Influence of Polymer Polarity on Photochromic Behavior of Naphthodipyran Doped in Different Polymeric Matrixes

Xiancai Zhao, Guang Wang, Kuo Zhang

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

ABSTRACT: Photochromic polymer films were prepared by doping the naphthodipyran into different polymers such as Polyvinylpyrrolidone (PVP), styrene-butadiene-styrene (SBS) triblock copolymer, and polymethyl methacrylate (PMMA) at different concentrations. The kinetics of the photochromism/decoloration in the thin films was quantified by fitting biexponential equations to their photochromic decay curves after UV irradiation. The results show that the fastest decoloration process was in SBS, and the slowest one was in PVP. The DSC results indicate that T_g of polymeric matrix has no obvious effect on the decoloration rate of naphthodipyran. The decreasing order of the decoloration constant of naphthodipyran was consistent with increasing polarity of polymer matrixes as PVP > PMMA > SBS. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4157–4164, 2012

Key words: photochromism; kinetics; naphthodipyran; decoloration; polymer film

INTRODUCTION

Photochromism is a reversible transformation of a chemical system. Photochromic compounds undergo a reversible change of molecular structures resulting in a change from colorless state to colored state visually when irradiated with ultraviolet (UV) light. After removing the UV irradiation, their original structure and color can be regained. Photochromic materials of organic compounds in heterogenous systems have been extensively studied for practical applications and elucidating primary photochemical reactions, for example, ophthalmic lenses, optical switches, optical filters, and temporary or permanent memory devices.[1–4] A group of photochromic compounds that have received considerable attention in industry are chromenes (benzopyrans) and some related naphthopyrans.[5–7] The use of diaryl-naphthopyrans in sun-protective ophthalmic lenses remains, by a wide margin, largest practical and commercial application. Their chemistry has been intensely developed, and increasingly complex derivatives with additional substituents and fusion to different heterocyclic systems have been studied to modulate their photochromic behavior and enhance their photochromic performance.[8–12] The photophysical processes of photochromic compound molecules in solutions and polymer matrixes lie on the geometrical and electronic properties of individual molecules, as well as the photochemical properties of the surrounding media.

The properties, such as the modulation of decoloration kinetics, maximum wavelengths of absorption, resistance to photodegradation, the ability to produce colored forms, and color reversibility are the important properties of photochromic materials for various applications. As the reversible property variation in photochromic materials is induced by molecular-level changes, several changes in physical and chemical properties can be observed when isomeric forms (merocyanines) trigger subsequent rearrangements of microenvironmental states upon light absorption. The characteristics of the host, such as the polarity, viscosity, and rigidity influence the decoloration kinetics of photochromic compounds in different polymer matrixes,[13–17] which critically affect the photophysical and photochemical functions of the photochromic materials.

Naphthopyrans are an important class of photochromic dyes because of their breadth of color generated, absence of background color, good thermal reversibility, fine control over fading kinetics, and good resistance to photochemical fatigue. The photochromism of naphthopyran was first reported by Becker and Michl in 1960s.[18] The photochromic reaction of the naphthopyran involves initial heterolytic cleavage of C(sp3)–O bonds on irradiation with UV-light and the molecule becomes a metastable amphoteric ion.[19] This would result in two colored
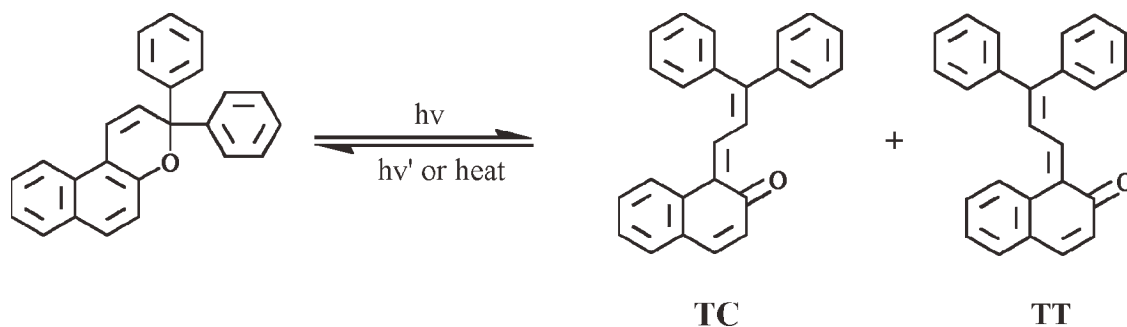
Scheme 1 The structure of the closed and opened forms of naphthodipyran during coloration by irradiation of UV-light and decoloration without light.

ring-opened structures, a transoid-*cis* (TC) and a transoid-*trans* (TT) merocyanine isomer (Scheme 1).[20] The TC isomer is more unstable than TT isomer and will transform into the TT isomer or revert to naphthopyran.

