomer were grafted onto the SBS polymer chains.^{26,27} All purified samples were collected and dried under vacuum conditions.

RESULTS AND DISCUSSION

Characterization of the Samples

Three samples of naphthopyran-grafted SBS were synthesized and their characteristics were examined (Table I). The grafting of the naphthopyran polymer on the PB block of SBS was confirmed by GPC technique. The grafting naphthopyran polymer should result in an increase in the average molecular weight of the SBS after the polymerization. Although the feed ratio of naphthopyran monomer to SBS was the same in the synthesis of three samples, the molecular weights of three samples were not the same. This difference was likely caused by lack of perfect controlling of the synthesis conditions. The three naphthopyran-grafted samples, **P1**, **P2**, and

Table I. Characteristics of the Samples

Acronym of polymer	M_w (g/mol)	M_w/M_n	T_g
SBS	10,7249	1.35	65.88
P1	12,2011	1.49	52.90
P2	12,3204	1.50	50.27
P3	12,5890	1.62	54.22

P3, have greater weight-average molecular weights and wider molecule weight distribution than that of pure SBS, which is normal in free radical polymerization method.

The naphthopyran-grafted SBS samples have a complex morphology with naphthopyran polymers embedded in the rubbery PB block. All their films are transparent like pure SBS, which indicates that the grafting naphthopyran polymers form a microphase and is confined in small microdomains.²⁵ On the contrary, when mixing the SBS and naphthopyran homopolymer with similar composition for comparison, the films of the mixture were not transparent.

The photochromic kinetics of the photochromic dyes are very sensitive to the T_g of the polymeric matrices in which they are attached.^{17,21,22,28} The higher T_g of polymeric matrix results in more rigidity and steric hindrance of the polymeric matrices.

The DSC heating curves of naphthopyran-grafted SBS samples and pure SBS are present in Figure 1. Three naphthopyran-grafted SBS samples had lower T_g than that of pure SBS (Table I), the differences of T_g among P1, P2, and P3 were not large. The decrease of T_g can be explained by the presence of naphthopyran polymer attached to SBS backbone, which disturbs the order of chains, and therefore, increases their mobility.²⁸ The DSC results indicated that the introduction of naphthopyran polymer into SBS decreases the rigidity of SBS and the length of linker between the double bond of acrylate and naphthopyran moiety in monomer has no significant effect on T_g of the grafted SBS matrices.

Photochromic Properties of Elastomers

When irradiated with UV light (365 nm), the initially colorless photochromic test elastomer films became highly colored

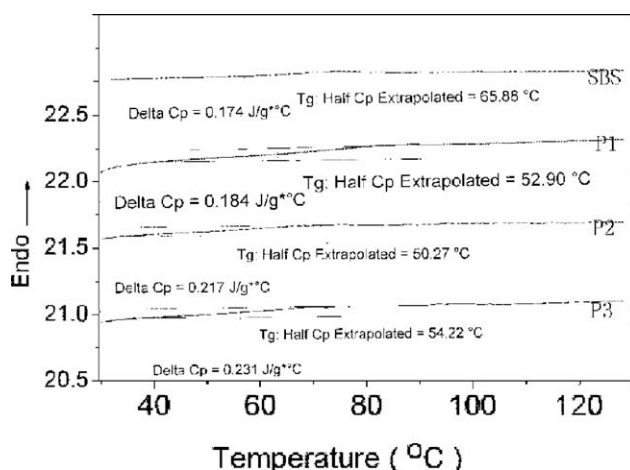


Figure 1. DSC heating curves of naphthopyran-grafted SBS samples and pure SBS.

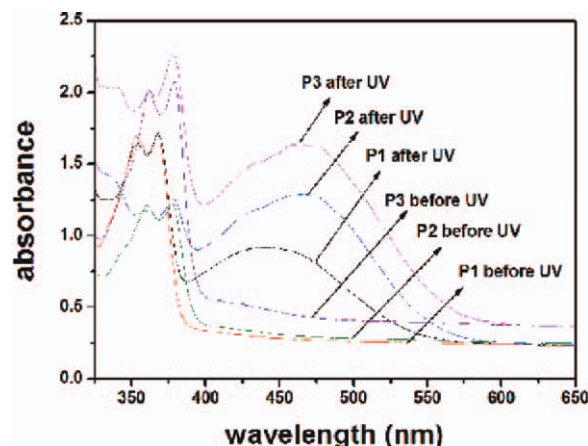


Figure 2. Absorbance spectra of naphthopyran-grafted SBS elastomers before and after UV irradiation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com)]

