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PHOTOCHROMISM OF SPIROOXAZINE DOPED OR BONDED IN POLYMER MATRICES

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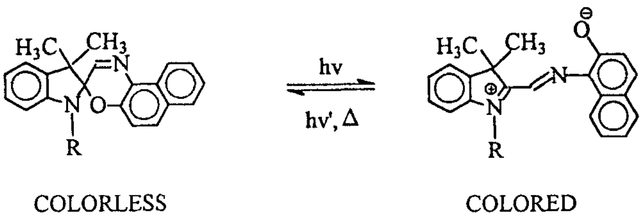
ABSTRACT

This study explores the thermal decoloration of a novel 1-[4′-(2″-methacryloxy)ethoxycarbonyl]benzyl-3,3-dimethyl-spiro[indoline-2,3′-[3*H*]-naphtho[2,1-*b*]-1,4-oxazine] (spirooxazine **III**), a photochromic colorant attached to a double bond either doped or bonded in PMMA matrices. Results indicate that the thermal decoloration rate decreases rapidly with an increasing concentration of spirooxazine in the doped system due to the availability of free volume within the polymer matrices. The thermal decoloration rate remains almost constant in the bonded system with an increasing concentration of spirooxazine **III**.

INTRODUCTION

Photochromism [1, 2] is being extensively studied because to its potential as an optical medium for optical disks, coatings for smart windows, photochromic decoration, optical switches and optical filters, etc. Among organic photochromic compounds, spirooxazine is one of the most well-explored group because of its excellent light fatigue resistance [3, 4] and color change upon photoirradiation. The photochromism of spirooxazine is shown in Scheme 1.

In general, a photochromic compound is doped in a polymer matrice for practical applications. The concentration is usually low in order to avoid phase separation of the colorant and the polymer matrix. If a higher concentration is



SCHEME 1. Photochromism of spirooxazine.

needed for stable performance in electronic applications, a reactive photochromic compound which can be bonded with the polymer matrix may meet the requirement [5]. A novel spirooxazine **III** was tailor-made for this study, and its behavior in polymer matrices has been explored.

EXPERIMENTAL

Materials

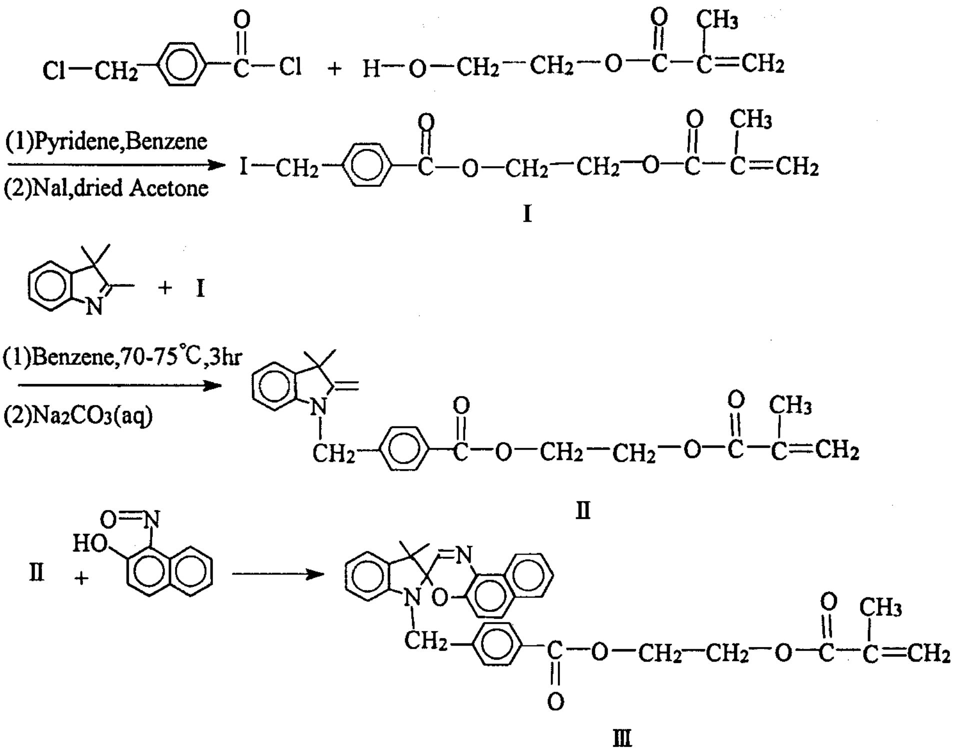
The synthesis of **III** is summarized in Scheme 2.

