

Synthesis and Photochromic Properties of Naphthopyran Polymer Containing Photocrosslinkable Coumarin Moiety

Bingjie Xie, Guang Wang, Xiancai Zhao

Department of Chemistry, Northeast Normal University, Changchun, 130024, People's Republic of China

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ABSTRACT: Naphthopyran homopolymer and copolymer containing coumarin in side chain were synthesized by atom transfer radical polymerization. Their photochromic properties were investigated using UV-vis absorption spectroscopy and their decoloration kinetics in films was quantified by biexponential fitting of their photochromic decoloration curves after UV irradiation. The results showed that the photochromism and photocrosslinking occurred simultaneously under UV irradiation, and the photocrosslinking of coumarin reduced the decoloration rate of naphthopyran. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3377–3382, 2011

Key words: photochromism; coumarin; naphthopyran; photocrosslinking; irradiation; polymer

INTRODUCTION

Photochromic polymers have recently received considerable attention owing to their potential application in many technologies such as optical switching, data recording and storage, nonlinear optics, and displays.^{1–4} Spiroxazine, spiroopyran, naphthopyran, and thiophene-derivates are photochromic moieties with excellent photochromic performance.^{5–8} Although photochromic behaviors of naphthopyran derivatives have been studied a lot,^{9–11} there are just several publications concerning naphthopyran polymers.^{12–15}

Naphthopyran is well-known photochromic compound, which undergo colorization from the naphthopyran form to its corresponding merocyanine form by irradiation of UV light and vice versa by heat or visible light.⁶ The kinetics of photochromism is important for naphthopyran to be applied in industrial application, and many factors such as viscosity, steric effect, ionic strength, solvent polarity, and complex formation affect the colorization and decolorization processes.¹⁶ The kinetics of photochromism can be adjusted by increasing the steric hindrance around the photochromic units in polymer matrix via photocrosslinking.^{5,16} The process of photopolymerization can increase the rigidity and

steric hindrance of polymer matrix. Photocrosslinking can provide some geometrical hindrance to the isomerization process of merocyanine form. To the best of our knowledge, there is no report about using the photocrosslinking to control the decolorization process of merocyanine form of naphthopyran group.

Coumarin and chalcone as photocrosslinkable groups can form dimer under UV light irradiation,^{6,17} which reduce the free volume around photoresponse units and increase the geometrical hindrance for photoresponse unit to change molecular structure. In this article, we introduced naphthopyran and coumarin as photochromic and photocrosslinkable unit in the side chain of copolymer, respectively. It is expected that the photocycloaddition of coumarin irradiated by UV light can reduce the free volume around naphthopyran units and further control the decolorization process of naphthopyran from the merocyanine structure to the naphthopyran form. The UV-vis absorption spectra and photochromic kinetics were used to evaluate the effect of photocycloaddition reaction on the stability of naphthopyran merocyanine in the copolymer. The structures of synthesized polymers and their photoreaction were shown in Scheme 1.

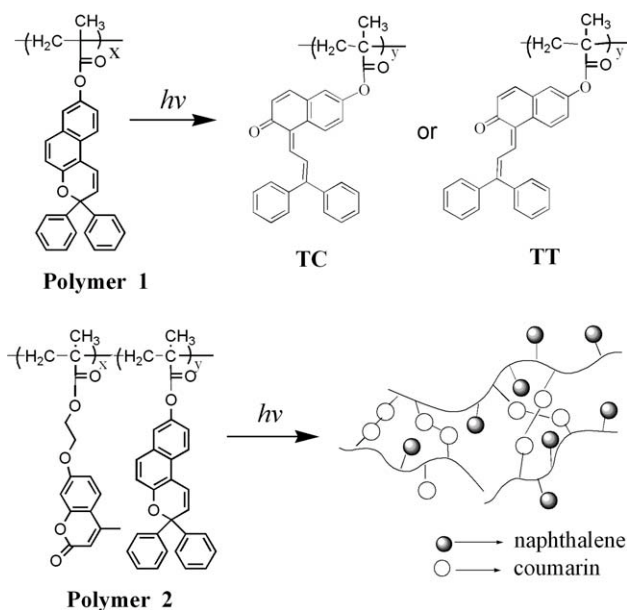
EXPERIMENTAL

N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA), 7-hydroxy-4-methylcoumarin, methacryloyl chloride, 2-bromoethanol, 1,1-diphenyl-2-propyn-1-ol, ethyl-bromoisobutyrate, and copper bromide were purchased from Aldrich Chemical (Shanghai, P.R. China) and used without further purification. THF was refluxed with sodium and distilled.

