

LIQUID CRYSTALLINE COUMARIN POLYMERS. II: PHOTO-CHEMISTRY OF SIDE-GROUP LIQUID CRYSTALLINE POLYMERS WITH COUMARIN MOIETIES

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Photochemical behaviors of a series of side-group liquid crystalline polymers with coumarin units were investigated by observations of UV-Vis absorption and fluorescence spectra with irradiation of UV light by using polymer films and solutions. By the irradiation of UV light with $\lambda > 300$ nm, photo-dimerization of coumarins was observed by using polymers with or without a substituent of ethoxycarbonyl group or ethoxycarbonylmethyl group at the 3 or 4 position of the coumarin ring. The photo-dimerizations of coumarin units were confirmed by photo-cleavage reactions with the irradiation of a light of 254 nm. It was revealed that the photo-dimerizations were affected by the substituents and/or the length of spacer.

Key words: coumarin, polymers, liquid crystals, photo-dimerization, photo-cleavage

1. INTRODUCTION

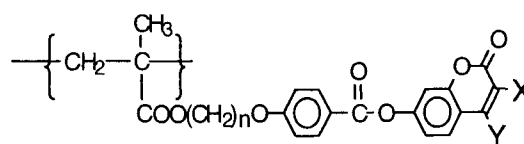
Recently, the study of photo-cross-linking liquid crystalline polymers has generated special attention, because they are useful in facilitating anisotropic networks¹⁾, information storage devices²⁾, etc. Most of the photo-cross-linkable liquid crystalline polymers contain the cinnamate ester group as a photo-reactive center, which undergoes photo-dimerization. On the other hand, it is well known that coumarin or its derivatives can also be photo-dimerized through the [2+2] cyclo-addition with an irradiation of UV light³⁾ and show fluorescence properties. Therefore, the introduction of the coumarin units into liquid crystalline polymer systems will be of great interest. The combination of liquid crystalline properties, photo-reactive properties and fluorescence properties by using coumarin unit would lead a new kind of functional materials.

We have been investigating liquid crystalline coumarin polymers with a tail group such as the ethoxycarbonyl or ethoxycarbonylmethyl group at the 3 or 4 position of the coumarin ring. It was found that the position of the ethoxycarbonyl group at the coumarin ring significantly affected liquid crystalline properties and optical properties⁴⁾. In this paper, we will describe the influence of some factors such as substituents, positions of substituents and length of spacer on the photo-reactions of their polymers, in order to develop new types of photo-sensitive polymers with liquid crystalline properties.

2. EXPERIMENTAL

Concentrations of the polymers in CH_2Cl_2 solutions were 7.5×10^{-5} mol/l. Polymer films were spin-coated from 2 wt-% of CHCl_3 solutions on quartz glass substrate. Photo-reactions were carried out by using a 500 W high pressure mercury lamp with a cut filter to remove light of $\lambda \leq 300$ nm (the energy was about 160 mW/cm² at 365 nm). Photo-cleavages were carried out by using a light of 254 ± 10 nm (0.3 mW/cm²).

3. CHARACTERIZATION OF POLYMERS



- P1, n=6, X=H, Y=H
- P2, n=6, X=H, Y=CH₂COOC₂H₅
- P3, n=6, X=H, Y=COOC₂H₅
- P4, n=6, X=COOC₂H₅, Y=H
- P5, n=0, X=COOC₂H₅, Y=H
- P6, n=2, X=COOC₂H₅, Y=H
- P7, n=11, X=COOC₂H₅, Y=H

Fig. 1 Structures of the polymers

Structures of the polymers for photo-chemical investigations are shown in Fig. 1. The preparation of these polymers was described in our previous paper⁴⁾. The number average molecular weight of P1 was determined as 8800 by gel permeation chromatography. The

number average molecular weights of the other polymers were determined in the range from 38000 to 46000⁴⁾.

Table I Characterization of polymers

Code	Phase behavior /°C	λ_a		λ_f	
P1	g 45 N 74 I	311 ^a	311 ^b	382 ^a	383 ^b
P2	g 47 I	311 ^a	311 ^b	382 ^a	382 ^b
P3	g 40 I	320 ^a	320 ^b	440 ^a	440 ^b
P4	g 46 SmA 187 I	332 ^a	332 ^b	403 ^a	418 ^b
P5	Cr < 250 ^c	332 ^a	332 ^b	403 ^a	418 ^b
P6	g 107 N 146 I	332 ^a	332 ^b	403 ^a	418 ^b
P7	g 21 SmA 195 I	332 ^a	332 ^b	403 ^a	418 ^b

g: glass state; N: nematic phase; I: isotropic state; SmA: smectic A phase; Cr: Crystal state. λ_a : Long-wave absorption maxima. λ_f : Fluorescence emission maxima. a) For solutions. b) For films. c) Decomposition was observed above this temperature by polarized optical microscopy.

