Synthesis and Photochromic Response of a New Photochromic Amorphous Molecular Material Based on Spirooxazine

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Keywords: photochromic amorphous molecular material, spirooxazine, glass formation, photochromism

1. Introduction

Photochromic materials have recently attracted renewed interest because of their potential technological applications for e.g. optical memories and switches [1]. In addition to reversible changes of optical properties attributed to photochromic reactions, photomechanical effect observed for photochromic materials are the current topics such as bending of liquid-crystalline polymer network films by photoirradiation [2,3], photoinduced surface relief grating formation [4-11], and reversible shape change of molecular crystals of diarylethene derivatives [12]. As practical applications usually require materials as solid films, there have been extensive studies on photochromic polymers and composite polymer systems where small photochromic molecules are dispersed in a polymer binder. In contrast to such polymeric materials, we have proposed a novel concept of photochromic amorphous molecular materials, namely, small organic photochromic molecules that readily form stable amorphous glasses, and created such materials based on azobenzene [11,13-17] and dithienylethene [18,19].

It is of interest to create new families of photochromic amorphous molecular materials other than azobenzene and dithienylethene families. Here we paid attention to spirooxazine. It is well known that spirooxazine analogues exhibit photochromism based on photochemical ring opening reactions to produce merocyanine forms and reverse photochemical and thermal cyclization reactions [20]. In the present study, we have designed and synthesized a new spirooxazine-based photochromic compound, 5-[bis(4-methylphenyl)amino]-1,3,3-trimethylspiro[indoline-2,3′-(3H-naphth[2,1-b][1,4]oxazine)] (BMSO) and investigated glass formation and photochromic response of BMSO.

![BMSO](image)

2. Experimental

BMSO was synthesized as follows: A benzene solution (20 ml) of 4-amino-N,N-bis(4-methylphenyl)aniline (10 g, 35 mmol) and 3-bromo-3-methyl-2-butanol (2.8 g, 17 mmol) was refluxed for 5 h under nitrogen atmosphere. The resulting solution was chromatographed on silica-gel using chloroform as an eluent to give 5-[bis(4-methylphenyl)amino]-2-methylene-1,3,3-trimethyl-indoline. The product (0.2 g) was dissolved in benzene (5 ml) and methyl iodide (0.2 g, 1.5 mmol) was added to the solution at 60 °C. The reaction mixture was stirred at this temperature for 2 h and then at 45 °C for 4 h. The solution was extracted with toluene and washed with aqueous solution of sodium hydroxide and water successively.
the solvent was removed under reduced pressure, the residue was dissolved in ethanol (10 ml) together with 1-nitroso-2-naphtol (80 mg, 0.46 mmol) and the solution was refluxed for 5 h under nitrogen atmosphere. The resulting solution was extracted with chloroform and washed with aqueous solution of sodium hydroxide and water successively. After the solvent was removed under reduced pressure, the residue was chromatographed on silica-gel by using a mixed solvent of toluene and hexane (1:2 v/v) as the eluent. Further purification by means of gel permeation chromatography by using an LC-908 recycling preparative HPLC (Japan Analytical Industry Co., Ltd.) with two columns, JAIGEL-1H and JAIGEL-2H (Japan Analytical Industry Co., Ltd.), followed by recrystallization from ethanol gave 80 mg of BMSO. MS(El): z/e = 523 (M+); 1H NMR (750 MHz, THF-d8): δ (ppm) = 8.56 (d, 1H), 7.75 (1H, s) 7.73 (1H, d), 7.69 (1H, d), 7.49 (1H, t), 7.33 (1H, t), 7.05 (1H, d) 6.98 (4H, d), 6.89 (1H, s), 6.88 (4H, d), 6.85 (1H, d), 6.49 (1H, d), 2.72 (3H, s), 2.24 (6H, s), 1.31 (3H, s), 1.24 (3H, s); 13C NMR (187.5 MHz, THF-d8): δ (ppm) = 151.4, 147.3, 145.0, 144.9, 141.9, 138.2, 132.0, 131.4, 130.9, 130.4, 130.3, 128.5, 127.5, 126.3, 124.8, 124.1, 123.6, 122.5, 120.6, 117.4, 108.3, 99.6, 52.5, 29.8, 25.7, 21.0, 20.8.

3. Results and discussion

A new photochromic amorphous molecular material, BMSO, was designed and synthesized. A nonplanar bis(4-methylphenyl)amino group was incorporated to provide molecule with glass-forming property. The synthetic route of BMSO is shown in Scheme 1.

BMSO was found to readily form an amorphous glass by cooling the melt sample. Fig. 1 shows DSC curves of BMSO. When the recrystallized sample was heated (Fig. 1a), an endothermic peak due to melting was observed at 155 °C. When the

melt sample was cooled on standing in air, an amorphous glass was formed. When the glass sample was heated (Fig. 1b), a glass-transition phenomenon was clearly observed at 83 °C. On further heating, no crystallization phenomenon was observed, suggesting that the glassy state of BMSO was quite stable.

BMSO was found to exhibit photochromism as amorphous film as well as in solution. Fig. 2 shows electronic absorption spectral change of BMSO amorphous film. When the film was irradiated with 365 nm-light, a new band appeared around 640 nm due to formation of the merocyanine (MC) form. When the irradiation

![Scheme 1](image1.png)  Synthesis of BMSO.

![Fig. 1](image2.png) DSC curves of BMSO. a) crystalline sample obtained by recrystallization from solution. b) glass sample obtained by cooling the melt. Heating rate: 5 °C/min.

![Fig. 2](image3.png) Electronic absorption spectral change of BMSO amorphous film. a) before photoirradiation. b) photostationary state upon irradiation with 365 nm-light.
was stopped after the reaction system had reached the photostationary state, the absorbance around 640 nm gradually decreased due to reverse thermal cyclization reaction to reproduce BMSO. Irradiation with visible light (>580 nm) was also found to induce the reverse cyclization reaction.

Further study on the kinetics of the thermal reverse cyclization reaction of photoproduced MC form has been performed. Fig. 3 shows the first order plots for the reactions in benzene solution and as amorphous film at 20 °C after the system has reached photostationary state upon irradiation with 365 nm-light. The reaction in benzene solution was found to follow the first order kinetics with a rate constant of 33 min⁻¹. On the other hand, the reaction as amorphous film did not follow the first order kinetics and the apparent first order rate constant was considerably smaller than that in benzene solution. The apparent first order rate constant at initial stage was estimated to be 0.15 min⁻¹, which was about two orders of magnitude smaller than that observed in benzene solution. The rate retardation of the reaction as amorphous film observed here was thought to be associated with a large volume needed for the reaction relative to the local free volume. Such rate retardation has been reported for azobenzene-based photochromic amorphous molecular materials with relatively large substituents [13,16,17].

In summary, a novel photochromic amorphous molecular material based on spiroxazine, BMSO, has been designed and synthesized in the present study. BMSO was found to readily form amorphous glass and exhibit photochromism as amorphous film as well as in solution. A variety of photochromic amorphous molecular materials based on spiroxazine will be created and their properties and applications will be investigated in the near future.

References