Correspondence to: G. Wang (wangg923@nenu.edu.cn).

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Scheme 1 Chemical structure of the polymers and the photoreactions under UV irradiation.

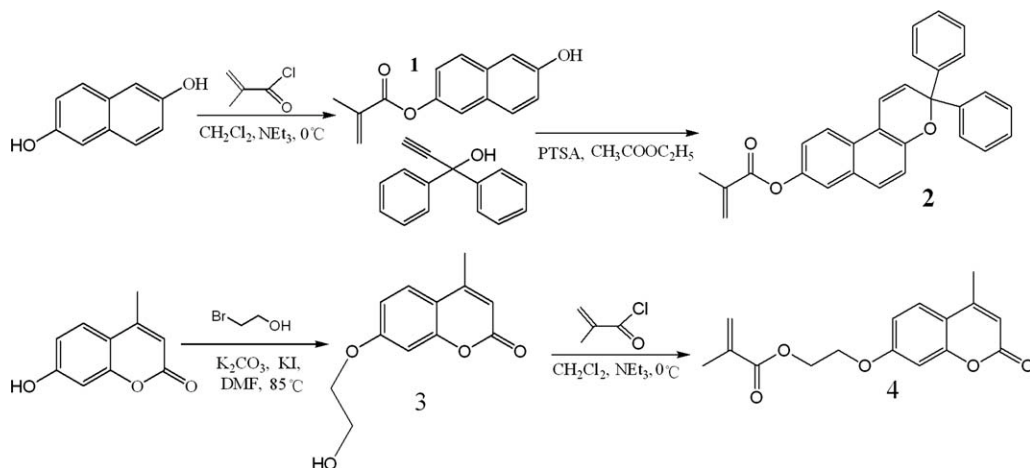
$^1\text{H-NMR}$ spectra were recorded on a Varian Unity Inova Spectrometer (500 MHz). Photoluminescence and UV-vis spectra were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer and a Varian Cary 500 spectrophotometer, respectively. Mass spectra were recorded on the LC-10A/MS equipment. Molecular weight and polydispersity were measured by gel permeation chromatography using a Waters-410 system; THF was used as the eluent and polystyrene standards for calibration. To investigate the effects of photocycloaddition of coumarin unit on the decolorization process of naphthopyran, a CHF-XM35-500W system light source with filters (~ 360 nm) was employed to provide parallel UV light.

Synthesis of methacryloyl coumarin and naphthopyran

The structures of the monomers and synthetic routes were illustrated in Scheme 2. A solution of 2,6-dihydroxynaphthalene (10.0 g, 62.5 mmol), triethylamine (13.0 mL, 93.6 mmol) was prepared in dried CH_2Cl_2 (100 mL). After it was stirred at 0°C for 30 min at nitrogen atmosphere, a solution of methacryloyl chloride (6.1 mL, 62.5 mmol) in 10 mL CH_2Cl_2 was added dropwise, then the reaction solution was stirred at room temperature for overnight, the precipitate was filtered off. The organic solution was washed with brine two times and dried with anhydrous magnesium sulfate. The purified compound **1** was obtained by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1 : 6). Yield, 7.12 g (31.22 mmol, 50%). $^1\text{H-NMR}$ (δ , CDCl_3): 7.65–7.60 (2H, t), 7.50–7.48 (1H, d), 7.21–7.10 (1H, dd), 7.06–7.04 (2H, d), 6.41 (1H, s), 5.79 (1H, d), 5.27 (1H, s), 2.10 (3H, s).

