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Photoreaction Behaviors of Two Liquid Crystalline Cinnamoyl Compounds with Different Phase in Solution and Mesomorphic States

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A novel nematic liquid crystal compound containing a cinnamoyl moiety (PCPC) and a typically cholesteric liquid crystal cholesteryl cinnamate (CC) were synthesized to explore the mechanism ofcinnamoyl compounds, and the chemical structures of photodimerization were confirmed by Fourier transform infrared spectroscopy and ^{1}H nuclear magnetic resonance spectral analysis. The photoreaction behaviors of these two cinnamoyl compounds in mesomorphic state and solution were investigated, UV-Vis spectral analysis was used to analyze the photoproduct. The results show that the photochemistry of PCPC in nematic state involves both photodimerization and photoisomerization, while CC shows a complex reaction which can be divided into three parts, and this has enabled us to present new data and interpretations regarding the [2+2] photocycloaddition reaction. Additionally, the results of UV-Vis spectral analysis in solutions strongly suggest that UV-Vis spectral analysis can be used to study the kinetic behaviors of cinnamoyl moiety photoreaction.

**Key words:** Cinnamoyl compound, Liquid crystal, Photoreaction behavior

I. INTRODUCTION

The photoreactions of cinnamic acid and its derivatives have attracted a continued interest [1−8]. The photochemistry of cinnamates involves two photoreactions upon irradiation in the ultraviolet-B (UVB) region of the electromagnetic spectrum [9−11]: the reversible E to Z photoisomerization that is favored in the early stages of UV irradiation [12, 13] and the irreversible photodimerization, leading to the formation of a cyclobutane ring (Scheme 1). According to the Woodward-Hoffmann rule, the photoinduced cycloaddition of two olefins to give their cyclobutane formation is allowed photochemically as a [2+2] reaction if the two reactive C=C bonds are within the topochemically stipulated distance (<4.2 Å) and parallel [14]. It is believed that during UV irradiation, photodimerization in solid state is the major photoprocess, while the *trans-cis* photoisomerization is the minor photoprocess [15, 16].

[2+2] photodimerization of cinnamic acid and its derivatives are among the most extensively studied organic solid-state reactions [17, 18], and may have potential applications in optical memory storage systems [19, 20]. A first systematic study on the photodimerization of cinnamic acid and its derivatives has been reported by Schmidt [21]. The topotactic nature of the obtained reaction products has been revealed by various techniques [22−28]. However, the precise solid-state structure of the product(s) of this photoreaction is still not completely understood. What is needed here, and indeed more generally in the field of solid state organic chemistry, is a suitable and straightforward method to follow the dimerization reactions and to confirm their topotactic nature [22].

Besides the applications in solid-state reaction, there have been many works devoted to the studies of the
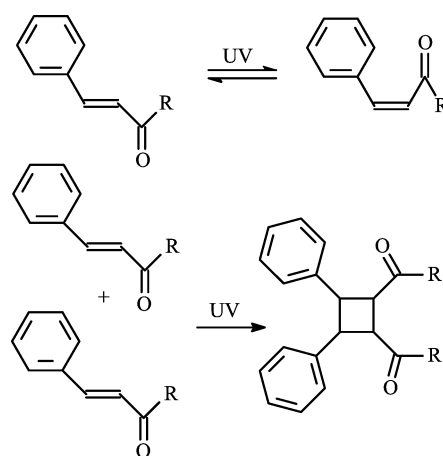
Scheme 1 E to Z photoisomerization and photodimerization of cinnamoyl derivatives.

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preparation and the applications of liquid crystalline polymer composed of cinnamoyl derivatives [29−36]. Because the photoisomerization of the C=C bond usually causes significant variation of the molecular volume due to the configurational change of the molecular structure, the variation is expected to be applied to control the reflected band and color of cholesteric liquid crystals [29−31], which is widely used in irreversible optical storage of electro-optical properties of liquid crystals. Furthermore, a polymer blend with cinnamate side chains could serve as a reversible photoinduced shape memory polymer [32], and cinnamoyl derivatives have been utilized as light-induced crack healing agents to repair fractures formed in the material by irradiation [33]. It is of considerable interest to follow the kinetics of mesomorphic state reactions, to proposed a model for the photodimerisation of trans-cinnamic acid derivatives help the practical application of mesomorphic state reactions, help accurately predicting product and yield.

In this work, a novel nematic crystal compound containing a cinnamoyl moiety and a typically cholesteric liquid crystal cholesteryl cinnamate were synthesized. UV-Vis spectral analysis was used to analyze the photoproducts of the two liquid crystal compounds in photoreaction of various states such as mesomorphic state and solution. The results of solution photoreaction strongly suggest that UV-Vis spectral analysis can be used to study the kinetic behaviors of cinnamoyl moiety photoreaction. We elaborate on differences of photoreaction behaviors of the two compounds in their mesomorphic state, and the relationship between photoreaction behavior and two different mesomorphic states are stated. Results have enabled us to present new data and interpretations regarding the [2+2] photocycloaddition reaction.

II. EXPERIMENTS

A. Materials

Cinnamyl chloride was purchased from Aldrich Chemical Co.. 4-pentyl-cyclohexyl phenol was purchased from Yantai Xianhua Chemical Co., Ltd. cholesteryl cinnamate (CC) was purchased from Beijing Sanshengtengda Technology Co., Ltd. Other reagents and all organic solvents were purchased from Beijing Chemical Reagent Co., China. The solvents used were distilled before use.

