

Synthesis and photochromic properties of novel spirooxazine

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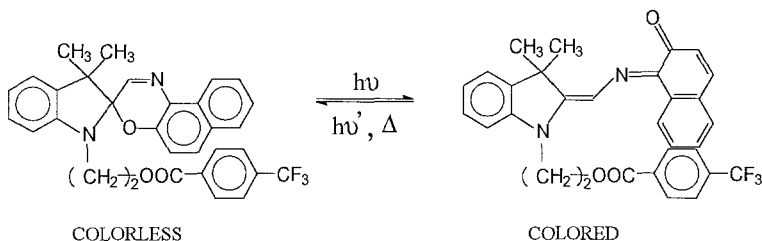
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Summary

Novel 1-[β -(4-trifluoromethyl benzoyloxy)ethyl]-3, 3-dimethyl-spiro[indoline-2, 3'-[3H]-naphtho[2,1-b]-1,4-oxazine](III) was prepared and their photochromic properties were investigated in polystyrene (PS) films. It is shown that the kinetics of thermal decoloration was decreased with increasing concentration of III in PS films.

Introduction

The photochromic organic compounds (1,2) have widely been studied because of their potential application in various photoactive devices (optical memory, optical switches, non-linear optics, etc.). The investigation of the photochromic compounds in different polymers has been the subject of many publications (3-5). Among different classes of photochromic materials, spirooxazines have attracted considerable interest because of their good fatigue resistance under a long period of irradiation in comparison with spiropyran derivatives (6). The basic principle of their photochromism consists of reversible heterolytic cleavage of the C(spiro)-O oxazine bond, followed by a rotation of one part of the molecule leading to coplanarity, yielding a colored open form upon exposure to UV light and return to colorless closed form by visible light irradiation or heat, as follows:



The search for a new spirooxazine with good properties to fit some practical applications has never been ceased, and is actually on the rise in the basic research. In this study, we have

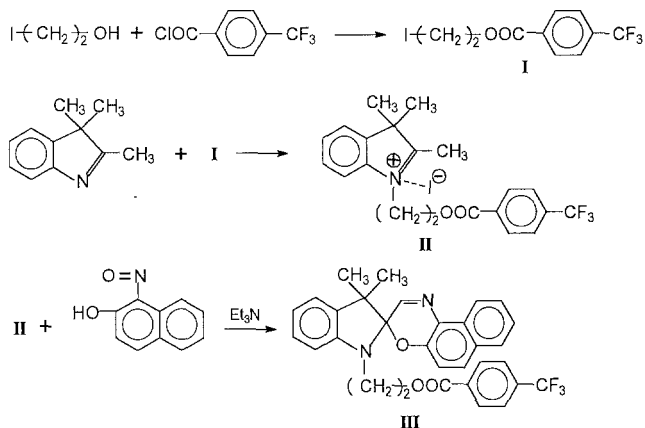
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synthesized a new spirooxazine (**III**) and investigated their kinetics of thermal decoloration in PS films.

Experimental

Materials

The synthesis of spirooxazine (**III**) is summarized in Scheme 1.



Scheme 1. Synthesis of spirooxazine (**III**).

1-Iodoethyl 4-(trifluoromethyl)benzoate (**I**)

A solution of 2-iodoethanol (1.7197 g, 0.01 mol) and 4-(trifluoromethyl)benzoyl chloride (2.2943 g, 0.011 mol) was stirred at 60–65 °C for 2.5 hours. After reaction the solution was stand at room temperature for overnight. The precipitate was filtrated off under suction, the filtrate was separated by column chromatography (silica gel-dichloromethane:n-hexane, 1:1, v/v, R_f=0.52) to give oily product. The yield was 2.9347 g (85%), bp 41–43 °C/48 mTorr. ¹H-NMR (CDCl₃, δ, ppm) : 3.41 (t, 2H, I-CH₂-, J=6.7Hz), 4.57 (t, 2H, -CH₂-O-, J=6.7Hz), 7.66 (d, 2H, ArH, J=8.3Hz), 8.12 (d, 2H, ArH, J=7.8Hz).

Analysis C₁₀H₈O₂F₃I (343.95)

calculated C 34.91 H 2.34

found C 34.95 H 2.43

1-[β-(4-Trifluoromethyl benzoyloxy)ethyl]-2,3,3-trimethyl indoleninium iodide (**II**) (7)

A mixture solution of **I** (2.9245 g, 0.0085 mol) and 2,3,3-trimethyl indolenine (1.5923 g, 0.01 mol) was heated at 80–85 °C with stirring for 6 hours. After reaction the solution was stand at room temperature for 3 days. The precipitate was isolated by filtration and washed with ethylether then recrystallization from ethanol to give golden crystals. the yield was 3.4204 g (82.4%), mp 106–108 °C. ¹H-NMR (CDCl₃, δ, ppm) : 1.58 (s, 6H, -CH₃, gem), 3.13 (s, 3H, N=C-CH₃), 5.38 (t, 2H, N-CH₂-, J=5.0Hz), 5.05 (t, 2H, -CH₂-O-, J=5.0Hz), 7.44–7.99 (m, 8H, ArH).