The goal of this work is to study, comparatively, the interaction between photochromic materials and the polymer matrixes. A naphthodipyran containing two pyran cycles was designed and synthesized. The photochromic behaviors of naphthodipyran doped in polymer matrixes with different polarity and rigidity such as PVP, SBS, and PMMA are studied. The structures of naphthodipyran, PVP, PMMA, and SBS were shown in Figure 1.

EXPERIMENTAL SECTION

Materials

The naphthodipyran compound was synthesized according to Scheme 2. Polyvinylpyrrolidone (PVP), styrene-butadiene-styrene (SBS) triblock copolymer, polymethyl methacrylate (PMMA), 2,6-dihydroxy-

naphthalene, and 1,1-diphenylpropyn-1-ol were purchased from Aldrich. Dichloromethane was distilled from phosphorous pentoxide prior to use.

^{1}H NMR spectra were recorded on a Varian Unity Inova Spectrometer (500 MHz) at room temperature and *d*-chloroform was used as solvent. The DSC curves were obtained using a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating rate of 10°C/min under nitrogen atmosphere. Mass spectra were recorded from Bruker Compass DataAnalysis 4.0 equipment. Elemental analysis data was obtained using the Euro EA EA3000 Elemental Analyzer.

Synthetic procedures for the preparation of naphthodipyran

There are several kinds of routes for synthesis of naphthopyran ring,[21–24] the naphthodipyran was synthesized by using dichloromethane and *p*-toluene-sulphonic acid (PTSA) as solvent and catalyst, respectively. The mixture of 2,6-dinaphthol (1.0 g; 4.89 mmol), 1,1-diphenylpropyn-1-ol (2.24 g; 10.6 mmol), and *p*-toluenesulphonic acid (PTSA, 0.0196 g)
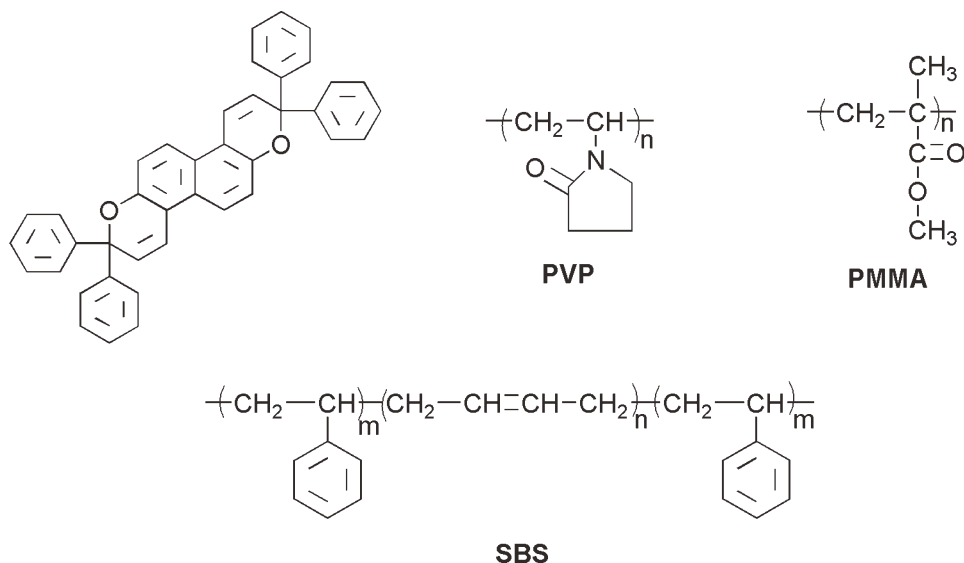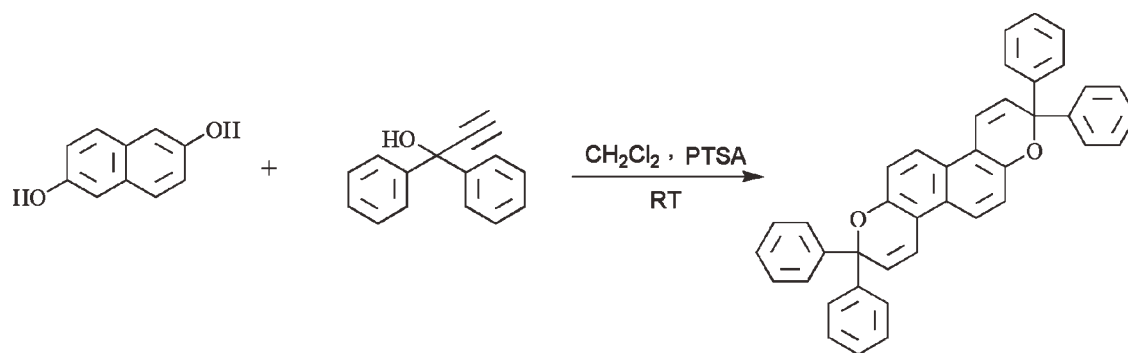