2-(4′-Iodomethylbenzoyloxy)ethyl Methacrylate (I) [6]

A solution of 2-hydroxyethyl methacrylate (6.45 g, 0.05 mol) in pyridine was treated with (4-chloromethyl)benzoyl chloride (9.45 g, 0.05 mol) at 10°C for 3 hours and at 40°C for 2 hours to give 2-(4′-chloromethylbenzoyloxy)ethyl methacrylate. The latter was stirred with sodium iodide in dried acetone at 40°C for 3 hours to give the crude material (**I**), and then the mixture was isolated by filtration. The filtrate was evaporated and recrystallized from a mixture of acetone and hexane (1:1) to give light yellow crystals. The yield was 14.6 g (78%), mp 53-55°C. ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.94 (s, 3H, $-CH_3$), 4.55 (m, 6H, $-CH_2-$), 5.60 (t, 1H, $-C{=}C-H$, J = 2.64 Hz), 6.13 (s, 1H, $-C{=}C-H$), 7.43-7.45 (d, 2H, ArH, J = 8.36 Hz), 7.96-7.98 (d, 2H, ArH, J = 8.36 Hz). Analysis of $C_{14}H_{15}O_4I$ (374.18): calculated, C 44.94%, H 4.04%; found, C 44.71%, H 4.09%.

1-[4′-(2″-Methacryloxy)ethoxycarbonyl]benzyl-3,3-dimethyl-2-methylene Indolenine (II) [5]

A mixture of **I** (3.74 g, 0.01 mol) and 2,3,3-trimethylindolenine (1.75 g, 0.011 mol) was heated at 75-80°C for 3.5 hours. The solid obtained was dissolved in a mixture of water and ethyl acetate and then made basic with sodium carbonate to pH 8. The Fischer base obtained was extracted three times with ether, dried over anhydrous magnesium sulfate, and passed through a 5-cm column of basic alumina. The etheral solution was evaporated, and then the crude material was flash chromatographed on silica gel using ethyl acetate/hexane (1:5) as the eluent to give an oily product. The yield was 2.71 g (67%). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.38 (s, 6H, $-CH_3$, gem) 1.92 (s, 3H, $-CH_3$), 3.84 (d, 2H, $=CH_2$, J = 14.56 Hz), 4.45 (t, 2H, $-CH_2-$, J = 9.32 Hz), 4.53 (t, 2H, $-CH_2-$, J = 9.24 Hz, 5.56 (t, 1H,



SCHEME 2. Synthesis of **III**.

—C=C—H, J = 2.72 Hz), 6.11 (s, 1H, —C=C—H), 6.45–7.97 (m, 8H, ArH). Analysis of $C_{25}H_{27}NO_4$ (405.49): calculated, C 74.05%, H 6.71%, N 3.45%; found, C 73.01%, H 6.61%, N 3.71%.

1-[4′-(2″-Methacryloxy)ethoxycarbonyl]benzyl-3,3-dimethyl-spiro[indoline-2,3′-[3*H*]-naphtho[2,1-*b*]-1,4-oxazine] (III)

A solution of Fischer base (**II**) (2.63 g, 6.5 mmol) and 1-nitroso-2-naphthol (1.12 g, 6.5 mmol) in 10 mL methanol was refluxed for 2 hours. The solvent was evaporated, and then the crude material was flash chromatographed on silica gel using chloroform as the eluent to give a light yellow product. The yield was 0.8 g (22%). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.39 (s, 3H), 1.46 (s, 3H), 1.94 (s, 3H), 4.30–4.56 (m, 6H), 5.58 (s, 1H), 6.14 (s, 1H), 6.29 (d, 1H, J = 7.72 Hz), 6.88–7.97 (m, 13H, ArH), 8.48–8.50 (d, 1H, ArH, J = 8.36 Hz), 7.76 (s, 1H, HC=N—). Analysis of $C_{35}H_{32}N_2O_5I$ (560.65): calculated, C 74.98%, H 5.75%, N 5.00%; found, C 74.35%, H 5.55%, N 4.9%.

