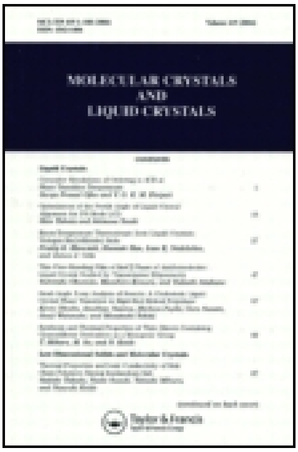

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Photochromism of Novel Spirooxazines II. Polarity Effect on Thermal Decoloration in Polymer Matrix

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PHOTOCHROMISM OF NOVEL SPIROOXAZINES
II. POLARITY EFFECT ON THERMAL DECOLORATION IN POLYMER MATRIX

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Abstract Polarity effect on photochromism has been investigated for three photochromic spirooxazines which are identical in structure except with different end groups ($-CF_3$, -H, $-CH_3$) on their side chain. End group with stronger electron-negativity (such as $-CF_3$) has a relatively strong polarity effect which in turn gives a faster thermal decoloration rate as confirmed by our measurements. In this non-linear relaxation process, KWW equation has been adopted for investigation.

INTRODUCTION

Photochromic organic compounds[1,2] have widely been studied because of their potential applications as optical media for optical disc, coatings for smart windows, optical switches and optical filters, etc. Among the organic photochromic compounds, spirooxazine is one of the most well explored group due to their excellent light fatigue resistance[3,4] and color change upon photoirradiation. In previous papers[5-7], we have described the synthesis and photochromic properties of novel spirooxazines doped or bonded in polymer matrices. Results show that thermal decoloration rate in the doped system is higher than in the bonded system. Since thermal decoloration rates are affected by the molecular structures around the photochromic molecules, we speculate that their polarities can impose different effect on the thermal decoloration of our synthesized spirooxazines. Thus experiments we conducted to verify our speculation and were further elucidated by KWW equation.[8]

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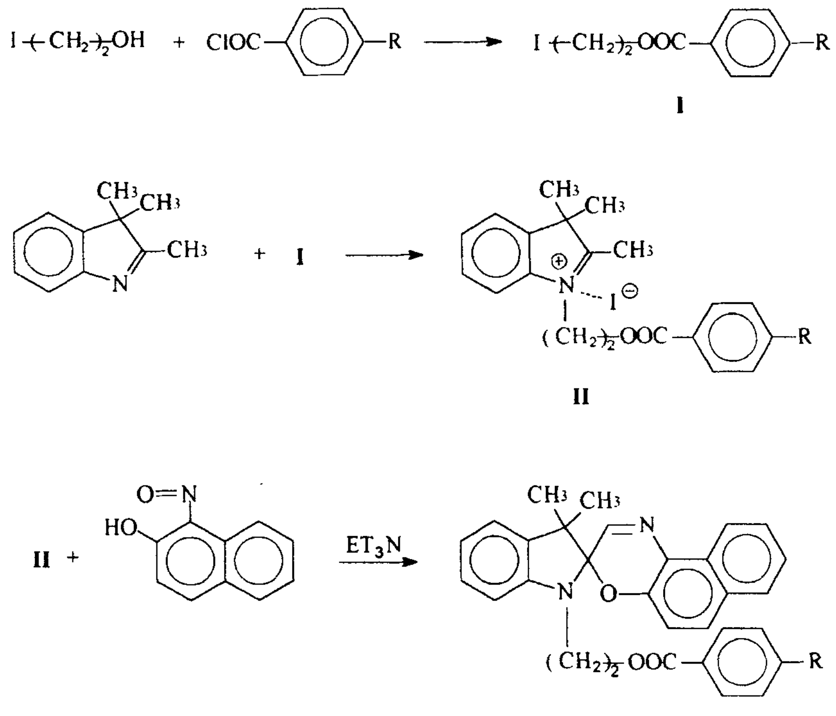
* corresponding author

EXPERIMENTAL

Materials

Synthesis of spirooxazines, 1-[β-(4-Trifluoromethyl benzoyloxy)ethyl]-3,3-dimethyl-spiro[indoline-2,3'-[3H]-naphthol[2,1-b]-1,4-oxazine] **(SO-CF$_3$)**, 1-[β-(4-methyl benzoyloxy) ethyl]-3,3-dimethyl-spiro [indoline-2,3'-[3H]-naphthol [2,1-b]-1,4-oxazine] **(SO-CH$_3$)** and 1-[β-(4-benzoyloxy)ethyl]-3,3-dimethyl-spiro[indoline-2,3'-[3H]-naphthol[2,1-b]-1,4-oxazine] **(SO-H)**, have been reported in our previous papers[5,6] The whole reaction procedure is summarized by the Scheme 1.