Figure 1 The structures of naphthodipyran, PVP, PMMA, and SBS.

Scheme 2 The route of synthesis for naphthodipyran.

in 20 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 over anhydrous sodium sulfate, the crude product was further purified by column chromatography (chloroform:petroleum ether = 1 : 3). The eluent was evaporated to give orange solid (0.9 g, 35%). ^{1}H NMR spectrum of naphthodipyran was shown in Figure 2, (δ, $CDCl_3$): 7.79 (d, $j = 9.0$ Hz, 2H), 7.46 (d, $j = 8.5$ Hz, 8H), 7.32–7.28 (m, 8H), 7.22–7.25 (m, 6H), 7.20 (d, $j = 9.0$ Hz, 2H), 6.26 (d, $j = 9.5$ Hz, 2H). HRMS (ESI-TOF), M = 540.65, Calcd for mole ([M + H^+]): 541.2123 Found, 541.1789. Anal. Calcd for $C_{40}H_{28}O_2$: C, 88.86; H, 5.22%. Found: C, 88.88; H, 5.21%.

Preparation of thin films

Polymer (0.4 g) was added to chloroform (20 mL) under stirring. After the mixture became clear, a specified amount (5 wt % of the polymer) of naphthodipyran was added to the polymer solution and stirred well. This solution was poured into a quartz glass and kept at room temperature for several hours to remove all traces of solvent. After staying at 50°C for 1 h in a vacuum, the resulting films were kept in the dark to prevent their degradation by direct sunlight prior to the spectroscopic measurements.

UV–Vis spectrophotometry

The photochromic properties of the polymeric films were analyzed by using a Varian Cary 500 UV-vis spectrophotometer. Samples were placed on the position of sample in the spectrophotometer at a slope of about 45° and their absorbance spectra were measured. The samples were then irradiated to a constant intensity with UV light (365 nm) to ensure that the sample has reached steady state coloration. A CHF-XM35 parallel light system with a 500 W xenon lamp with 5 cm beam diameter was used as the UV source of irradiation. The absorbance decay was then measured in the dark within 60 min. The wavelength of the maximum absorption (λ_{max}) of
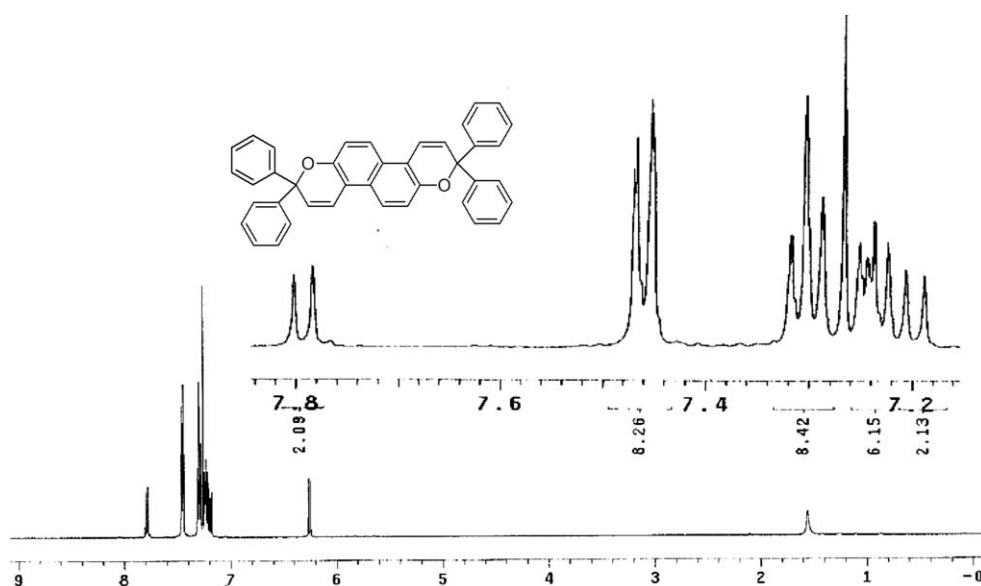

