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Short communication

# Synthesis and properties of spiroxazine polymer having photocrosslinkable chalcone moiety

Sung-Hoon Kim[a,*], Chi-Hee Ahn[a], Sam-Rok Keum[b], Kwangnak Koh[c]

[a] *Department of Dyeing and Finishing, Kyungpook National University, Daegu 702-701, South Korea*
[b] *Department of New Material Chemistry, Korea University, Jochiwon, Choongnam 339-700, South Korea*
[c] *College of Pharmacy, Pusan National University, Pusan 609-735, South Korea*

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**Abstract**

New spiroxazine polymer, polymer **9**, containing chalcone moiety has been prepared and its photochromic behaviour has been investigated. This polymer showed effective retardation of decolouration by virtue of photocrosslinking.

*Keywords:* Photochromism; Photocrosslinking; Spiroxazine polymer

## 1. Introduction

Photochromism has attracted much attention recently from the viewpoint of optical applications because of interest in refractive index or absorbance changes through optical extraction. The development of time-resolved or flash spectroscopy and, more recently, the use of laser photophysical means opened new approaches to the study of the excited states and transient species involved in the photoreactivity of photochromic molecules.

In recent years, photochromic and thermochromic spiropyrans and spiroxazines have been receiving considerable attention, due to their potential application in many new technologies, such as data recording and storage, optical switching, displays, and non-linear optics [1,2].

Photohardening of polymers is an area of considerable importance to the paint and printing industries, and the process includes photopolymerization of monofunctional monomers and photocrosslinking of polymers. Photohardening of the polymers is brought about by the formation of polymer networks with the aid of reactions involving photocrosslinkable functional groups. In order to increase the density of the polymer matrix, photocrosslinking can be induced under irradiation of the same light source that is usually utilized for including photochromism.

Among many promising photocrosslinkable groups, a chalcone group has been well studied and can be used in photocrosslinkable side chain polymers. The effect of photocrosslinked chalcone moiety on the stability of photochromism was investigated intensively [3–5]. We report herein the synthesis and photochromic property of spiroxazine polymer containing chalcone unit in the side chain.

## 2. Polymer synthesis

The synthesis of intermediates and monomers were carried out according to the synthetic route outlined by

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* Corresponding author. Tel.: +82 53 950 5641; fax: +82 53 950 6617.
*E-mail address:* shokim@knu.ac.kr (S.-H. Kim).

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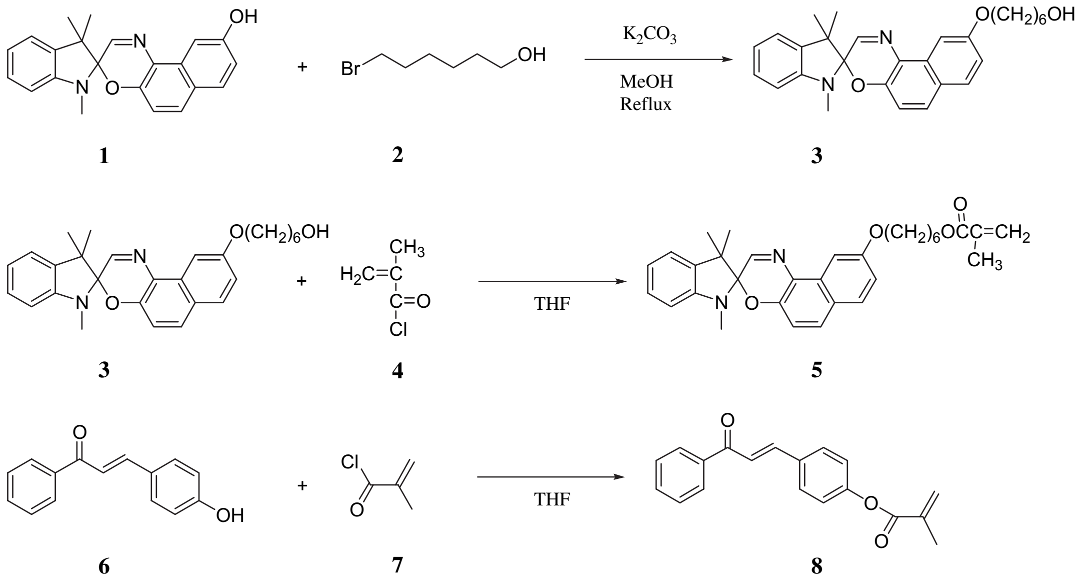
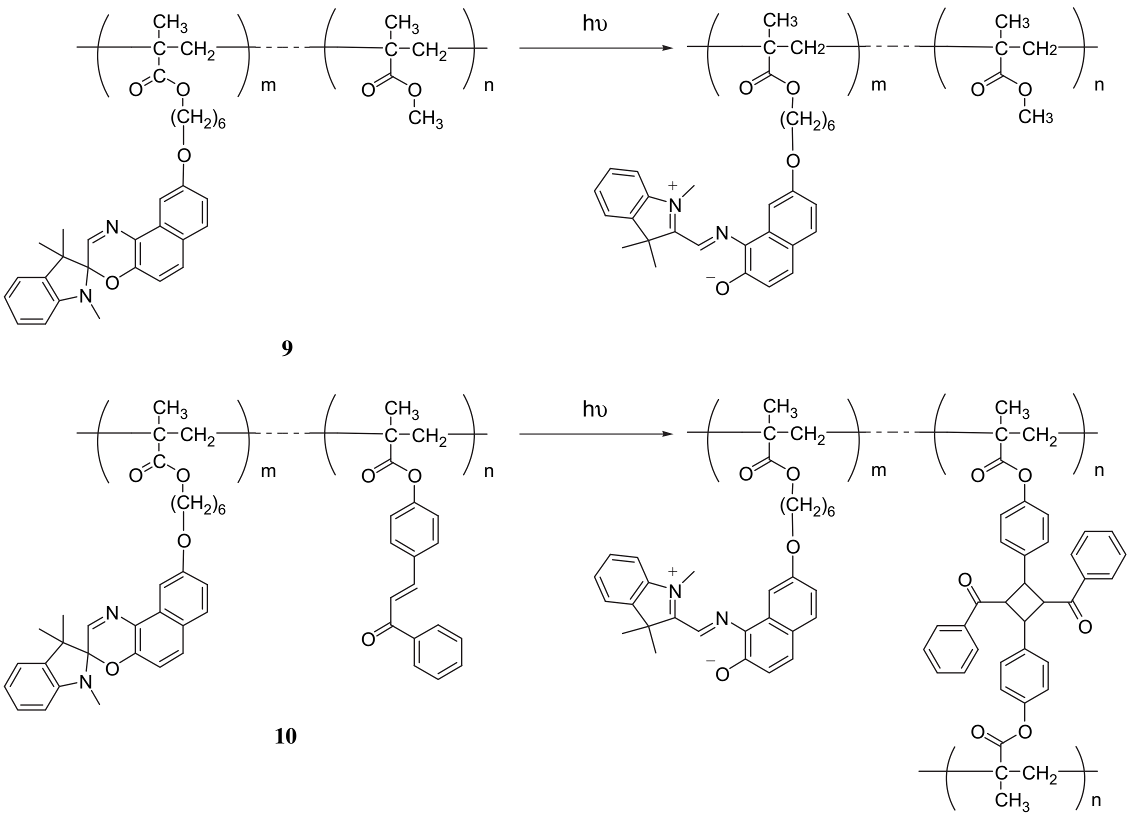