Toluene-*p*-sulfonic acid (PTSA, 0.624 g, 4.59 mmol) was added into the ethyl acetate solution of compound **1** (7.12 g, 31.22 mmol) and 1,1-Diphenyl-2-propyn-1-ol (7.80 g, 37.46 mmol) at room temperature and stirred for 45 h. The reaction mixture was washed with water and brine. The organic solution was dried with anhydrous magnesium sulfate, the monomer **2** was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1 : 3). Yield, 5.30 g (12.65 mmol, 40.6%). MS (m/e): 419 (M $^+$). $^1\text{H-NMR}$ (δ , CDCl_3): 7.98–7.95 (1H, d), 7.62–7.59 (1H, d), 7.49–7.46 (5H, t), 7.34–7.20 (9H, m), 6.38 (1H, s), 6.30–6.27 (1H, d), 5.78–5.76 (1H, t), 2.08 (3H, s).

The monomer **4** was synthesized to refer to the literature.¹⁸ $^1\text{H-NMR}$ (δ , CDCl_3): 7.52–7.49 (1H, d), 6.90–6.87 (1H, d), 6.83 (1H, s), 6.14 (2H, s), 5.60 (1H, s), 4.54–4.51 (2H, t), 4.30–4.27 (2H, t), 2.39 (3H, s), 1.95 (3H, s).



Scheme 2 Synthesis of methacryloyl coumarin and naphthopyran.

Synthesis of polymers

Scheme 1 showed the chemical structures of our new synthesized polymers using atom transfer radical polymerization. The polymers were prepared using CuBr complexed with PMDETA as catalyst and ethyl bromoisobutylate as initiator,¹⁹ the synthetic steps are depicted as follow.

Synthesis of polymer 1

Monomer 2 (0.4 g, 0.96 mmol), ethyl-bromoisobutyrate (0.0039 g, 0.02 mmol), CuBr (6 mg), and PMDETA (7 mg) were added to a dried round-bottle flask with a stir bar. The flask was degassed and backfilled with nitrogen for three times, then 1.0 mL THF was added by a syringe, the mixture was stirred until a homogeneous solution formed. Then PMDETA (7 mg) was added by syringe, and the solution was stirred until the Cu complex was formed, which was easily visualized through the appearance of light green. 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 60°C for 20 h. The reaction mixture was diluted with THF and passed through an alumina column. Afterward, the polymer was precipitated in methanol three times. $M_n = 17,000$ and $M_w/M_n = 1.52$.

Synthesis of polymer 2

The polymer 2 was prepared under the same condition with the polymer 1 while the feed ratio is as follow: Monomer 2 (0.2368 g, 0.57 mmol), monomer 4 (0.1632 g, 0.57 mmol), ethyl-bromoisobutyrate (0.0039 g, 0.02 mmol), and CuBr (6 mg) in 1 mL THF. $M_n = 17,300$ and $M_w/M_n = 1.36$.

Preparation of polymer films

Thin films of polymers and coumarin were prepared by spin coating of polymer solution on quartz plate with a concentration of 40 mg/mL in CHCl₃ solution at 1800 r/min, after the solvent evaporated; the film was dried in the vacuum at 35°C for 6 h. The thickness of polymer films is determined by DEKTA 6M Stylus profiler. The film of coumarin monomer (compound 4) was used to prove that the UV irradiation can elicit the [2 + 2]cycloaddition reaction between coumarin molecules.