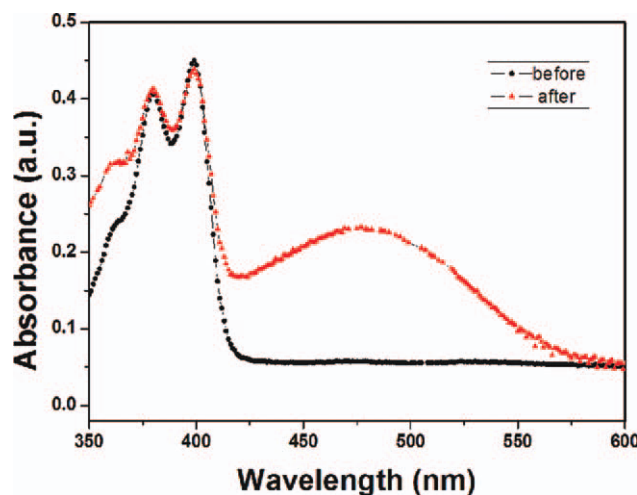**Figure 2** ^{1}H NMR spectrum of naphthodipyran.

Figure 3 UV–vis absorbance spectra of naphthodipyran doped in the PMMA before (-●-) and after (-▲-) irradiation of UV light (365 nm) for 60 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
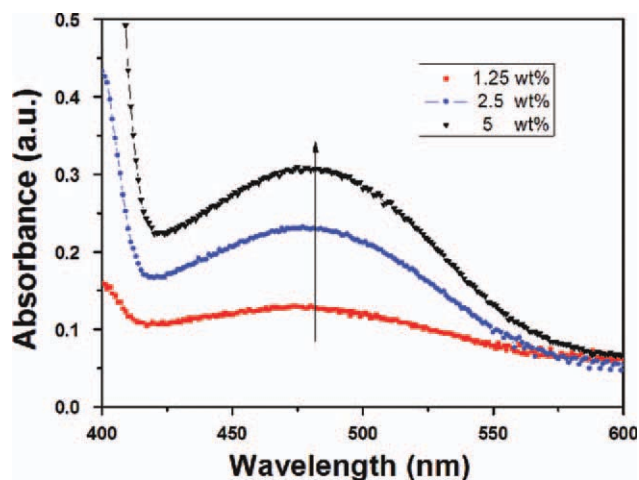

Figure 4 UV–vis absorption spectra of naphthodipyran doped in PMMA matrix with different concentrations, after 60 min of UV light (365 nm) irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the ring-opened form (colored) of naphthodipyran was obtained by plotting the UV spectrum of the sample. All of the experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Photochromic properties