accompanied by the isomerization of naphthopyran from the ring-closed form (CF) to the merocyanine structure. As shown in Scheme 1, exposure of the CF of naphthopyran to continuous UV irradiation results in a distribution of two colored merocyanine isomers: *trans-cis* (TC) isomers and *trans-trans* (TT) isomers. The TC form is a major component with short life in merocyanine composition, on the contrary, the TT form is a minor component with longer life.²⁰ The TT isomer reverts to the CF through two-step process, TT → TC → CF. The thermal decoloration behavior can be attributed to decaying of the above two merocyanine isomers with different first-order rate constants, k_1 and k_2 . Therefore, the isomerization of TT form to CF form is the dominating process and k_1 can be used to represent the decaying rate of two ring-opened naphthopyran.

The new absorbance peaks (λ_{max}) of ring-opened forms of naphthopyran are situated at 450, 468, and 474 nm for P1, P2, and P3 samples, respectively (Figure 2). It is noteworthy that all naphthopyran-grafted SBS samples exhibited a bathochromic shift (about 25 nm) in the wavelength of their open forms with respect to the lengths of linkers. The differences among the absorbance peaks of ring-opened naphthopyran are likely caused by the different length of linker in monomer. When the linker is longer, there is more distance between naphthopyran and SBS main chain, therefore the interaction between SBS main chain and naphthopyran would be smaller, which causes different effects of PB block on the ring-opened naphthopyran. On termination of the UV irradiation, the samples decolorized spontaneously in the dark because of the thermal back reaction of naphthopyran (Figure 3). The switching speed of photochromism of naphthopyran was very fast, the absorbance intensity of ring-opened naphthopyran reached the maximum in 3 min after UV irradiation and the decoloration finished just within 5 min for all samples.

The cyclic experiments reversibility between coloration and decoloration of the naphthopyran-grafted SBS in films can be examined continuously quite well for numerous cycles. Figure 4 shows the experimental result of sample P2, which indicates that the photochromism of naphthopyran in SBS films has

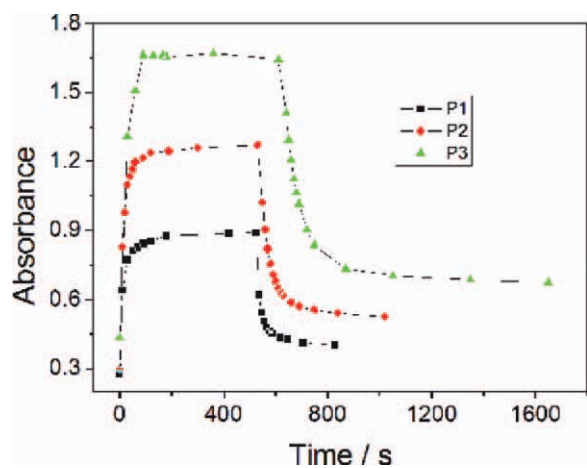


Figure 3. Absorbance intensity at λ_{\max} versus time for the coloration and decoloration of P1, P2, and P3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

good reversibility. The results show that the decoloration of naphthopyran in three elastomer films are not complete. The extent of decoloration of naphthopyran in P1 was larger than that in P2 and the extent of decoloration in P3 was the smallest (Figure 3). For P2 sample, the decreased extent of absorbance intensity of ring-opened form was less than 12% after nine cycles, which is favorable for naphthopyran to be used in practical application. Figures 3 and 4 also indicate that the decoloration of naphthopyran in three elastomers was not complete, the color remained partly in the samples. On the contrary, the absorbance intensity of ring-opened form at λ_{\max} can be almost fully recovered after UV irradiation.

Stretching-Induced Change of Photochromic Performance

The naphthopyran-grafted SBS is a thermoplastic elastomer and has the same transparency as pure SBS. Thin films of three samples showed good mechanical strength that could be repeatedly stretched at room temperature. The thicknesses of P1, P2, and P3 films were 168, 183, and 176 μm , respectively. For three naphthopyran-grafted SBS samples, the stretched films can induce a similar change of photochromic performance. The

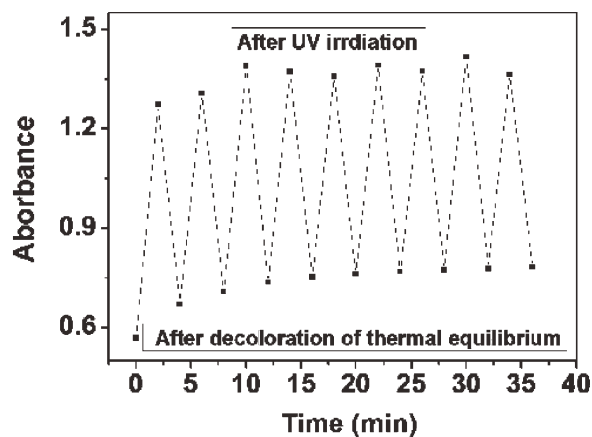


Figure 4. Photochromic cycles of naphthopyran between CF and merocyanine in P2 under UV irradiation and thermal bleaching.