Irradiation apparatus and UV measurements

The irradiation light source was CHF-XM35 parallel light system with a 500 W xenon lamp and a filter to generate UV light (~ 360 nm, 20 mW/cm²). A Var-

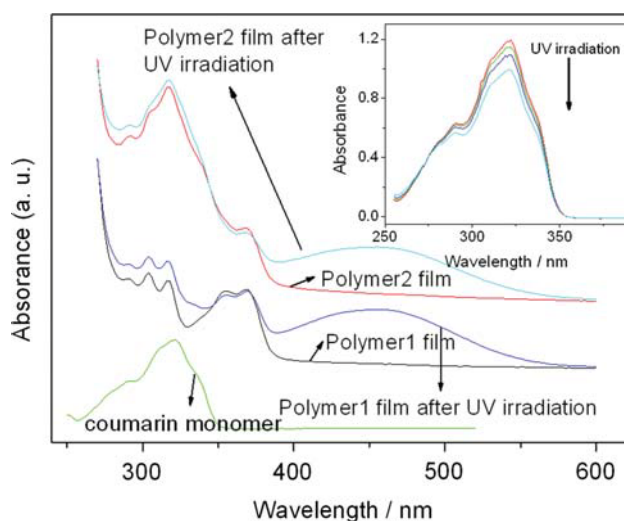


Figure 1 UV-vis absorption spectra of coumarin and polymers in film before and after UV irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ian Cary 500 UV-vis spectrophotometer was used to record the UV spectra as a function of time. Measurements of UV spectra and irradiation of the sample by the UV light were carried out simultaneously. The irradiation light source was put above the polymer film, which was put on the position of sample at about 45°C slope in the spectrophotometer. The thermal decoloration of irradiated polymer film is put in UV-vis spectrophotometer cell position and kept in dark at room temperature.

Manipulation data using Origin 7.5 software

The evolution of absorption peak intensity as a function of time of absorption decay was studied for polymer films after UV irradiation at the wavelength of 454 nm. The time-dependent decay curves were fitted by biexponential decay using Origin 7.5 software. The pre-exponential constants (A_0 , A_1 , and A_2) and kinetic constants (k_1 and k_2) of the biexponential kinetic equation deduced from the best fitting was used to analyzed the photochromic kinetics of the naphthopyran polymer films.²⁰

RESULTS AND DISCUSSION

Absorption spectral analysis of photochromic copolymers

Figure 1 shows the absorption profiles of the polymer 1 film with 320 nm thick and polymer 2 film with 280 nm thick before and after UV irradiation. Before UV irradiation, polymer 1 has four absorption peaks situated at 304, 316, 354, and 369 nm, respectively, which can be assigned to the absorbance of the naphthopyran group. Compared with polymer 1,

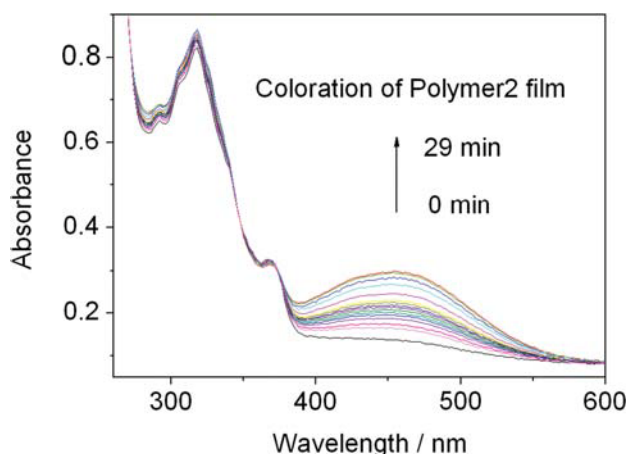


Figure 2 Absorption spectra changes of polymer 2 film upon UV irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymer 2 has two main absorption peaks (316 and 369 nm). Referring to the absorption spectrum of coumarin in Figure 1, the peak at 317 nm came from coumarin group and covered the peaks at 304 and 317 nm of naphthopyran. After UV irradiation, a new absorption peak appeared at 454 nm for either polymer 1 or polymer 2, which indicated that ring-open reaction of naphthopyran from closed form to merocyanine form took place. The intensity of absorption peak at 317 nm of polymer 2 decreased with the time of irradiation, which also showed that the UV irradiation elicited the [2 + 2]cycloaddition reaction between coumarin units. To prove this hypothesis, the evolution of the absorption spectrum of the film of coumarin monomer under UV irradiation was investigated (Fig. 1, insert). The result showed that the absorption intensity at 320 nm of coumarin film decreased with the UV irradiation. This result further illustrate that the [2 + 2]cycloaddition reaction of coumarin units in polymer 2 under UV irradiation can take place.