The absorption spectra of naphthodipyran doped in the PMMA, PVP, and SBS were recorded before and after irradiation of UV-light. The UV–vis absorbance spectra of naphthodipyran doped in the PMMA before and after irradiation (365 nm light) were shown in Figure 3. It can be seen that no peak were observed at all in the range of 425–575 nm before UV irradiation. However, when the film was irradiated by 365 nm light, a well-formed peak with the maximum wavelength of 474 nm was clearly observed. The maximum wavelength of the absorption was blue shift from 481 to 474 nm when changing the polymer matrixes from SBS to PMMA, as shown in Table I. The polarity and the hydrogen bonding ability of the polymer matrix can induce shifting of the maximum absorbance of the photochromic compound. The polarity as well as the hydrogen bonding ability of PMMA are similar with that of PVP, but are larger than that of SBS. It

should be emphasized that the inter-dipole interaction between the chromophore and the polymer chains also plays the principal role in the observed blue shift.[25] The more polar the polymer is, the more the blue shift is. This is due to the stabilization of the ring-opened structure relative to the interaction between ring-opened naphthodipyran and polymer matrixes. The polarity and hydrogen bonding ability of polymer matrixes have obvious effects on the photochromic kinetics of photochromic compounds.[26–29]

Figure 4 shows the UV–vis absorption spectra of naphthodipyran incorporated into the PMMA matrix with different concentrations after UV 365 nm-light irradiation for 30 min. The intensity of the absorption peaks increased with the increase of naphthodipyran concentration in the polymeric matrix.

Figure 5 shows the optical absorbance change during coloration of naphthodipyran doped in PMMA polymeric matrix by the irradiation of UV light (365 nm). As irradiation time is increased, the optical intensity at 474 nm increases exponentially (inset of Fig. 5). The intensity of the 474 nm absorption band nearly reaches a plateau after irradiation for 52 min, indicating long irradiation time can cause saturation of the optical intensity. Upon cessation of the UV light, the samples decolorize spontaneously in the dark because of the thermal back-reaction that occurs as open form of the naphthopyran which undergoes ring closure, this process is accompanied by decreasing of absorbance band of ring-opened naphthopyran. Figure 6 presents the decoloration of naphthodipyran doped in the PMMA polymeric matrix after irradiated for 52 min, by continuously recording its optical absorption spectra at different time in the dark.
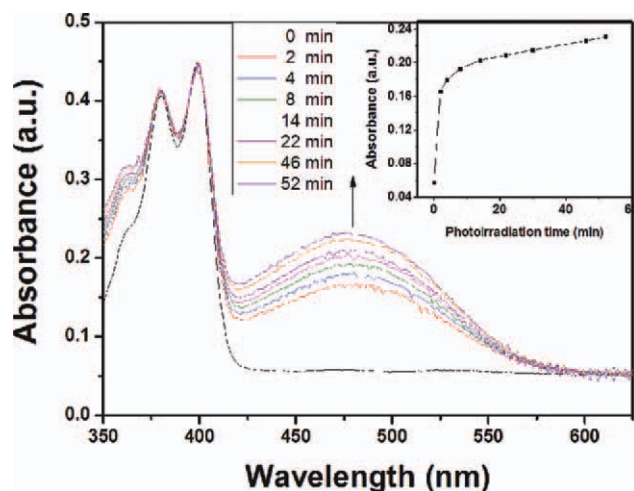
TABLE I
The λ_{max} Values of the Opened Form of Naphthodipyran Doped into PMMA, PVP, and SBS

Matrixes	PMMA	PVP	SBS
T_g (°C)	127.2	90.2	65.9
λ_{max} (nm)	474	476	481

Figure 5 Optical absorbance spectra change during coloration of naphthodipyran doped in the PMMA matrix by irradiation of UV light (365 nm) versus irradiation time. The absorbance intensity increase at 474 nm is shown in the inset. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7 Optical absorbance spectra change during coloration of naphthodipyran doped in the PVP matrix by irradiation of UV light (365 nm) versus irradiation time. The absorbance intensity increase at 476 nm is shown in the inset. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The same trends of increase of absorption intensity with irradiation time as well as the thermal decay upon decoloration were also observed when the naphthodipyran was doped in PVP or SBS matrix. Figures 7 and 8 shows the result of naphthodipyran in PVP matrix. Photoirradiation of samples for 20 min at room temperature results in an exponential increase of absorbance intensity at λ_{max} of the ring-opened naphthodipyran. Figure 9 shows the plots of the absorbance intensity at λ_{max} of naphthodipyran in the PMMA, PVP, and SBS polymeric matrix as a function of irradiation time.

