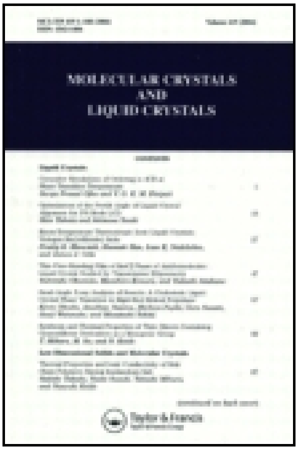

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Stable Colored and Fluorescent Patterns Derived from Photochromic Spiropyran and Photoacid Generator

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When the poly(methylmethacrylate) films containing 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-indole] (SP1) and N-(1,8-naphthalene dicarboximidyl)-10-camphorsulfonate (NIC) were irradiated by UV light, a salt was formed from the reaction of phenolate in the merocyanine form (the photo-product of SP1) and the photo-generated acid. The original absorption of the film at 338 nm decreased and a new absorption band appeared at 400 ~ 500 nm due to the salt formation between the photo-generated acid and the merocyanine form of SP1. The resulting yellow films showed an orange-red emission centered around 520 nm, while the original colorless films have no fluorescence. The irradiation of film through a mask produced a finely resolved pattern and the patterned image was quite stable over several months of storage in the dark at room temperature. The photo-irradiation of the film also induced the refractive index change as large as 0.0022.

Keywords: patterned image; photoacd generator; photochromic; spiropyran

INTRODUCTION

Photochromic compound spiropyrans (SPs) experience structural transformation from the closed colorless spiro structure to the open colored merocyanine form by absorbing UV light (Scheme 1, path a). Such photochemical transformation involves the changes of polarity, dipole moment, fluorescence and refractive index as well. Their unique features attract considerable attention for the potential applications including optical data storages, molecular switching devices and optical waveguides [1–4]. The colored merocyanine form of the SPs,

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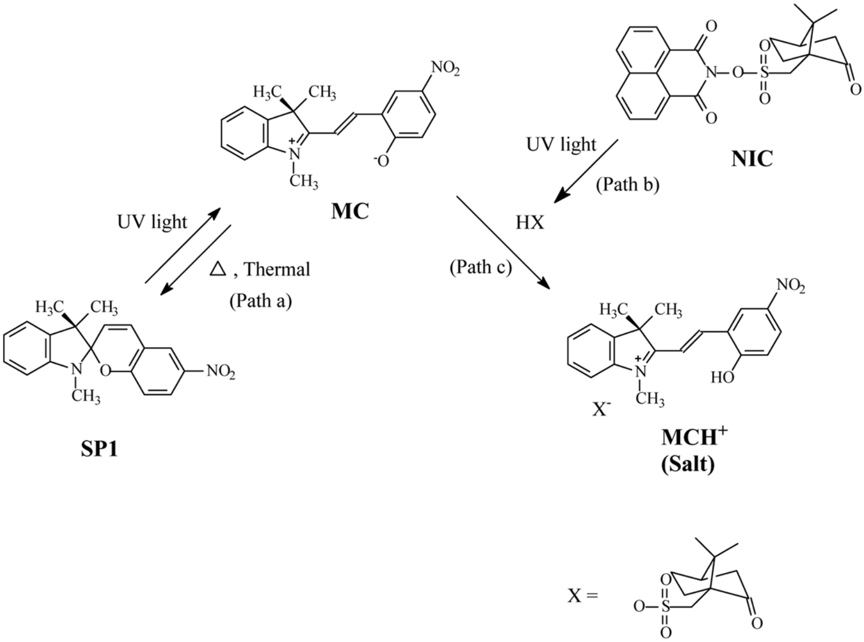

SCHEME 1 Schematic representation of formation of salt for (MCH*) from spiropyran (SP1) by illumination of UV light in the presence of photoacid generator (NIC).

however, is unstable as it relaxes back to its initial colorless state even in the dark at room temperature [5–7]. Since such short lifetime of the colored merocyanine species is one of the major obstacles to restrict the applications of the spiropyran, many researchers have focused their efforts on stabilizing the merocyanine form through forming J-aggregate, chelating with a metal ion, being incorporated into polyion complex or clay [8–12].