Photochromism of polymer films

There is a new absorption peak at 454 nm for both polymer 1 and polymer 2 after UV irradiation. The intensity of this new absorption peak increase with the time of irradiation. During the irradiation, the color of polymer film changed to pink from original pale yellow. Figure 2 shows the spectra change of polymer 2 coloration under UV irradiation, the new absorption peak appeared indicated that the UV irradiation induced the photochromism of naphthopyran. The absorption intensity at 454 nm of polymer 1 and polymer 2 reached the maximum after UV irradiation for 6 min and 29 min, respectively. The absorption of coumarin to irradiation light as well as the retard effect of photocrosslinking of cou-

marin on cycle ring process of naphthopyran may be the reason that it took a longer time to reach the maximum absorption for polymer 2 than for polymer 1.

After the absorption intensity at 454 nm reached a saturation state under UV irradiation, the polymer films were put on the cell position of the UV-vis spectrophotometer in the dark and the absorbance spectra was recorded to investigate the decay performance. The absorption intensity at 454 nm of polymer 1 and polymer 2 decreased with the time, which indicated that naphthopyran occurred decoloration reaction from the open merocyanine form to closed naphthopyran form. Figure 3 shows the evolution of the absorption spectra of thermal decoloration of polymer 1 film, the optical intensity decreased to thermal equilibrium between merocyanine form and ring-closed naphthopyran for 365 min. The polymer 2 film had similar decoloration performance, but the decreasing rate was slower than that of polymer 1 film. It needed 660 min for polymer 2 to reach the thermal equilibrium. Figure 4 presents the change of optic intensity at 454 nm for polymer 1 and polymer 2 in films with irradiation time and gave the insight into the overall comparison for decreasing trend. These results indicated that the decoloration rate of polymer 1 was larger than that of polymer 2, which shows the crosslinking reaction of coumarin reduced the free volume and increased the steric hindrance surrounding the naphthopyran unit.

To investigate the reversibility of coloration and decoloration, we also repeat the circular experiment of coloration and decoloration of polymer 2 in film, the result is shown in Figure 5. This result indicates that the decoloration of naphthopyran in polymer 2 is not completely, the color is remained partly. On

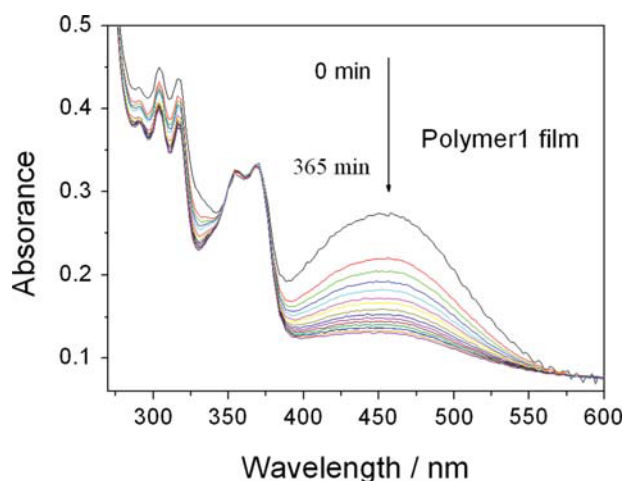


Figure 3 The absorption spectra change of polymer 1 during decoloration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