Table 1 gives their phase behaviors, long wave absorption maxima arising from the transitions of the coumarin ring and their

emission maxima. The influence of structures on their thermal and optical properties could be seen clearly from this table⁴⁾.

4. PHOTO-CHEMICAL PROPERTIES

Fig. 2 shows the change of UV-Vis spectra of **P1-P4** films with different tail groups by the irradiation of $\lambda > 300$ nm. For all of the polymers, the continuous decrease of their long-wave absorption by the irradiation was observed, which would be due to the consumption of the coumarin unit caused by some photo-reactions. In the cases of **P1** and **P2**, both their long and short wavelength absorbances decreased with the time of photo-irradiation, which is the typical characterization of the photo-dimerization of simple coumarin units. On the other hand, for **P3**, the change of its UV-Vis spectra at the short wavelength was complicated. With the increase of the irradiation time, the absorbance at short wavelength increased then decreased. For **P4**, its absorption band at 270 nm increased with the irradiation, whereas an other absorption band at about 300 nm disappeared soon after the photo-irradiation.

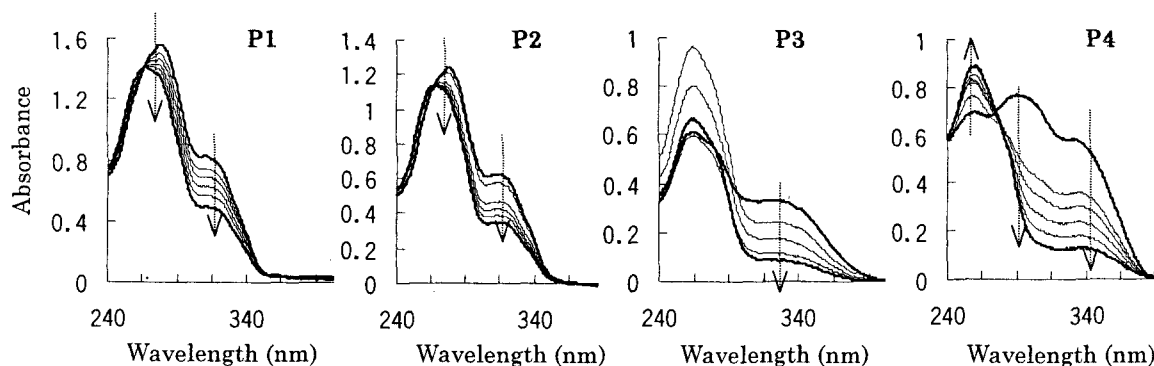


Fig. 2 The change of UV-Vis spectra of **P1-P4** films with the irradiation of $\lambda > 300$ nm. The irradiation time for **P1**, **P2**, and **P4** is 0 min, 2 min, 4 min, 8 min, 16 min, and 32 min, respectively. The irradiation time for **P3** is 0 min, 2 min, 4 min, 8 min, and 16 min, respectively.

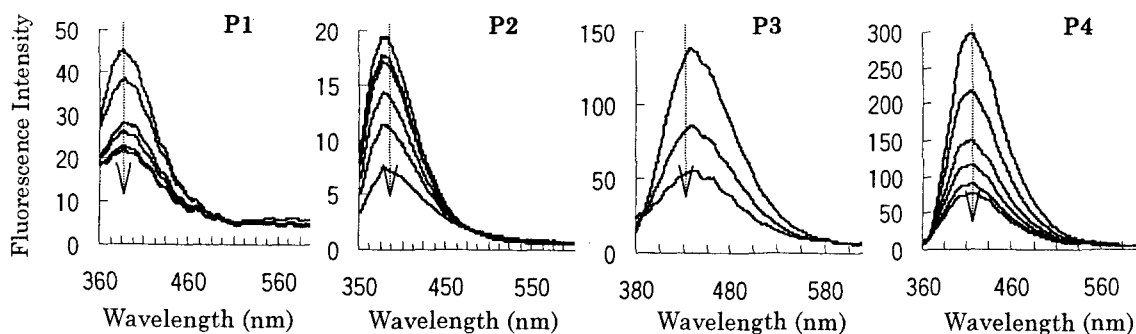


Fig. 3 The change of fluorescence spectra of **P1-P4** films with the irradiation of $\lambda > 300$ nm. The irradiation time for **P1**, **P2**, and **P4** is 0 min, 2 min, 4 min, 8 min, 16 min, and 32 min, respectively. The irradiation time for **P3** is 0 min, 4 min, and 16 min, respectively.

The photo-reactions were also confirmed by the change of fluorescence spectra as shown in Fig. 3. For all of the polymers, the continuous decrease of their fluorescence intensities by the irradiation was observed, which would be due to the decrease of the amount of coumarin unit.