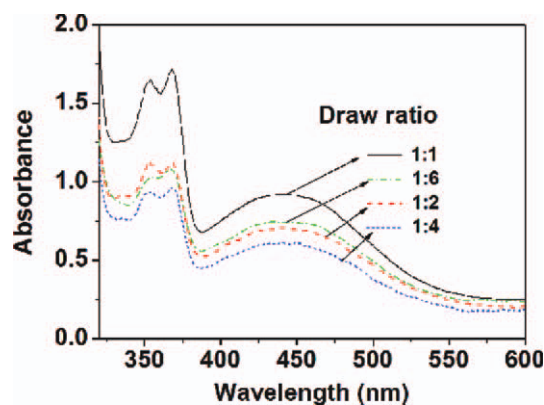


Figure 5. Absorbance spectra of P1 in film before and after stretching. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

decoloration rate constant k_1 of naphthopyran in the elastomer samples showed similar variation trend with the increasing of the draw ratio. After stretching, the absorbance intensity of three samples decreased with increasing of the draw ratio. This may be attributed to the decrease of naphthopyran concentration in the films relative to that before stretching. When the draw ratio reached to 1 : 6, the absorbance intensity reverted to increase. Figure 5 shows the change of absorbance spectra of P1 sample at different draw ratios. Although the absorbance intensities decreased with the increasing of draw ratio, the absorbance peak has small shift after stretching. This shift may be due to the rigid change of microenvironment around naphthopyran molecules. The above result indicates that the stretching of film does not affect the molecular structures of ring-opened and ring-closed naphthopyran.

The decoloration process of ring-opened naphthopyran is accompanied by decreasing of absorbance band of ring-opened naphthopyran. Data in Table II indicate that the maximum absorption intensity (A_0) at λ_{\max} of ring-opened naphthopyran increase with the increasing of the linker of monomers under the same draw ratio. P1 and P3 samples showed the smallest and the largest values of A_0 , respectively. The maximum absorption intensity is likely in proportion to the concentration of naphthopyran in SBS elastomers.

These three polymers P1, P2, and P3 showed similar pattern of decoloration rate. The decoloration rates can be studied by monitoring the variation of the absorption intensity at λ_{\max} of the colored form against time. The samples were continuously irradiated to a constant intensity with UV light at room temperature for 200 s, and then the absorbance spectra of polymer films in the dark were measured consecutively in the same wavelength range. $T_{1/2}$ is the time taken by the sample to fade to half of its original absorption value and provides insight into the overall decoloration kinetics. The $T_{1/2}$ was determined by plotting the absorbance intensity at λ_{\max} as a function of time. Figure 6 represents the variation trend of the absorbance intensity of P2 sample with time, which is a typical example of three naphthopyran-grafted SBS samples. Because there is larger background absorbance (about 0.3–0.45; Figure 2), so the absorbance intensity at

Table II. Photokinetic Analysis of the Decoloration of Naphthopyrans in SBS Elastomers in Films Before and After Stretching

Drawing ratio	A_0	A_1	k_1/s^{-1}	A_2	k_2/s^{-1}	A_{th}	$T_{1/2}/s$	λ_{max}/nm
P1	0.8924	0.32746	0.1271	0.15697	0.0189	0.40517	15	443
P1 , 1 : 2	0.6277	0.26918	0.1288	0.09319	0.0102	0.25979	19	447
P1 , 1 : 4	0.5202	0.20772	0.0861	0.07487	0.0099	0.27679	12	444
P1 , 1 : 6	0.7225	0.26521	0.1011	0.10489	0.0117	0.33986	16	442
P2	1.2692	0.27735	0.0953	0.46737	0.0199	0.53848	36	465
P2 , 1 : 2	0.8931	0.07905	0.0887	0.17548	0.0199	0.48603	33	465
P2 , 1 : 4	0.6334	0.18994	0.0506	0.12257	0.0116	0.31848	42	468
P2 , 1 : 6	0.6789	0.14717	0.0845	0.16153	0.0205	0.32099	34	470
P3	1.6629	0.48397	0.0301	0.41908	0.0088	0.68365	56	468
P3 , 1 : 2	1.0573	0.1919	0.0882	0.33686	0.0214	0.53402	24	467
P3 , 1 : 4	0.6334	0.33793	0.0247	0.13443	0.0066	0.46672	40	472
P3 , 1 : 6	0.7867	0.18313	0.0371	0.09401	0.0114	0.37457	30	471