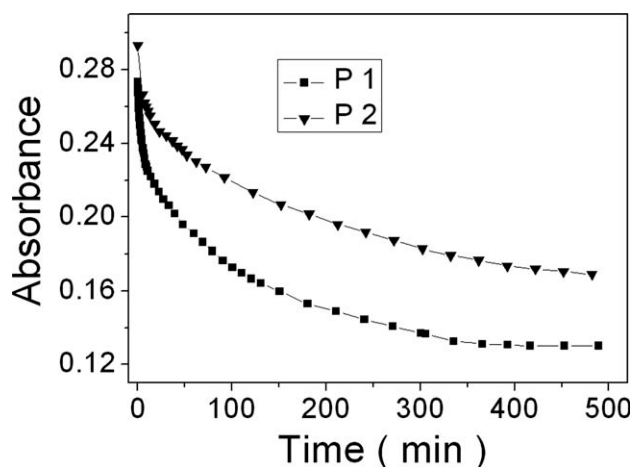


Figure 4 The evolution of optical intensity at 454 nm of polymer 1 and polymer 2 in films with decay time.

the contrary, the absorbance intensity of ring-opened form at 452 nm can be recovered nearly after UV irradiation. The absorbance extent decreased nearly 30% after five cycles, which is unfavorable for naphthopyran to be used in practical application. The dissociation of coumarin dimer is not complete under our experimental condition, the remainder crosslinking of coumarin prohibit naphthopyran in polymer 2 to transform completely form ring-opened form to ring-closed form. This is the reason that the color of ring-opened naphthopyran is remained partly after thermal bleaching. The following factor, such as the content of coumarin in copolymer, film preparation, the condition of decoloration, etc. can affect the reversibility of coloration and decoloration of naphthopyran in copolymer film, the research work on improving photochromic reversibility is undergoing in our group.

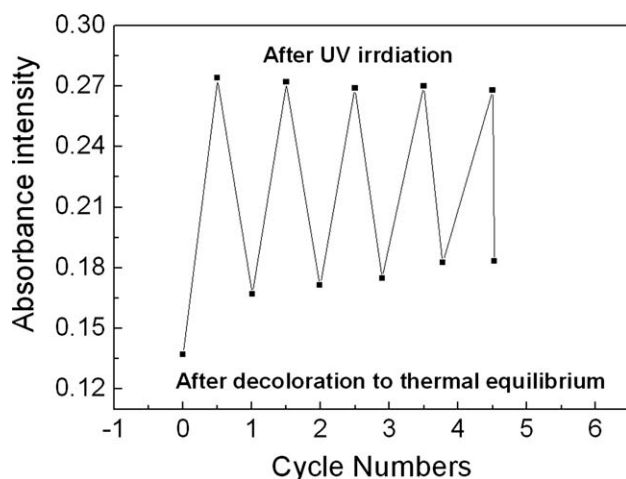


Figure 5 Photochromic cycles of naphthopyran between closed form and merocyanine in polymer 2 under UV irradiation and thermal bleaching.

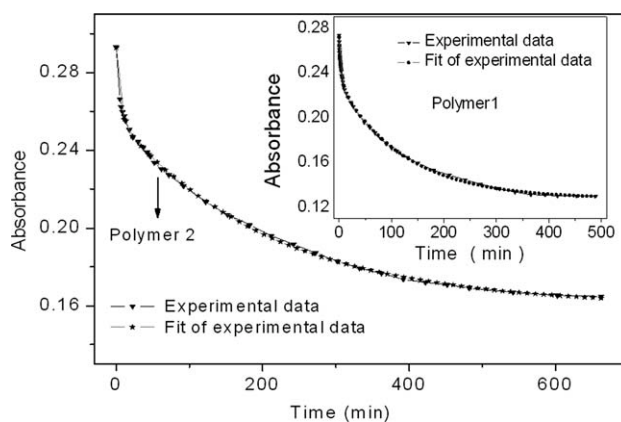


Figure 6 Biexponential fits for the thermal decoloration in the dark of polymer 1 (insert) and polymer 2.

Kinetics of photochromism

The thermal decoloration of naphthopyran polymer films was investigated in the dark at room temperature after the optical intensity reached the maximum under UV irradiation. The decoloration occurred spontaneously in the dark due to the thermal back-reaction from merocyanine form to closed naphthopyran form. The kinetic properties of spectra decaying were studied by monitoring the absorption intensity against the time at the maximum wavelength (454 nm) of the merocyanine form. The following empirical equation^{21,22} was used to analyze and compare the thermal ring closure kinetics of photochromic polymer 1 and polymer 2.