R= H, CH$_3$, CF$_3$

SCHEME 1 Synthesis of spirooxazines (SO-H, SO-CH$_3$ and SO-CF$_3$)

Sample Preparation

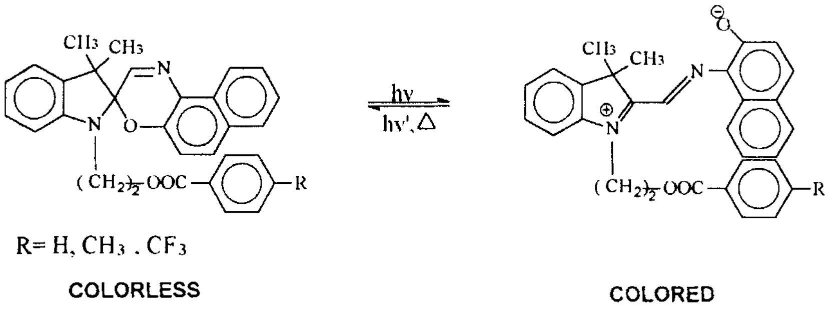
PMMA films of 2-μm thickness containing 3 wt % of doped SO-H, SO-CH$_3$, SO-CF$_3$ were prepared from benzene by solvent-cast method and were evacuated at room temperature overnight and subsequently heated under vacuum for 3 hours at 80 °C to eliminate the residual solvent.

Measurements of Thermal Decoloration

The PMMA films containing 3 wt % of spirooxazines were exposed to 4W Xe lamp for 10 minutes and then the absorption spectra were measured by an Otsaka MCPD-1000(311C) spectro multichannel photodetector. The photodetector can measure the whole spectrum between 300 and 1100 nm within 20 ms. All data collected were transferred to a personal computer for analysis. Absorption measurements were performed at ambient temperature. The absorption maximum (λ_{max}) was observed at 600 nm.

RESULTS AND DISCUSSION

Photochromic spirooxazines with different polarities have been synthesized in our laboratory. They have different functional groups, $-CF_3$, $-CH_3$, and -H attached to their side chains as shown in Scheme 2. Electronegativities of these electron-donor and electron-acceptor groups reveal different polar effect. In order to analyze the polarity effect on the thermal decoloration of spirooxazines in PMMA, the extent of deviation from first-order kinetics and rates of thermal decoloration which were based on Kohlraush-Williams-Watts (KWW) equation[8,9] were under investigations.



SCHEME 2 Photocoloration and thermal decoloration are two major features in photochromism.

Based on our measurements, the absorbance vs. time plot as shown in Figure 1, reveals that the sample SO-CF_3 in PMMA has the sharpest change of slope among the three spirooxazines. This indicates that functional group $-CF_3$, with the strongest electronegactivity or electron-withdrawing capability among the three, demonstrates the most polarity effect on the rate of thermal decoloration, i.e. it has the fastest thermal decoloration rate. On the other hand, functional group $-CH_3$, being a electron donor, exhibits the slowest thermal decoloration rate while the end group -H has thermal decoloration rate in between the two. These results are in accordance with what we speculated, that spirooxazines with different polarities can impose different effect on the thermal decoloration rate.

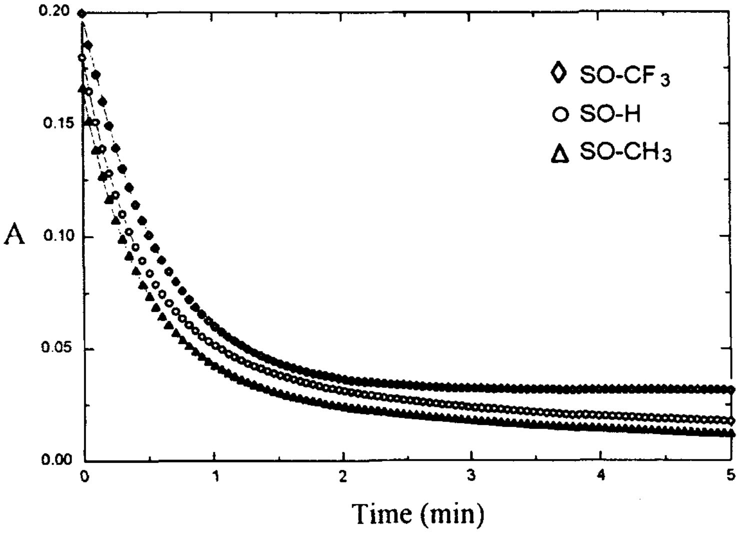


FIGURE 1 Thermal decoloration of PMMA with different spirooxazines

Experimental results indicate that the thermal decoloration is a non-linear relaxation process, the effect of polarity can further be elucidated by KWW equation as shown below. The experimental absorbance vs. time plot can be expressed numerically by the equation[10]

$$A(t) = C_1\exp[-t/t_1] + C_2\exp[-t/t_2] + C_3 \quad (1)$$

where A is the absorbance of colored species, t_1 and t_2 are the first and second decay times, respectively; and C_1, C_2 and C_3 are constants as given in Table I.

