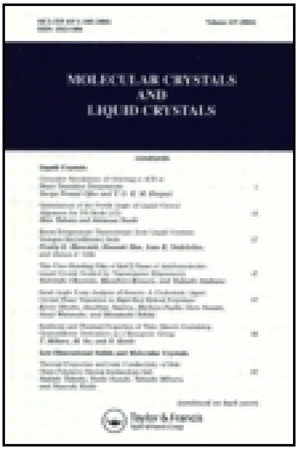

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# Preparation of Photochromic Cellulose Derivatives Containing Spirobenzopyran

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# Preparation of Photochromic Cellulose Derivatives Containing Spirobenzopyran

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New cellulose acetate derivatives substituted with 6-(*p*-alkoxyphenyl)carbonyl-spirobenzopyran (COSP) were prepared from base-catalyzed etherification of cellulose acetate by 6-(*p*-bromohexyloxyphenyl)carbonylspirobenzopyran. The degree of COSP substitution was controlled by the feed amount of COSP and reached to max. 46 wt %. $T_g$ of the resultant COSP bound cellulose (CA-COSP) was increased as the COSP substitution is increased. CA-COSP was soluble in aprotic polar solvents, to allow preparation of photochromic film by solution process. Reversible photochromic property was observed from the CA-COSP film by using two light sources of UV and visible light.

*Keywords:* photochromic property; cellulose derivative; spirobenzopyran

## INTRODUCTION

Photoregulation of polymers containing photochromic functional groups has been the subject of many investigations[1]. Such photochromophore bound polymers are highly promising materials for application in photochromic displays as well as in photoregulated devices. Recently, we have reported synthesis and polymerization of 6-(*p*-alkoxyphenyl)carbonylspirobenzopyran (COSP), which showed improved thermal stability with faster photochromic response compared to 6-nitrospirobenzopyran[2]. The photochromic effect and application potential of COSP bound polymer could be much improved by modifying polymer structure. As a polymer backbone we have investigated cellulose derivatives due to their abundance and unique properties such as optical clarity, toughness, chemical resistance, processibility, compatibility, and particularly, ease of chemical modification[3]. In this paper, we report syntheses and photochromic property of new cellulose acetate derivatives containing spirobenzopyran moieties (CA-COSP, **1**).

## EXPERIMENTALS

**Reagents and Materials:** All reagents and solvents were purchased from Aldrich Chem. Co. and TCI and used after appropriate purification procedures. 6-(ω-Bromohexyloxyphenylcarbonyl)spirobenzopyran (**2**) was synthesized from the reaction of 6-(hydroxyphenylcarbonyl)[2] with 2 mol. eq. of 1,6-dibromohexane in the presence of potassium carbonate in acetonitrile at 83 °C. **2** was obtained in 86 % yield (m.p. 117 °C) after column chromatography with ethyl acetate/hexane (1:6 v/v) as an eluent. Cellulose acetate (CA, DS = 1.88) was prepared by a base-catalyzed hydrolysis of commercial cellulose acetate (Aldrich, DS=2.45) according to literature[4].

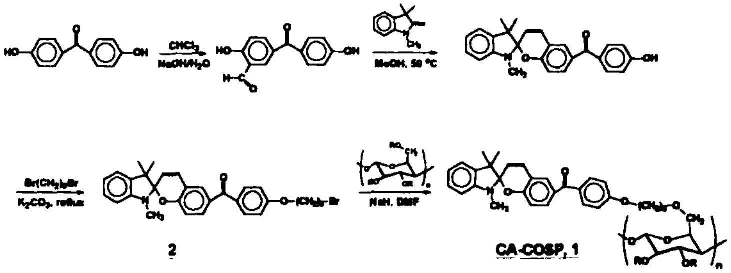
**Synthesis of CA-COSP (1):** CA (0.50 g, 2 mmol of anhydroglucose unit) was dissolved in 50 ml of DMF at nitrogen atmosphere. To the above solution, was added sodium hydride (1 eq. of **2**) and stirred for 1.5 h at room temperature. 2.51 g (4.48 mmol, 2 eq. of OH groups in CA) of **2** was added in one portion and the solution was stirred at 65 °C for 24 h. After cooling to room temperature, the mixture was poured into 95 % methanol and the precipitates was collected and dried. Reprecipitation of the resulting solid from DMSO into methanol/water mixture (1:1 v/v) was performed twice, and the final brown powder was dried in a vacuum oven at 40 °C.