Figure 10 shows the absorbance intensity at λ_{max} of opened-form naphthodipyran in polymeric matrixes during decoloration in dark versus time. The slopes of decay curves of the opened form of naphthodipyran doped in the PMMA, PVP, and SBS are different, which may be caused by the different transformation kinetics of naphthodipyran from the opened form to the closed form in the different polymeric matrixes. This is due to the different polarity of the organically modified polymeric matrixes, which indicates that the polymeric matrixes used in the present study can induce different change in the
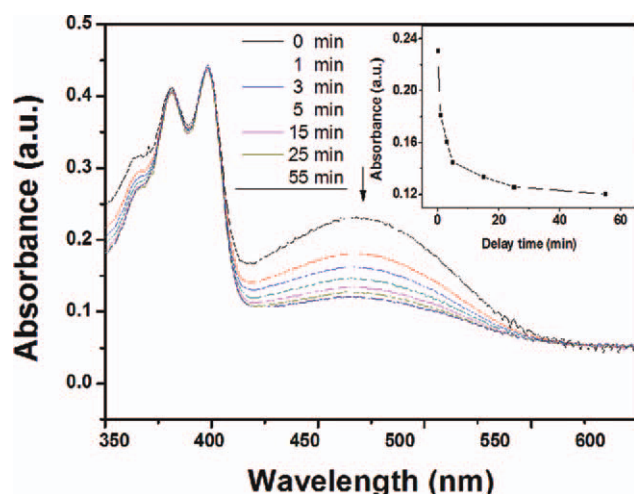

Figure 6 Optical absorbance spectra change during decoloration of naphthodipyran doped in the PMMA matrix after irradiation of UV light (365 nm) versus time. The absorbance intensity decay at 474 nm is shown in the inset. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
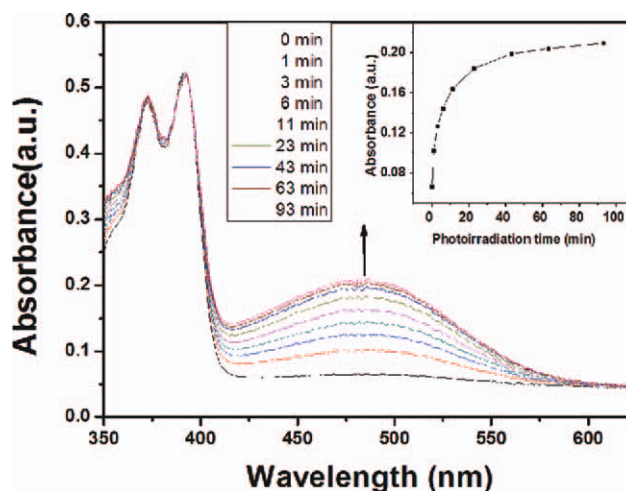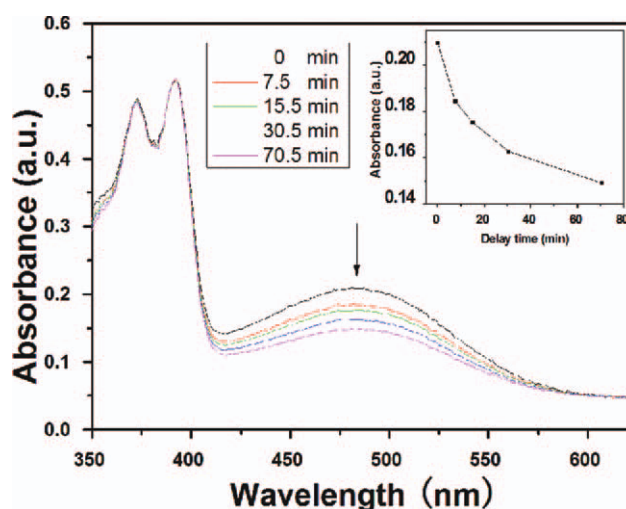