Scheme 1.

Scheme 1. Intermediate **3** and monomers **5** and **8** were prepared according to the literature [6–9]. Chalcone residue was introduced as a pendant group to polymer **10** by copolymerization of monomer **5** with monomer **8**. The copolymerizations were carried out in DMF solution in the presence of AIBN as the initiator. A representative condition is 0.975 mmol of monomer **5**, 0.0975 mmol of monomer **8** and 0.0195 mmol of AIBN. The molecular weights of the resulting polymers **9** and **10** were estimated by gel-permeation chromatography (GPC) to be in the range $M_n = 1.16 \times 10^4 – 1.39 \times 10^4$ and polydispersity of the polymers were in the range



Scheme 2.

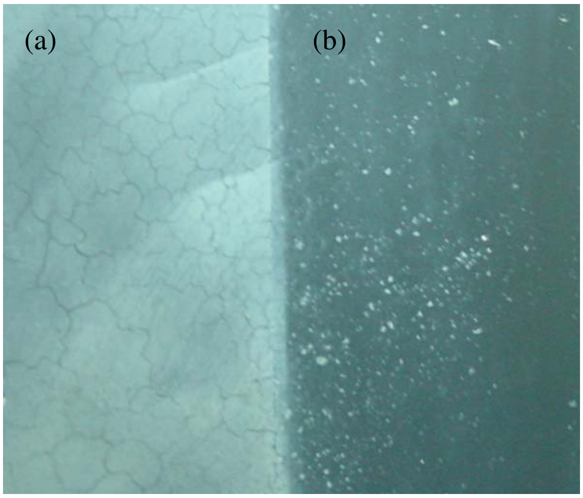


Fig. 1. Polymer **10** exposed and developed in $CHCl_3$: (a) exposed area, (b) unexposed area.

5.53–5.29, respectively. The glass transition temperature ($T_g$) of polymers **9** and **10** are 104 °C and 107 °C, respectively.

## 3. Photochromism

Photochromic molecules are usually embedded in solid matrix for both fundamental and practical studies so that photochromism is affected markedly by the nature of the matrix. In negative resists the photochemistry that occurs on irradiation renders the material less soluble in the developer; the unirradiated parts of the coating are washed away and a negative polymer image of the original pattern remains on the substrate. Photoreactive polymers containing chalcone moiety behave as a negative resist resulting from photocycloaddition. Crosslinks are formed by photoaddition between an excited chalcone group of one chain with a ground state chalcone group belonging to another chain (Scheme 2).