Synthesis of Photochromic Copolymers (poly(MMA-*co*-III))

A series of poly(MMA-*co*-**III**) copolymers containing different molar ratios of **III** in the feed were prepared by solution polymerization in benzene at 70°C using 0.25 wt% AIBN as the initiator. The copolymers were isolated and purified by repeated precipitation with ether and dried under reduced pressure. The photochromic groups content in the copolymers was evaluated by elemental analysis (according to the nitrogen content). PMMA and photochromic **III** are the host and guest, respectively, in the copolymer.

Characterization of the Polymers

Glass transition temperatures of the copolymers were measured by differential scanning calorimetry (DSC). The DSC measurements were performed with a Du Pont TA910 instrument. Gel permeation chromatography with Waters Co. columns using THF as solvent was carried out to determine the average molecular weights of the copolymers.

Sample Preparation

PMMA films of about 2-μm thickness containing different concentrations of doped **III** were prepared from benzene by the solvent-cast method and were evacuated at room temperature overnight and subsequently heated under vacuum for 3 hours at 80°C to eliminate the residual solvent. Copolymer [poly(MMA-*co*-**III**)] films of about 2-μm thickness containing different contents of the spirooxazine group were prepared by spin-coating a 20% polymer solution in chloroform on a glass slide.

Measurements of Thermal Decoloration

Polymer and copolymer films containing different contents of the spirooxazine group were exposed to a W-4 lamp for 20 minutes and then the absorption spectra were measured on an Otsuka MCPD-1000(311C) spectro multichannel photodetector. The photodetector can measure the whole spectrum between 300 and 1100 nm within 20 ms. Absorption measurements of thermal decoloration of samples were deformed at ambient temperature. The absorption maximum (λ_{max}) was observed at 570 nm.

RESULTS AND DISCUSSION

Photochromisms of organic compounds doped or bonded in bulk polymers are different from those in solutions. It has been reported [7–14] that their thermal decoloration does not follow simple first-order kinetics except for temperature above the T_g of the polymer matrices, and they are affected by the environment around the photochromic molecules; for example, chain segmental mobility in the polymer matrix, available free volume in the matrix, polymer polarity, volume change accompanied by structural changes of the photochromic molecules, the existence of different isomers, and the distribution of photochromic molecules. Many authors have proposed different models to describe those thermal decoloration behaviors, such as two simultaneous first-order processes [7], a distribution of environments in the polymer matrix [17], or a defect diffusion model [18]. However, in this study we are interested in the thermal decoloration phenomena of a

TABLE 1. Molecular Weight and T_g of Copolymers

Polymer	Molecular weight M_w	M_n	Content[d] of III, wt%	T_g, °C
PMMA	129,580	75,897	0	120.5
Copolymer 10[a]	120,145	82,507	7.5	126.9
Copolymer 25[b]	132,898	96,489	22.3	127.4
Copolymer 35[c]	125,292	79,415	32.0	126.9

[a] 10 wt% of spirooxazine III in the feed.

[b] 25 wt% of spirooxazine III in the feed.

[c] 35 wt% of spirooxazine III in the feed.

[d] Determined by elemental analysis (according to nitrogen).

novel photochromic spirooxazine **III** which is capable not only of doping but also of bonding with a polymer matrix such as PMMA.

The spirooxazine content in copolymers synthesized by the addition reaction is a function of photochrome **III** concentration in the feed. Table 1 summarizes the data and also shows the molecular weights and glass transition temperatures (T_g). Addition of spirooxazine **III** to PMMA may lead to a increase of the T_g of these copolymers when the spirooxazine is less than 7.5 wt% (Fig. 1). Results indicate that T_g is almost the same for polymers with a spirooxazine content above 7.5 wt% and lies in the 126.9–127.4°C range.

The thermal decoloration rates of different concentrations of spirooxazine **III** doped or bonded in polymer matrices are shown in Tables 2 and 3, respectively. Experimental data are expressed by the KWW equation [19] in the form $-\log(A - A_0) = Kt^{\alpha} + C$, where K is the rate constant, α is the order of the reaction, C is a constant, A is the absorbance, and t is the time in seconds. The α values found (0.098 and 0.063) are much less than unity. In other words, the rate deviates from