λ_{max} of opened-form naphthopyran in elastomers cannot fade to half of the maximum value. Therefore, the $T_{1/2}$ was calculated as the time that the absorbance intensity at λ_{max} of opened-form naphthopyran decreased to the half of the difference between the maximum absorbance intensity and the equilibrium absorbance intensity after decoloration. All $T_{1/2}$ data are presented in Table II. When comparing the decoloration rates of **P1**, **P2**, and **P3** before and after stretching, we observed that the stretching of films causes changes of decoloration rates. For each sample, the difference of decoloration before and after stretching was small, and the changes presented irregular trend with the variation of the drawing ratio. Before stretching, the $T_{1/2}$ of naphthopyran in **P3** was the largest and that in **P1** was the smallest. After stretching, the $T_{1/2}$ value of **P1** was smaller than that of **P2** but was greater than $T_{1/2}$ of **P3**. This relation was different from that of the linker length between the double bonds of acrylate and naphthopyran moiety in naphthopyran monomer. These results indicate that the length of linker in monomer affects the decoloration $T_{1/2}$ of naphthopyran in SBS elastomers, but this effect has no obvious regularity with respect to the length of linker.

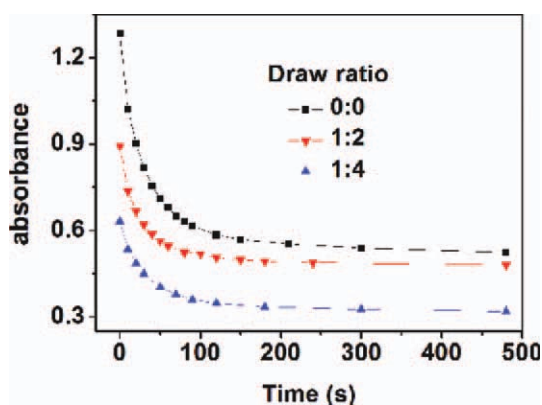


Figure 6. The plot of absorbance intensity at the λ_{max} of ring-opened naphthopyran in **P2** in different drawing ratio with time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

The photochromic decoloration kinetics can also be presented by the following empirical biexponential equation:^{29–31}

$$A(t) = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} + A_{th}$$

where $A(t)$ is the optical density at λ_{max} of opened form, A_1 and A_2 are the contributions to the initial optical density A_0 . A_0 is the maximum absorption intensity at λ_{max} of opened form after long time of continuous irradiation. k_1 and k_2 are the exponential decay rate constants of fast and slow components, respectively, and A_{th} reflects the thermal equilibrium between the two forms. This equation is often used to analyze the decoloration behavior of some photochromic units and confirms that the decay process follows a biexponential model.^{21,22,30} The values of constants of the equation were found from fitting the experimental data of polymer films using Origin 7.5 computer program. The correlation coefficient of the curve fitting (R) was greater than 0.999. Figure 7 shows the excellent agreement between the biexponential fit and experimental data of **P3** before and after stretching. The samples **P1** and **P2** revealed the same results as **P3**, their fit curves were almost superimposed over experimental curves. This result indicates that biexponential model is suitable for analysis of photokinetics of naphthopyran in SBS elastomers.

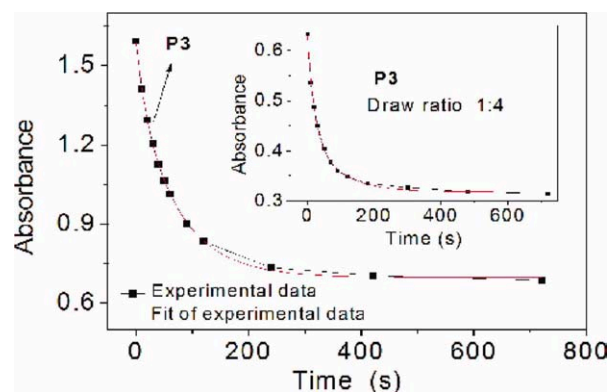


Figure 7. Biexponential fits for the thermal decoloration in the dark of **P3** before and after stretching (inset). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