Fig. 4 gives the decay rates of the four polymers in their solutions and films, calculated according to the ratio of their long wave-length absorption intensities after and before photo-irradiation (i.e. A/A_0), respectively. It was observed that, in both solutions and film states, the reaction rates followed the order of $P3 \approx P4 \gg P1 \approx P2$. Each polymer in solution has a faster reaction speed than that in film. The comparison of their decay rates of the four polymers showed that the introduction of $C_2H_5OCOCH_2$ group didn't have obvious influence about the photo-reaction. However, the introduction of an electron-withdrawing group (i.e. C_2H_5OCO group) caused the increase of the rate of photo-reactions. This phenomenon is different from the results of some investigations on the photo-reactions of coumarins, which indicated that the introduction of an electron-withdrawing group decreased the ability of the photo-reactions^{5,6}. Therefore, it is necessary to confirm whether the photo-reactions of $P3$ and $P4$ are photo-dimerizations or not. As

the coumarin units were attached in the side-group of the polymers, the photo-dimerization should cause the cross-linking to afford the insoluble products. All of the polymers became insoluble in chloroform after 20 min photo-irradiation, although they were soluble before irradiation. Solid state ^{13}C NMR spectroscopy of the irradiated sample of $P4$ was measured. A peak at about 55 ppm was observed after 10 h of irradiation, which indicated that the double bond of the coumarin unit was photo-dimerized to give cyclobutane unit in the polymer system. This result was accordance with study of the dimer of its model compound. Further investigation was carried out by the irradiation of photo-reacted polymer films with a light of 254 nm as shown in Fig. 5. For $P1$, $P2$, and $P4$, the recovery of their absorption bands at the long and short wavelength was observed, which showed that the dimer was clove and the coumarin unit was recovered. The recovery of the coumarin absorption identified that the photo-reactions with the irradiation of light over 300 nm were mainly photo-dimerization. For $P3$, only its absorption band at long-wavelength was recovered by the irradiation of 254 nm light. Therefore, we can not exclude the occurrence of some other photo-reactions besides the photo-dimerization of $P3$.

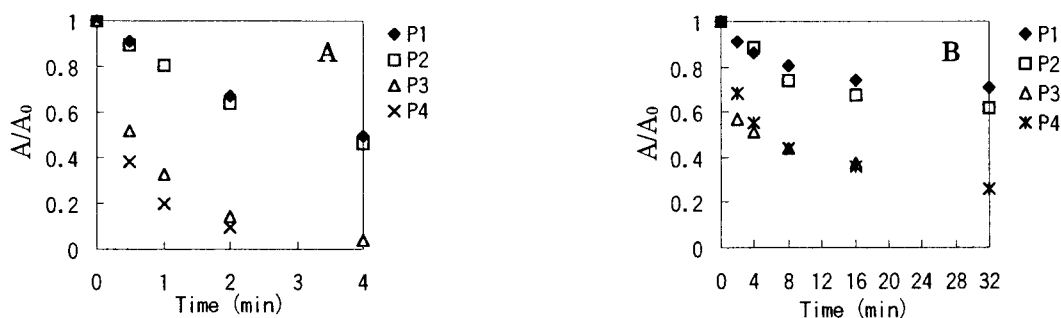


Fig. 4 The decay rates of $P1$ – $P4$ in solutions (figure A) and films (figure B).

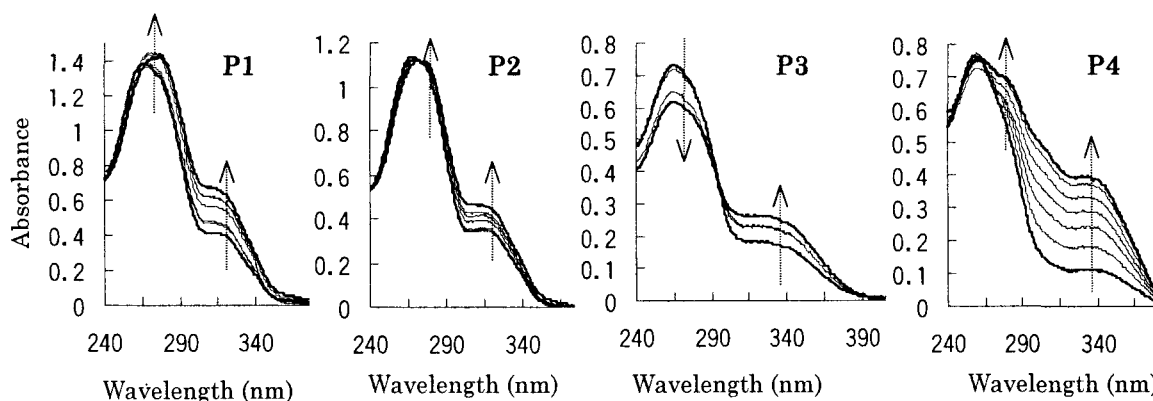


Fig. 5 The change of UV-Vis spectra of the photo-reacted $P1$ – $P4$ films with the irradiation of $\lambda \approx 254$ nm. The irradiation time for $P1$, $P2$, and $P4$ is 0 min, 2 min, 4 min, 8 min, 16 min, 32 min, and 64 min, respectively. The irradiation time for $P3$ is 0 min, 4 min, 8 min, and 16 min, respectively.