[2+2]Cycloaddition in the ground state of two C=C double bonds is forbidden by orbital symmetry, but it is symmetry allowed if one of the reactants is in the excited state. Polymer **10** is coated on a glass substrate, dried, and exposed to UV radiation pattern; it is then treated with chloroform as a developer (Fig. 1).

The photochromic reaction in question is caused by the reversible heterolytic cleavage of the C(spiro)–O bond under UV irradiation, yielding the coloured form that can return to the colourless form by ring closure under visible light irradiation or in the dark. Newly synthesized copolymers were soluble in THF and could afford a thin solid film by dip-coating onto a glass substrate. Electronic absorption spectra changes of polymers **9** and **10** upon UV irradiation in thin solid film are depicted in Fig. 2.

The visible range absorption increased gradually by UV irradiation which is ascribed to the generation of the open merocyanine form from the closed spiro form. When the samples of polymers **9** and **10** were left in the dark at room temperature after irradiation, the absorbance at 600 nm decreased slowly. Spectra measured after UV irradiation are proportional to each other in the visible region, indicating that only one species was formed. This allowed the absorption to be monitored at $\lambda_{max}$ (600 nm) as a function of time to obtain the thermal colour fading rate ($k$) of the transformation from the open merocyanine form to closed spiro form via a first-order reaction Eq. (1):

$$A_t - A_\infty = A_i \exp(-kt) \quad (1)$$

where $A_i$ is the absorbance at 600 nm, $A_t$ the absorbance at 600 nm at time $t$ after UV irradiation. $A_\infty$ and $k$ refer to the absorbance at 600 nm after 50 s and the first-order colour changing rate constant, respectively. In this thermal colour change process, the kinetic analysis predicts the logarithm of the difference between $A_\infty$ and $A_t$ at time $t$ to be linear with time, the slope giving the decolouration rate constant, $k$. First-order plots

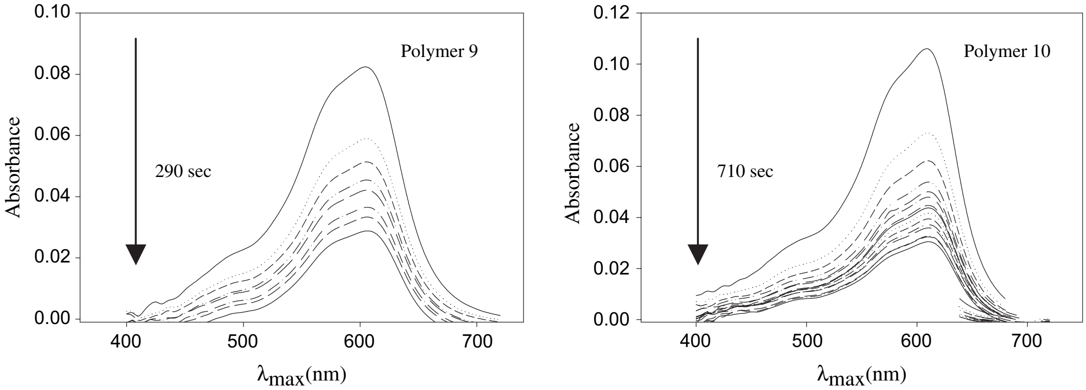


Fig. 2. Visible spectral changes of polymers **9** and **10** upon UV irradiation.

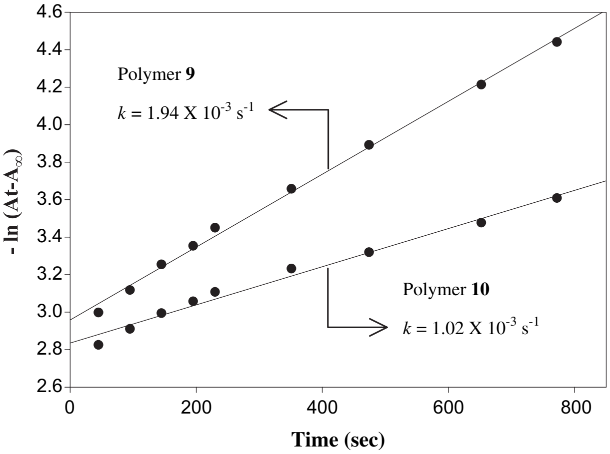


Fig. 3. Plot of $-\ln(A_t - A_\infty)$ as a function of time according to Eq. (1) for the decolouration of polymers **9** and **10**.

according to Eq. (1) for the polymers **9** and **10** are shown in Fig. 3.

The first-order decolouration rate constant of polymer **10** in the thin solid film state was smaller than that of polymer **9** ($k = 1.94 \times 10^{-3}\ s^{-1}$ for polymer **9**, $k = 1.02 \times 10^{-3}\ s^{-1}$ for polymer **10**); which indicates that open-to-close occurs more readily in polymer **9** than in polymer **10**. We believe that the photocrosslink of chalcone moiety can induce steric hindrance during photochromism and it can also retard the rate of photochromic decolouration process.

## Acknowledgements

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