In our recent studies, we observed that an acid treatment on the spiropyran under irradiation of UV light produced a quite stable salt form between the merocyanine form and the acid [13]. The resulting merocyanine salts exhibited a negative photochromism as the colored open form was more stable than its colorless counterpart.

Since a photoacid generator (PAG) produces a corresponding acid when it is exposed to UV light [14–15], irradiation of UV light on the films containing both PAG and SP would produce a stable salt form between the generated acid and merocyanine (the photo-product of SP) in the film. In this work, we present a successful generation of a stable colored and fluorescent image by UV irradiation on the films containing SPs and PAG.

EXPERIMENTAL

Materials and Film Preparation

1′,3′-Dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-indole] (**SP1**) and poly(methylmethacrylate) (**PMMA**) were purchased from Aldrich Chem. Co. and used without further purification. *N*-(1,8-naphthalenedicarboximidyl)-10-camphorsulfonate (**NIC**) were purchased from Uray Co. (Korea) and was employed as a photoacid generator. NIC has an absorption maximum at 335 nm with a molar extinction coefficient of 3.3×10^5.

For image patterning and refractive index change experiments, 2–3 μm thick films were typically prepared by spincasting a filtered solution of SP1 (5 mg), NIC (6.5 mg), and PMMA (100 mg) in chloroform (1 ml) on glass substrate or silicon wafer. The resulting transparent colorless films were exposed to UV light using a medium-pressure mercury lamp operated at 80 W for 1 min to produce patterned image or refractive index change in the film.

Instruments

The absorption spectra were recorded by UV/vis absorption spectroscopy (UV-2550, Shimadzu Co.). The fluorescence spectra were obtained from FluoroMax-2 fluoro-spectrophotometer. The refractive indices of the films were measured using a prism coupler with 830 nm diode laser as a monitoring probe beam and a silicon photodetector.

RESULTS AND DISCUSSION

After examining several commercially available photacid generators, N-(1,8-naphthalenedicarboximidyl)-10-camphorsulfonate (NIC) was chosen because it has maximum absorption at 335 nm and hence relatively large overlap of absorption with the SP1.

Since NIC underwent cleavage of N-O bonds upon UV absorption and produced camphorsulfonic acid as a photo-product [16], the formation of salt between camphorsulfonic acid and SP1 with the UV irradiation was examined in the solution as a model reaction. A solution of SP1 and camphorsulfonic acid in THF was prepared and the absorption spectrum was recorded. Upon UV irradiation the initially colorless solution readily turned yellow and a new absorption band appeared at $400 \sim 500$ nm as shown in Figure 1. This new

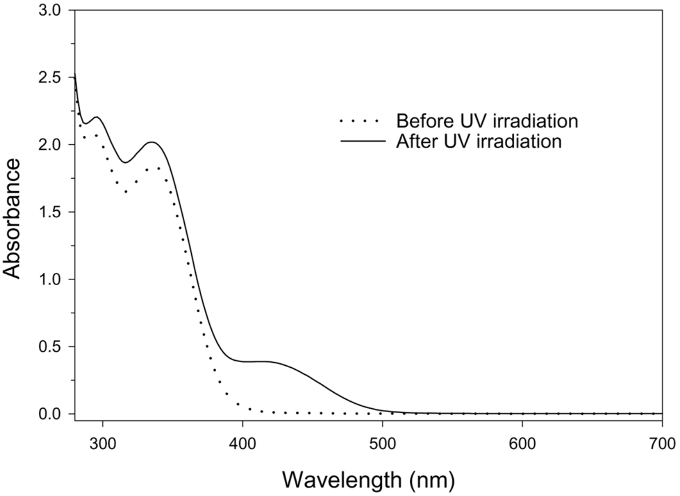

FIGURE 1 The absorption spectra of SP1 and camphorsulfonic acid in THF solution before and after irradiation of UV light at 365 nm.