TABLE I A(t) of three spirooxazines

Compounds	A(t)
$SO\text{-}CF_3$	$0.1683\exp[-t/0.57] + 0.04071\exp[-t/3.858\times10^7] - 0.00917$
SO-H	$0.1235\exp[-t/0.4233] + 0.03527\exp[-t/2.486] + 0.00706$
$SO\text{-}CH_3$	$0.1181\exp[-t/0.4001] + 0.04716\exp[-t/1.823] + 0.01482$

Take logarithm and differential of A(t)

$$- \mathrm{d} \ln A(t) / \mathrm{d}t = k \qquad (2)$$

where k is a characteristic rate constant for a simple exponential decay of a colored species. If we further assume that k is a function of time, then

$$- \mathrm{d} \ln A(t) / \mathrm{d}t = K(t) \qquad (3)$$

by integration

$$\ln A(t) / A(0) = [-\int_0^t K(t)dt] \qquad (4)$$

If we simply relate K(t) with KWW eq. which is known to describe various types of non-linear relaxation process in disordered solid.[8,9]

$$K(t) = R\, t^{\alpha-1} \quad (0 < \alpha \leq 1) \qquad (5)$$

where α concerns with the derivation from the first order reactions, and R concerns with absolute reaction rates

$$- \mathrm{d} \ln A(t)\, \mathrm{d}t = R\, t^{\alpha-1} \equiv \Psi \qquad (6)$$

and

$$\ln \Psi = (\alpha - 1) \ln t + \ln R \qquad (7)$$

where

$$\Psi \equiv - \frac{(-C_1/t_1)\exp[-t/t_1] + (-C_2/t_2)\exp[-t/t_2]}{C_1\exp[-t/t_1] + C_2\exp[-t/t_2] + C_3}$$

When $\ln \Psi$ vs. $\ln t$ plots give straight line, the values of α and R can be calculated from the slope and the interception as given in TableII.

During the first time interval from (t=0 to t=36 sec) the product of $\alpha \times R$ of these spirooxazines are 0.881, 0.853 and 0.708 for SO-CF_3, SO-H and SO-CH_3 respectively. The relative order may reflect quantitatively its polarity effect on thermal decoloration during the first 36 seconds. These studies also illustrate that only the first one minute of thermal decoloration kinetics can be meaningful represented by KWW Equation.

TABLE II Thermal decoloration kinetics of spirooxazines in PMMA films
[$K(t) = R\,t^{\alpha-1}$ ($0 < \alpha \leq 1$)]

	Time Interval (min)	R	α	$R \times \alpha$
SO-CF3:	0 - 0.6	1.0623	0.83	0.8817
	0.6 - 1.2	0.8226	0.10	0.0823
SO-H:	0 - 0.6	1.138	0.75	0.8535
	0.6 - 1.2	0.8610	0.04	0.034
SO-CH3:	0 - 0.6	0.9974	0.71	0.7082
	0.6 - 1.2	0.7556	0.03	0.0227

CONCLUSION

The non-linear relaxation process as described by KWW equation has been adopted to investigate the photochromism of these three spirooxazines. The polarity effect indicates that the stronger in electronegativity leads to a faster thermal decoloration rate.

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REFERENCES

1. R.C. Bertelson, in Photochromism, edited by G. H. Brown (Wiley-Interscience, New York 1971), pp. 733-840.
2. R. Guglielmetti, N.Y.C.Chu, G. Gauglitz, K. Ichimura, J. Michl, U. P. Wild, A. Renn, N. Hampp and C. Brauchle, in Photochromism, Molecules and Systems, edited by H. Durr and H. Bouas-Laurent(Amsterdan: Elsevier, 1990), pp. 854-975.
3. S. Kawauchi, H. Yoshida, N. Yamashina, M. Ohira, S. Saeda and M. Irie; Bull. Chem. Soc. Jpn., 63, 267 (1990).

4. N. Y. C. Chu, Can. J. Chem., 61,300 (1983)
5. Ming-Siing Wang and Andrew Teh Hu, Polym. Bull., 33, 275(1994)
6. Ming-Sing Wang, Chien-Liang Yeh and Andrew Teh Hu, Polymer International, 38,101 (1995)
7. Andrew Teh Hu, Wen-Hishin Wang and Hong-Ji Lee, J. Macromol. Sci. A. Pure Appl. Chem., A33(6), 803(1996)
8. G. Williams and D. C. Watts, Trans. Faraday Soc., 66, 80 (1970)
9. Y. Munakata, T. Tsutsui and S. Saito, Polym. J., 22, 843 (1990)
10. Jeffrey I. Steinfeld, J.S. Francisco and W.L.Hase, Chemical Kinetics and Dynamics, (Prentic-Hall, 1989), p.123.