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

where $A(t)$ is the optical intensity at 454 nm of the open forms, A_1 and A_2 are the contributions to the initial optical intensity A_0 . A_0 is the maximum absorption intensity at 454 nm of open form after long time of continuous irradiation. k_1 and k_2 are exponential decay rate constants of fast and slow components, respectively; and A_{th} reflected the thermal equilibrium between the two forms. This equation presents that the decay process is biexponential model and was used to analyze decoloration behavior of some photochromic units.²¹⁻²⁵ For naphthopyran, the decoloration rate of opened form (TC) and (TT) to closed form are fast and slow, respectively, (Scheme 1). These constant values were obtained from the fit of the experimental data for polymer films by using Origin 7.5 and the correlation coefficients (R) was greater than 0.999. Figure 6 indicates the excellent agreement between the biexponential fit and experimental data of polymer 1 and polymer 2.

Table I presents constant values deduced from the fit of the experimental data for films of polymer 1

TABLE I
Kinetic Constants of the Biexponential Equation for the Decoloration of the Opened form of Naphthopyran Moieties in Different Polymers

Constants	Polymer 1	Polymer 2
Ath	0.13	0.16
A ₁	0.037	0.036
k ₁	0.25	0.19
A ₂	0.11	0.096
k ₂	0.0082	0.0084
t _{1/2}	300 (min)	850 (min)

and polymer 2. Naphthopyran in polymer 1 and polymer 2 has same bleaching trend, the decoloration rate is very fast at the beginning of thermal bleach, which is accompanied by ring-close reaction from TC to ring-closed naphthopyran. After the most of TC isomer transformed to the closed form, the transforming of TT isomer to ring-closed naphthopyran is dominating thermal bleach process, that is, the latter part on the curves in Figure 4. Comparison of the decoloration performance between polymer 1 and polymer 2 shows that the introduction of coumarin unit into polymer reduced the decoloration rate of naphthopyran. The k_1 and k_2 of polymer 1 ($k_1 = 0.25 \text{ min}^{-1}$, $k_2 = 8.2 \times 10^{-3} \text{ min}^{-1}$) were larger than those of polymer 2 ($k_1 = 0.19 \text{ min}^{-1}$, $k_2 = 4.8 \times 10^{-3} \text{ min}^{-1}$), respectively, which showed that polymer 1 has faster decoloration rate than polymer 2. These results indicated that the cycle closure process of naphthopyran in polymer 1 film has smaller resistance than that in polymer 2 film. Measured $t_{1/2}$ values (the time taken for the intensity of the photo-generated color to half of its original value) are also beneficial for comparing kinetics of decoloration process. The $t_{1/2}$ of polymer 1 (300 min) was lesser than half of that of polymer 2 (850 min). This result also showed that the steric hindrance during the cycle closure process of naphthopyran moieties is smaller in polymer 1 than that in polymer 2, in other words, the decoloration rate of polymer 1 is larger than that of polymer 2.

The above results means that photocrosslinking between coumarin moieties during the irradiation of UV light can reduce the distance between polymer chains and give smaller free volume required by transforming from open merocyanine to closed naphthopyran form. It also could be saying that the photocrosslinking of coumarin can form bigger geometrical hindrance and increase the rigidity and steric hindrance of polymer matrix, which also retarded the decoloration rate of open form of naphthopyran. These results mean that introduction of coumarin into the photochromic copolymer can increase steric hindrance after UV irradiation during photochromism and can be used to control the decoloration kinetics of photochromic polymer.

CONCLUSIONS

The naphthopyran-containing monopolymer and copolymer with coumarin were designed and synthesized. The kinetics of naphthopyran decoloration in polymers showed that the photocrosslinking reaction of coumarin moieties during photochromism could increase the steric hindrance around naphthopyran in polymer and decrease the decoloration rate. We believed that the photocrosslinking of coumarin could be used to control decoloration rate of photochromic moieties in polymer.

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