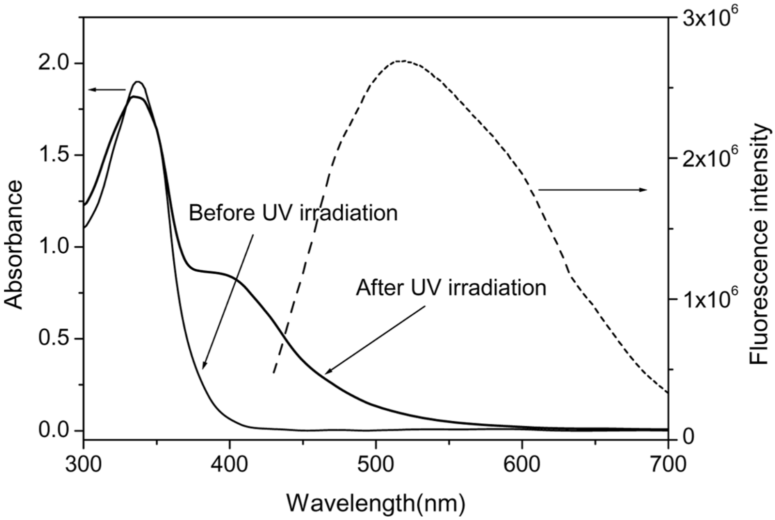

FIGURE 2 The absorption and fluorescence spectra of the PMMA films containing SP1 and NIC upon irradiation of UV light. The fluorescence spectrum was obtained after UV irradiation (excitation wavelength:400 nm).

absorption must be due to the salt formation between the merocyanine and the acid [17–18]. This result showed that the phenolate anion in the merocyanine form was efficiently protonated by camphorsulfonic acid to result in the salt form, MCH^+. The thermodynamically stable MCH^+ form showed a negative photochromism as the colored open form was more stable than its colorless closed counterpart. Similar result was also observed in our previous studies [13(a)], where SP1 was treated with toluenesulfonic acid or dodecylbenzene sulfonic acid under UV light irradiation.

About 2–3 μm thick films were prepared from the chloroform solution containing NIC, SP1 and PMMA. The resulting transparent colorless films had a maximum absorption at 338 nm as shown in Figure 2. When the films were exposed to UV light, the absorption at 338 nm decreased and a new absorption band appeared at 400 ~ 500 nm similar to the solution case in Figure 1. This suggested that even in the solid state, the reaction between camphorsulfonic acid (the photo-product

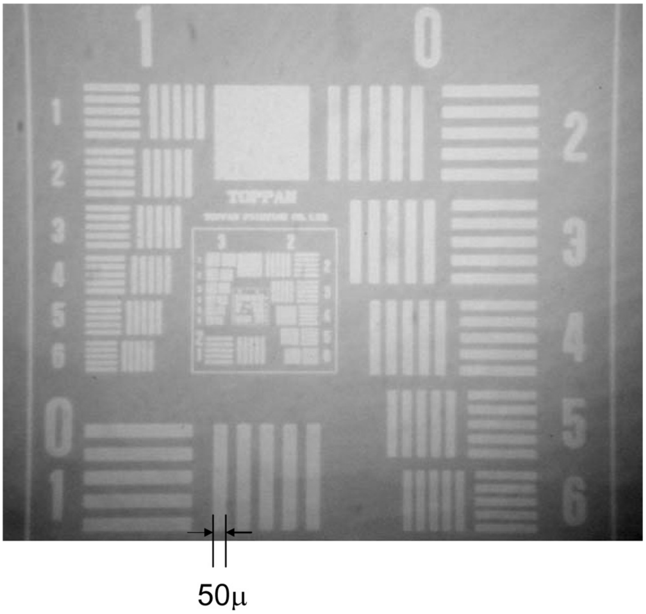

FIGURE 3 Photo-induced patterned image of the PMMA film containing SP1 and NIC on a glass substrate after exposure to UV light through a chrome mask. (SP1 content: 5wt%) The originally colorless portions, which were not exposed to UV light, were colored blue-violet by irradiation of a weak TLC lamp light (365 nm) to enhance the contrast of the picture.

of NIC) and the merocyanine form (the photo-converted product of SP1) yielded the merocyanine salt (Scheme 1). The result also indicated that the proton transfer from the photo-generated acid to MC was facile even in the solid state and MC had enough life-time to react with the acid. The produced merocyanine salts were so stable that the new absorption had little change over several months at room temperature in the dark state.