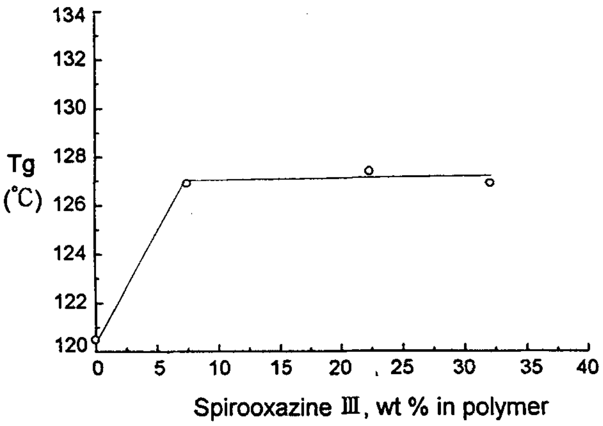


FIG. 1. T_g vs wt% of III in copolymers.

TABLE 2. Thermal Decoloration Rates of **III** Doped in Polymers

Concentration of **III** in polymer, wt%	Thermal decoloration rate
7.5	$-\ln(A - A_0) = 5.3481t^{0.098} - 1.2860$
17	$-\ln(A - A_0) = 2.9166t^{0.098} + 0.2767$
25	$-\ln(A - A_0) = 0.5202t^{0.098} + 1.4860$

simple first-order kinetics due to steric hindrance in the bulk polymer matrices. This is in agreement with literature data [13-16]. When the *K*s are plotted against the concentration, the curves of Fig. 2 result. At lower concentration of spirooxazine **III**, the thermal decoloration rate constant in the doped system is higher than that in the bonded system. We surmise that the polymer matrix has much more available free volume in the doped system to allow for the formation of the colored open form with less restrictions. It also provides higher mobility in the doped system to convert the colored open form back to the original colorless closed form by rotation and translation, as shown in Scheme 1. In the doped system the thermal decoloration rates decrease rapidly with increasing concentration of spirooxazine **III**. This implies that the decoloration rate is quite sensitive to the concentration used in the system. However, in the bonded system the decoloration rate decreases only slightly with increasing concentration. For practical applications the thermal decoloration rate may be considered to be constant, i.e., a concentration-independent variable within certain limits. Further, a much higher concentration (up to 35 wt%) of spirooxazine can be introduced into the system without phase separation and aggregation since the copolymer, poly(MMA-*co*-**III**), is created. This provides an opportunity for a high concentration of photochromic colorant, such as spirooxazine **III**, in polymer matrices for stable on-off performance in electronic applications.

CONCLUSION

A novel reactive spirooxazine **III** has been synthesized and characterized. This spirooxazine possesses not only photochromic phenomena but also a reactive double

TABLE 3. Thermal Decoloration Rates of **III** Bonded in Copolymers

Concentration of **III** in copolymer, wt%	Thermal decoloration rate
7.5	$-\ln(A - A_0) = 3.1037t^{0.063} + 0.1197$
22.3	$-\ln(A - A_0) = 2.8505t^{0.063} - 0.2886$
32.0	$-\ln(A - A_0) = 2.4745t^{0.063} + 0.3329$

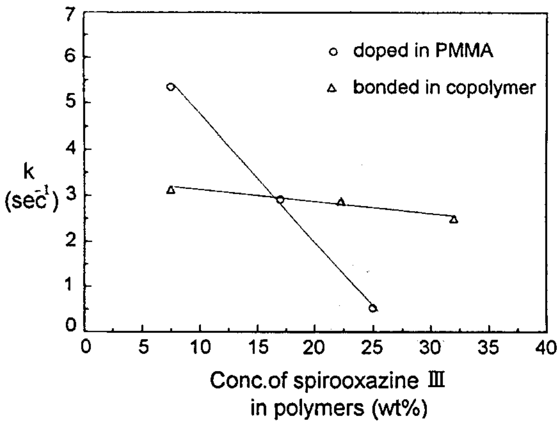


FIG. 2. Comparison of kinetics of doped and bonded **III** in polymer matrices.

bond which can result in vinyl polymerization. This reactive spirooxazine was doped and bonded, respectively, in PMMA to compare their thermal decoloration rates. The KWW decay function was used, and it was found that the thermal decoloration rate in the doped system is higher than in the bonded system. The thermal decoloration rate decreases rapidly with an increasing concentration of spirooxazine in the doped system but is almost constant in the bonded system. This indicates that there is no phase separation and aggregation in the bonded system, even if the spirooxazine reaches 30 wt%.

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