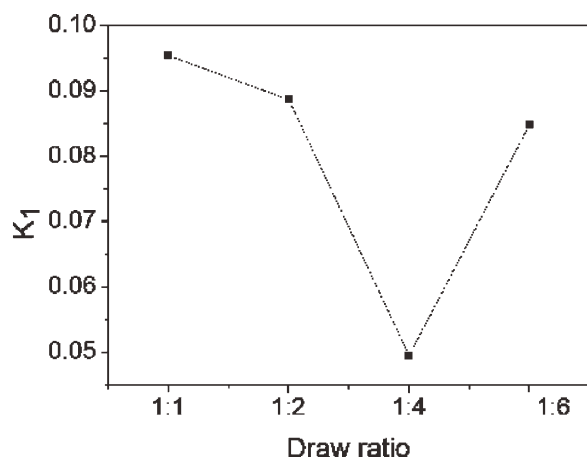


Figure 8. The plot of the decoloration rate k_1 of naphthopyran in P2 as a function of stretching ratios of P2 film.

Decoloration kinetics of naphthopyran in solid matrices is complicated and is influenced by the dispersing environment, free volume, steric hindrance, and chemical composition of the matrices. The decoloration rates of naphthopyran incorporated into SBS are smaller than that of incorporated into the other polymeric matrices, such as, poly(dimethylsiloxane), poly and poly(*n*-butyl acrylate), and poly(methyl acrylate).^{9,20} Naphthopyran moiety is incorporated into the PB chain in the SBS block copolymer and forms small microdomains around PB chain segments. The environment around naphthopyran may provide a larger restriction and steric hindrance for naphthopyran molecule to its rotational mobility and isomerization.

A comparison of the decoloration kinetics of naphthopyran-grafted SBS samples with respect to the length of linker and stretching of the films shows that both linker and stretching film had modulation effect on the decoloration rates of naphthopyran in P1, P2, and P3 samples. Figure 3 and Table II present the trend of change in decoloration rate of naphthopyran. First, the decoloration rate constant k_1 decreases with the increasing of the linker length both in the original films and in the stretched films at the same draw ratios. For the shorter linkers, naphthopyran moieties are closer to the PB backbone and it receives little influence of steric hindrance of PS chain segment. PS is the harder block of SBS than PB and makes larger restriction to the photochromic isomerization of naphthopyran moieties. Second, for any film, the stretching film affects obviously the decoloration rate constant k_1 . Although there is no regular change of decoloration rate constants of naphthopyran in three samples with draw ratios, k_1 in three naphthopyran-grafted SBS samples has similar evolution with the increasing of draw ratio. This effect of stretching film has also been examined indirectly by Evans and coworkers^{9,21,22} that showed decoloration rate constants of naphthopyran in other polymer matrices present regular change with the naphthopyran concentration. The stretching can change the free volume and steric hindrance around naphthopyran molecules that in turn affects the decoloration rates. The experimental results indicated that the stretching causes complicated change of internal matrices of elastomers, so the decoloration rate constant k_1 shows no regu-

lar change trend with the change of the draw ratios. This may be because of the stretching that makes irregular change of microenvironment and further irregularity effects on the decoloration rate constant k_1 . In different stretching ration, the SBS main chains gave different environment around naphthopyran, such as, rigidity and free volume. However, the decoloration rates constants k_1 of naphthopyran in the elastomers revealed similar change performance with the draw ratios.

Figure 8 shows the plot of the decoloration rate constant k_1 of naphthopyran as a function of stretching ratios in P2 film. The decoloration rates constants k_1 of naphthopyran in other two samples followed similar trend of variations with stretching ratio. The irregular change trend of k_1 with drawing ratio further confirmed that the influence of stretching is larger than that of naphthopyran concentration on the decoloration constant k_1 .

The above results indicated that the decoloration rate constant k_1 of naphthopyran in SBS samples can be tuned by both the length of linker in monomer and the stretching of film samples. Compared with other amorphous photochromic polymers, the naphthopyran-grafted SBS samples offer both good processability of thermoplastic elastomers and photochromic performance of naphthopyran. Moreover, the decoloration rate constant k_1 of naphthopyran in SBS can be tuned via dual-mode, the length of linker in naphthopyran monomers and stretching of films.

CONCLUSION

Three naphthopyran-grafted thermoplastic SBS elastomers were prepared by grafting different naphthopyran polymers onto SBS backbone through radical polymerization. It was found that the fading speed of naphthopyran in elastomer films can be tuned by both drawing films and changing length of linker between the double bond of acrylate and naphthopyran moiety in monomer. The dual-mode tuning of decoloration rate of naphthopyran may appear to be mainly of fundamental interest. We believe that such elastomers can be exploited for such device applications by mechanically tuning the decoloration speed of photochromic dyes through stretching the films. More studies are underway to obtain the systemic tuning of decoloration rate of naphthopyran in SBS elastomers.

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