Figure 8 Optical absorbance spectra change during decoloration of naphthodipyran doped in the PVP matrix after irradiation of UV light (365 nm) versus time. The absorbance intensity decay at 476 nm is shown in the inset. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
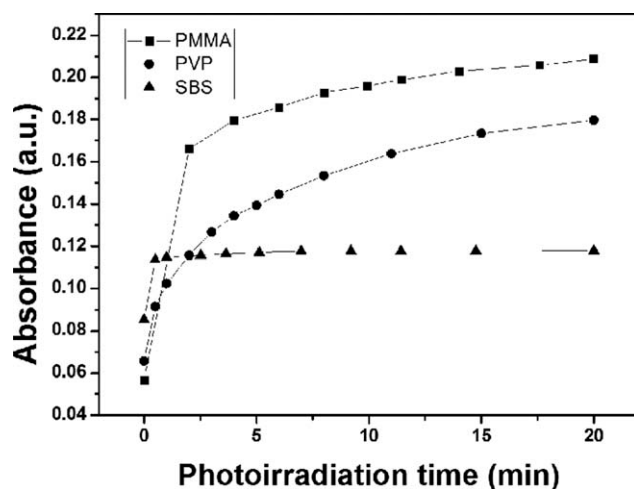
Figure 9 Optical absorbance at λ_{max} of naphthodipyran doped in the PMMA, PVP, and SBS polymeric matrix during the coloration process by irradiation of UV light (365 nm) versus irradiation time.

microenvironment of naphthodipyran, especially in PVP.

Kinetics of the thermal bleaching of naphthodipyran in different polymer matrixes

The kinetics of the thermal back or ring closure reaction (decoloration) was studied following the fading of color at the maximum absorption of the opened form of naphthodipyran. To take into account the inhomogeneous distribution of free-volume in the polymeric matrixes and to compare the photodynamics among them, a biexponential model was used to quantify the kinetics of the photochromism in these polymeric matrixes. As it is the case in polymers, the kinetics of the thermal bleaching reaction
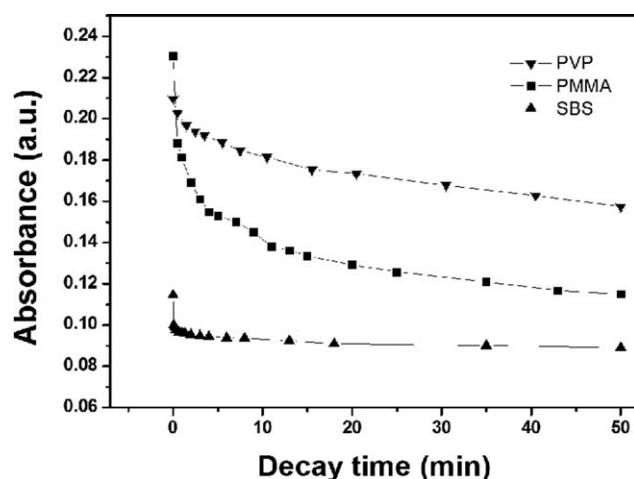

Figure 10 Optical absorbance at λ_{max} of naphthodipyran doped in the PMMA, PVP, and SBS polymeric matrix during decoloration after irradiation of UV light (365 nm) versus time.

TABLE II
Kinetic Constants of Biexponential Equation for the Decoloration of the Opened Form of Naphthodipyran Doped in Different Matrixes

Sample	Ath	A1	K_1/s^{-1}	A2	K_2/s^{-1}
SBS	0.08834	0.017735	19.531	0.00884	0.0707
PVP	0.1176	0.06736	0.4972	0.0513	0.0337
PMMA	0.11266	0.05448	2.6654	0.06353	0.0725

from metastable to stable naphthodipyran does not proceed as first-order kinetics. In fact, it is generally accepted that the common observation of nonexponential isomerization kinetics in polymer matrixes indicates the site-specific matrix effects by imposing a distribution of localized barriers to the steric requirements of the reaction.[30–31] Attribution of the deviation from first-order kinetics to the conformational statistics of the matrixes was confirmed by the approach to a single-exponential decay pattern. The results can be analyzed by using Gaussian model developed by Albery et al., which has been applied to porous silica by Saito and co-workers.[32] The basic assumption of the model is that the distribution of rate constant, k is due to a normal distribution of free energies leading to a Gaussian. Kinetic data concerning the thermal back reaction of naphthodipyran in polymer matrixes has been previously analyzed as a biexponential process.[13] The following empirical equation was used to analyze and compare the thermal ring closure kinetics of the photochromic test samples,[19,28] where $A(t)$ is the optical density of

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

naphthodipyran at λ_{max} and A_1 and A_2 are contributed to the initial optical density A_0. A_{th} reflect the thermal equilibrium between the closed and merocyanine forms of naphthopyran.