**Instrumental Measurements:** Spectroscopic characterizations were performed by using FT-IR (Shimadzu, 300 SE) and 400 MHz $^1$H-NMR (Bruker). Thermal analyses were done by differential scanning calorimetry (DSC, TA Instruments, DSC 2010) and thermogravimmetry analyses (TGA, TA Instruments, TGA 2050). UV/Vis spectra of CA-COSP films (**1**) were obtained by UV/Vis spectrophotometers (Shinco S-2100 and GuidedWave Spectrophotometer with optical fiber probe). The light sources for the photo-induced absorbance change of CA-COSP film (6 μm thick) were an UV lamp (365 nm, 8 μW/cm$^2$, Spectroline, ENF-240C), a Xe lamp (Oriel) attached with a monochromator and a He-Ne laser (Melles Griot, 10 mW, 633 nm).

## RESULTS AND DISCUSSION

Synthesis of CA-COSP is summarized in Scheme 1. The degree of substitution

(DS) of COSP in CA-COSP (1) with respect to the amount of 2 and NaH used was studied by comparing IR and NMR spectra of 1 with those of COSP and CA. The existence of COSP moiety in the resulting polymer could be confirmed from IR spectra. Strong absorption at 953 cm$^{-1}$, a characteristic peak of $C_{spiro}$-O stretching was found when 2 equivalent of 2 (based on OH groups in CA) was used. The substitution of COSP was also confirmed by $^1$H-NMR spectrum. Comparison of peak integration in $^1$H-NMR spectrum revealed that about 45.5 % of OH groups in CA were substituted by COSP. When 1 and 0.5 equivalent of 2 were used, 8.7 and 0.9 % of OH groups were substituted with COSP, respectively.



SCHEME 1. Synthetic scheme of CA-COSP

DSC thermograms of 1 showed that the glass transition temperature was 150.6 °C for CA-COSP of DS=45.5 and increased for those with lower DS of COSP (175.1 and 195.9 °C for DS=8.7 and 0.9, respectively). Initial thermal degradation was found at 239 °C (for DS=45.5) in TGA curve of 1. Those with lower DS of COSP showed higher degradation temperature (>306 °C) than that of DS=45.5.

Film (6 μm thick) of CA-COSP with DS=45.5 was prepared from the solution casting of 1 in DMSO. The color of the CA-COSP film was instantaneously changed from colorless to blue upon exposure to UV light. Such color change could be attributed to the isomerization from a transparent spiropyran form to a colored merocyanine form of COSP[2]. Fig. 1 shows spectral change of the CA-COSP film by UV irradiations (254 and 365 nm, respectively). New absorption band centered at 580 nm was appeared and increased by prolonged excitation with UV light. Absorbance increase by 365 nm excitation was higher than that by 254 nm as compared in Fig. 1(c).

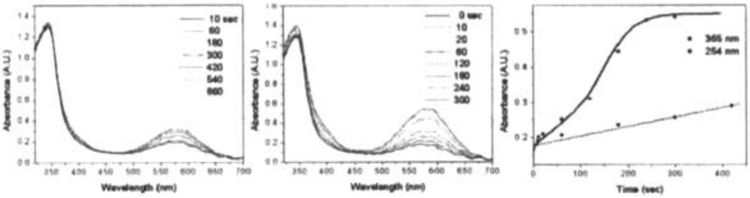


FIGURE 1. UV spectral changes of CA-COSP film: Under irradiation with UV light of (a) 254 nm and (b) 365 nm, and (c) absorbance change at 580 nm against irradiation time.

The colored film of CA-COSP was reversibly bleached to colorless film upon excitation with visible light. Fig. 2 shows absorbance change at 580 nm by visible light (He-Ne laser, 633nm) for the colored CA-COSP film prepared by 365 nm excitation for 1 and 2 min (denoted as 365-1-633 and 365-2-633 in Fig. 2, respectively). Decrease of absorbance was much accelerated by visible light as compared to that by spontaneous dark reaction (denoted as 365-1-dark and 365-2-dark in Fig. 2, respectively). The photochromic bleaching could arise from effective photo-induced conversion of merocyanine to colorless spirobenzopyran form. Such reversible photochromic properties shine light on the application of CA-COSP film into photonic devices.

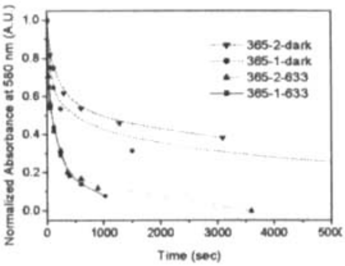


FIGURE 2. Change of absorbance at 580 nm for CA-COSP film against time under various conditions after irradiating with 365 nm light for 1 and 2 min

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