Analysis C₂₁H₂₁O₂NF₃I (375.14)

calculated C 50.12 H 4.21 N 2.78

found C 48.32 H 4.19 N 2.69

Synthesis of 1-[β -(4-Trifluoromethyl benzoyloxy)ethyl]-3,3-dimethyl-spiro[indoline-2,3'-[3H]-naphtho[2,1-b]-1,4-oxazine] (III) (8)

A mixture solution of II (2.5155 g, 0.005 mol) and 1-nitroso-2-naphthol (0.9524 g, 0.0055 mol) in 50 ml ethanol was heated to a gentle reflux at about 80 °C. To this solution was added dropwise triethylamine (1 g, 0.01 mol) over a period of 30 minutes, and the mixture was refluxed for 3 hours. The solution was then cooled and the solvent was evaporated under reduced pressure. The resulting dark brown paste was separated by column chromatography (silica gel-dichloromethane:n-hexane, 1:1, v/v, R_f=0.37) and recrystallized from acetone to give light brown crystals. The yield was 1.5239 g (57.5%), mp 151-153 °C. ¹H-NMR (CDCl₃, δ , ppm) : 1.33 (d, 6H, -CH₃, gem, J=5.1Hz), 3.57-3.76 (m, 2H, N-CH₂-), 4.48-4.60 (m, 2H, -CH₂-O-), 7.76 (s, 1H, -N=CH-C), 6.74-8.55 (m, 14H, ArH).

Analysis C₃₁H₂₅N₂O₃F₃ (530.18)

calculated C 70.18 H 4.75 N 5.28

found C 69.93 H 4.76 N 5.48

Sample preparation

Polystyrene films of 20-30 μ m thickness which containing different concentrations of III (1wt%, 2wt% and 3wt%) were prepared by using the solvent-cast method from benzene and were evacuated at room temperature overnight and subsequently heated under vacuum for 3 hours at 80 °C to eliminate the residual solvent.

Measurements of thermal decoloration

The polystyrene films containing different concentrations of III were exposed with 150W Xe lamp for 20 min. and then the absorption spectra were measured on an Otsuka MPCD-1000(28C) spectro multichannel photodetector. The photodetector can measure the whole spectrum between 220 nm and 800 nm within 16 ms. Absorption measurements of thermal decoloration of samples were performed at ambient temperature. The absorption maximum (λ_{max}) was observed at 580 nm.

Results and Discussion

Reactions of photochromic compounds embedded in polymer matrices are different from those in solutions. It has been reported that, the thermal decoloration did not follow a simple first order kinetics except for the temperature above T_g of the polymer matrices (9-11). The thermal decoloration in polymer matrices are affected by the environment around photochromic molecules, for example, chain segmental mobility of matrix, available free volume of the matrix, polymer polarity, volume change accompanied by the structural changes of photochromic molecules, the existence of different isomers and distribution of photochromic molecules. Many authors have proposed different models to describe those thermal decoloration behaviors, as two simultaneous first order processes (12,13), a distribution of environments in the polymer matrix (14) or a defect diffusion model (15).

In this study, Fig.1 shown the thermal decoloration of novel spirooxazine III embeded in PS films is completely different from those observed in homogeneous solutions. The thermal decoloration behavior deviated from simple first order kinetics, and is affected by the concentration of III, with the lower concentration of III approach to steady state more quickly than higher concentration III in PS films. The thermal decoloration rates of PS films with different novel spirooxazine III concentrations are listed in Table 1. The rates were obtained

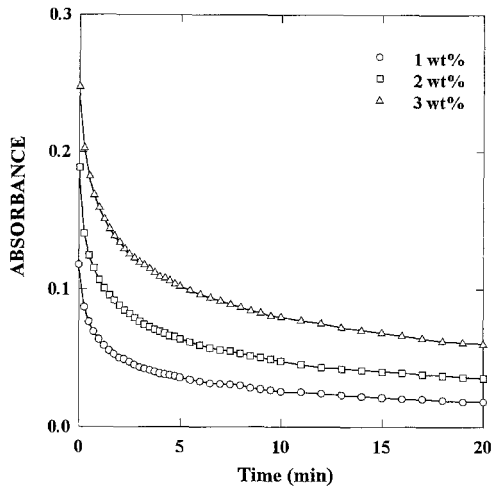


Fig.1 Thermal decoloration of PS with different spirooxazine III content.

by mathematical curve fitting from experimental kinetics data in Fig.1, indicating that the kinetics of thermal decoloration decreases with increasing concentration of III in PS films. In this experiment, the nature of photochromic compound and polymer matrix are the same. The only difference is the concentration of photochromic compound III. It is clear that the available free volume of PS matrices plays a crucial role in the thermal decoloration. At low concentration of III, PS has much more available free volume to allow the formation of the colored open form with less restriction, and also provides higher mobility to convert the colored open form to the original colorless closed form by the rotation and translation. Base on the results in Table 1., we propose a general model similar to the Kohlraush-Williams-Watts (KWW) equation, which is known to describe various types of non-linear relaxation processes in disordered solids (16) to present the kinetics of thermal decoloration of III in PS films:

$$\log(A - A_0) = -k t^\beta - c$$

where A is the absorbance of colored form at time t, A_0 is the absorbance of colored form before UV irradiated, k is rate constant, β is the extent of deviation and c is the constant.

Table 1. Thermal decoloration rate of spirooxazine III in the Polystyrene films.

Spirooxazine III	Thermal decoloration rate
1 wt%	$\log(A - A_0) = -0.2975 t^{0.35} - 0.9162$
2 wt%	$\log(A - A_0) = -0.2669 t^{0.35} - 0.7174$
3 wt%	$\log(A - A_0) = -0.2290 t^{0.35} - 0.5822$

Conclusion

A novel spirooxazine III has been synthesized. Its kinetics of thermal decoloration in PS films is given in the Table 1.

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