In this simple model, the merocyanine form of the naphthodipyran in the polymer of PMMA, PVP, and SBS matrixes was thermally decolorized with different rate constants as shown in Table II. From the viewpoint of a uniform distribution of free volume, the separated constants k_1 and k_2 should be understood as empirical mean values between the fast and the slow kinetic constants. The kinetic constant (k_1 and k_2) is consistent with the stability of the opened form of naphthodipyran in the polymeric matrixes. The results show that the stability in PVP is larger than that in PMMA, and that in SBS is the smallest. These kinetic parameters of the thermal fading for naphthodipyran doped in polymeric matrixes are also dependent on the polarity and hydrogen bonding ability of the matrixes. In general, the polymer matrixes with polarity and hydrogen bonding ability give more restriction effect on the isomerization of
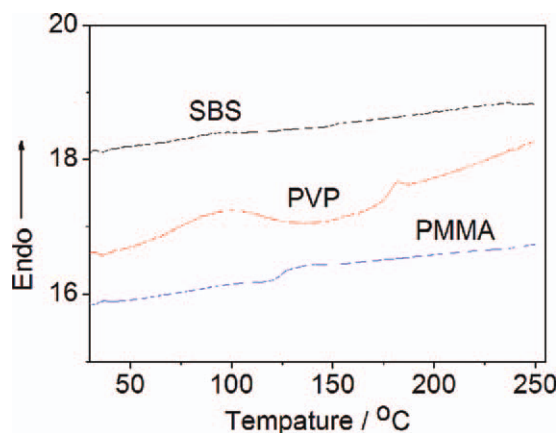
Figure 11 DSC heating curves (second scan) for SBS, PMMA, and PVP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

photochromic molecules.[27,33] The lowest kinetic constant obtained for the PVP matrix indicates that opened form of naphthodipyran is more stable in the PVP than in PMMA matrix. The kinetic constant of naphthodipyran is the highest in nonpolar matrix SBS. The higher polarity and hydrogen bonding ability of the polymeric matrixes cause more compact interaction between opened form of naphthodipyran and the polymeric matrixes.[34] On the other hand, the SBS polymeric matrix has the lowest polarity and no hydrogen bonding ability, which results in the highest kinetic constant values of thermal back reaction of naphthodipyran in the polymer.

The effect of T_g of polymeric matrix on the kinetics of naphthodipyran

The bleaching kinetics of photochromic dyes are very sensitive to the T_g (as well as steric hindrance of the polymeric matrix) of the polymeric matrix in which the dyes are contained. Rigidity of PMMA and PVP polymers (glassy polymers with high T_g) are bigger than that of SBS. Figure 11 shows the differential scanning calorimeter (DSC) curves of naphthodipyran-doped PMMA, PVP, and SBS. Their T_g are presented in Table I and are 127.2, 90.2, and 65.9°C, respectively. The difference between PVP and PMMA is nearly 40°C, but the kinetic constants (k_1, the fast kinetic constants) of naphthodipyran in PVP and PMMA matrixes have smaller difference, this result indicated that the T_g of polymeric matrix has small effect on the kinetic constants of naphthodipyran. On the contrary, the difference of T_g between SBS and PVP is above 25°C, the kinetic constant (k_1, the fast kinetic constants) of naphthodipyran in SBS is 40 times than that in PVP. The noncorrelation between T_g and the kinetic constant of naphthodipyran further proved that the polarity of polymeric matrix is the dominating effect on the

photochromic process of naphthodipyran but the polymeric T_g has no obvious effect.

CONCLUSION

The kinetic constant of the decoloration of photochromic naphthodipyran in polar polymer matrixes (PMMA and PVP) is bigger than that in nonpolar polymer matrix (SBS), which shows that the open form of naphthodipyran is more stable in polar matrixes than in nonpolar matrix. The greater polarity of the polymer matrix in which the naphthodipyran is doped causes more compact interaction between the opened form of naphthodipyran and polymer matrix. This result illustrates that the polarity of polymer matrixes can be used to tune the kinetics of photochromic molecule in polymer matrixes.

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