We investigated the influence of the length of spacer on their photo-reactions by using P4~P7 with the same tail group. The decay rates calculated according to A/A_0 at their long wavelength absorption bands in solutions and films were shown in Fig. 6. It was observed that the reaction rate of P5 without a spacer was a little slower than those of P4, P6, and P7 in solutions, whereas in film states, the reaction rate of P5 was much slower than those of P4, P6, and P7. The two films of P4 and P7 with a long spacer exhibited nearly similar rates of dimerization. Therefore, the results suggested that a suitable length of spacer was existed for the acceleration of photo-dimerizations in the film states. Probably, a long spacer decreased the glass transition or melting point and ensured the mobility of the side-group in the solid states, which resulted in that the dimerization of the coumarin units occurred easily.

As described above, the photo-reactions with the irradiation by using the light longer than 300 nm caused the cross-linking of the polymers. Therefore, the photo-cross-linking should have some influence on their thermal properties, which could be reflected from the DSC measurements and POM observation of the irradiated polymers films. As an example, Fig. 7 shows the DSC curves of P4 before and after 10 h photo-irradiation. It was found that its clearing point corresponding to the transition from SmA to I phase disappeared caused by the photo-cross-linking. Meanwhile, its typical bâtonnet texture of SmA phase before photo-irradiation could not be observed after photo-irradiation.

5. CONCLUSION

In this paper, the influence of substituents and length of spacer on the photo-reactions of liquid crystalline polymers with coumarin units was investigated. The results showed that the ethoxycarbonyl group of the 3 or 4 position at the coumarin ring had a significant influence on their photo-dimerizations to improve the rates of reactions. It was also found that a long spacer could accelerate the rates of photo-dimerizations in the film states. Furthermore, the liquid crystallinity of these polymers disappeared after the photo-irradiation with the light over 300 nm, which would be due to that the dimer of coumarin unit disturbed the orientation of side-group.

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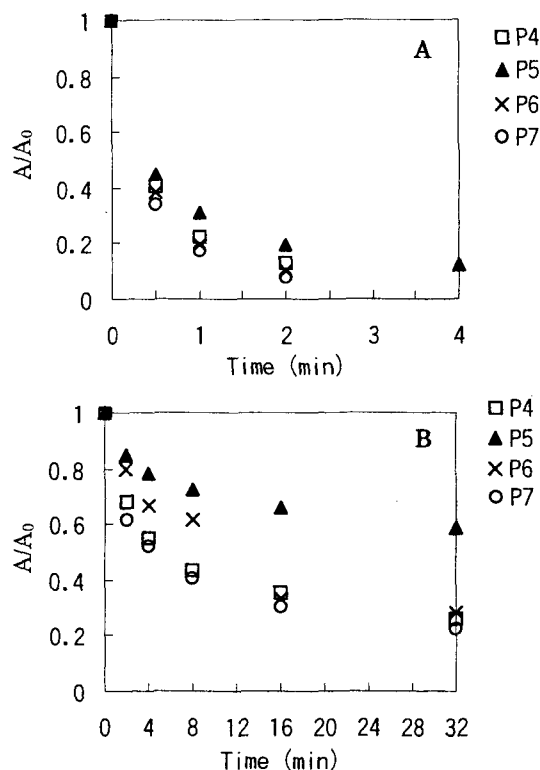


Fig. 6 The decay rates of the polymers of P4~P7 with the same tail group but different length of spacer in solutions (figure A) and films (figure B) with the irradiation of light of $\lambda > 300$ nm.

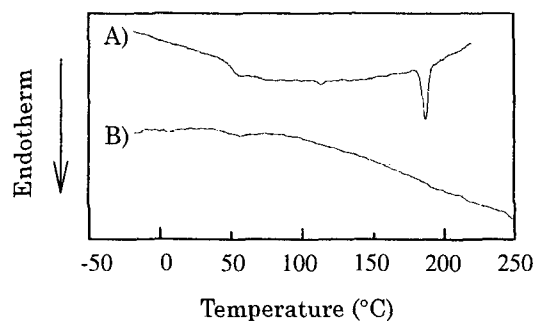


Fig. 7 DSC curves of P4 before (A) and after photo-irradiation (B) by using the light of $\lambda > 300$ nm for 10 h.