The stability of the produced salts was manifested in the emission experiment. The above yellow films showed a broad emission centered around 520 nm (Fig. 2) when excited at 400 nm, while SP1 does not show any significant fluorescence because most of the absorbed energy is used to transform SP form into MC form. This feature could be useful in the application for the fluorescence optical storage system.

The PMMA films containing SP1 and NIC on a glass substrate was exposed to UV light through a mask for 1 min. As shown in Figure 3, a clear colored pattern appeared. The yellow lines, which were the exposed area to UV light through the photomask, were finely patterned. The generated images were quite stable and have remained over several months of storage in the dark at room temperature.

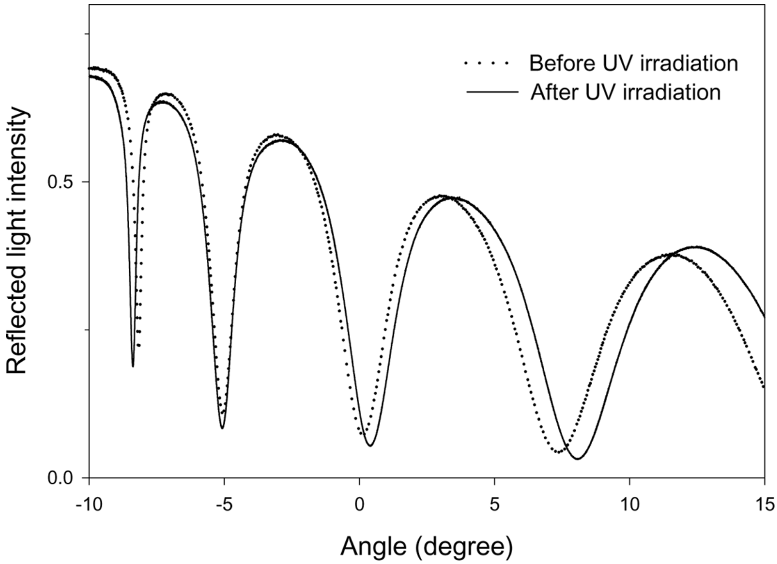

FIGURE 4 Incidence angle dependence of reflected light measured by a prism coupler using a probe beam of 830 nm for the PMMA film containing SP1 (5 wt%) and NIC before and after UV irradiation.

Photo-irradiation of the photochromic spiropyrans also induced refractive index change. The refractive indices of the films before and after UV light irradiation were evaluated by a prism coupling method using a probe beam of 830 nm [19]. PMMA films (ca. $2 \sim 3\,\mu$m film thickness) with a different ratio of SP1 contents were prepared by spincoating on a silicon wafer. Figure 4 shows the incidence angle dependence of the reflected light intensity for the PMMA film containing SP1 (5 wt%) and NIC before and after UV irradiation which was measured by prism coupler using a probe beam of 830 nm. The refractive index of the film containing 5 wt% SP1 was 1.4886 and 1.4908 before and after UV irradiation, respectively. This difference of refractive index (0.0022) was significant as the photoinduced refractive index change of 0.0006 was large enough to fabricate optical modulator based on polycarbonate doped with a photochromic diarylethene derivatives [20].

In conclusion, we here presented a new strategy for preparing of a stable colored and fluorescent imaging using a photochromic spiropyran and a photoacid generator. The in-situ generation of the photoacid and the merocyanine form in the films by UV irradiation could be useful for the production of stable and fluorescent patterned images, which may find use in the optical data storage medium and processing.

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