B. Sample preparation

The mesomorphic sample of CC at 175 °C and the mesomorphic sample of PCPC at 140 °C were filled into a 25 μm thick indium tin oxide (ITO) coated glass cells by capillarity. The inner surfaces of ITO coated

glass cells were coated with a 3.0% polyvinyl alcohol (PVA) aqueous solution. The deposited film was dried at 80.0 °C for 30.0 min and subsequently rubbed with a textile cloth along one direction. Polyethylene terephthalate (PET) films of 25 mm thickness were used as the cell spacers. The samples were filled into the cells by capillary action.

C. Measurements

FTIR spectra were recorded on a Nicolet 5700 (America) FTIR spectrophotometer. Samples were thoroughly mixed with KBr and pressed into pellet form. ^{1}H NMR spectra were obtained on a Bruker AV600 (Darmstadt, Germany) NMR spectrometer, and chemical shifts were reported in ppm with tetramethylsilane (TMS) as an internal standard. The thermal properties of the polymers were analyzed at a heating rate of (10 °C/min with a NETZSCH DSC 204 F1 differential scanning calorimeter (Germany). The UV-Vis absorption and transmittance spectrum was taken on a Hitachi U-3010 (Japan) UV-Vis spectrophotometer.

D. Irradiation experiment

A 200 W high-pressure mercury lamp (wavelength 365 nm) is used for the irradiation experiments. The intensity of UV light is 50 mW/cm^2 and the radius of spot size is 1.5 cm. The samples were put in the focus of the high-pressure mercury lamp for the irradiation experiments. Then energy E_t is used to stand for irradiation time.

E. Synthesis of novel monomers with cinnamate moieties

Cinnamoyl moiety (PCPC, 4.92 g, 20.0 mmol) and cinnamyl chloride (6.66 g, 40.0 mmol) were dissolved in dry tetrahydrofuran (THF) (50 mL). The reaction mixture was stirred at 60 °C for 6 h. The resulting solution was washed with water and evaporated to dryness. The crude product was recrystallized from THF. The PCPC and CC are shown in Scheme 2. Fourier transform infrared spectroscopy (FTIR) (KBr, $v_{\max}$ in cm^{-1}): 2919, 2848(CH$_2$), 1730(C=O in −C=C−COO−); 1631(C=C), 1506(C−C in Ar). ^{1}H NMR(CDCl$_3$, in ppm): 0.916(t, 3H, CH$_3$, J=7.2), 1.064(dd, 2H, cyclohexyl), 1.278(m, 9H, cyclohexyl-H CH$_2$), 1.436(dd, 2H, cyclohexyl), 1.893(dd, 4H, cyclohexyl), 2.49(t, 1H, cyclohexyl), 6.643(d, 1H, H-CCHPh, J=16.2 Hz), 7.089(d, 2H, O−Ar−H, J=8.4 Hz), 7.236(t, 2H, O−Ar−H, J=16.2 Hz), 7.509(t, 3H, Ph−H), 7.593(s, 2H, Ph−H), 7.867(d, 1H, CHC−HPh, J=15.6 Hz). Phase transition temperature (Fig.1(a)): 137 °C (crystal to nematic), 167 °C (nematic to isotropic liquid).
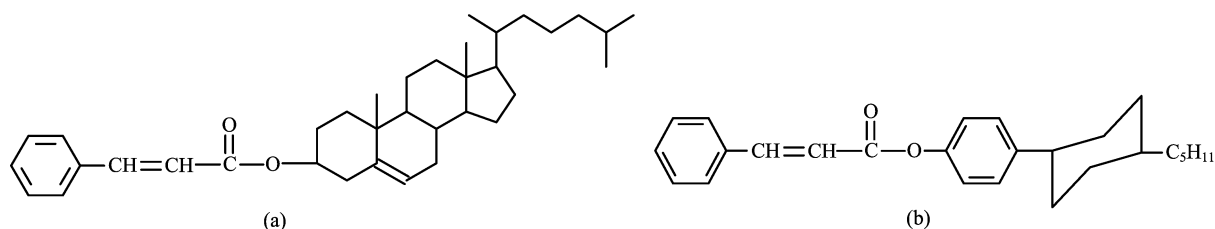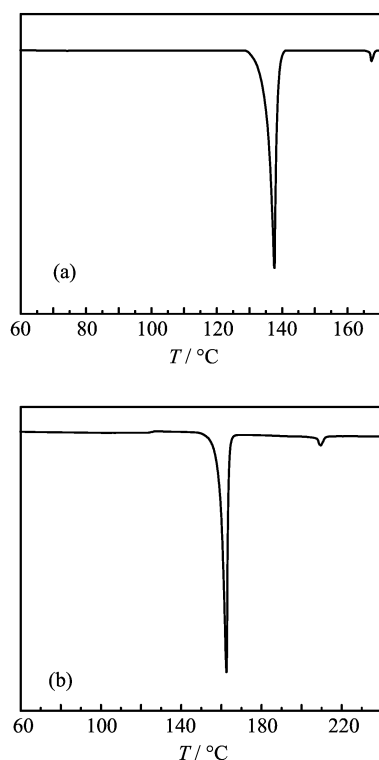
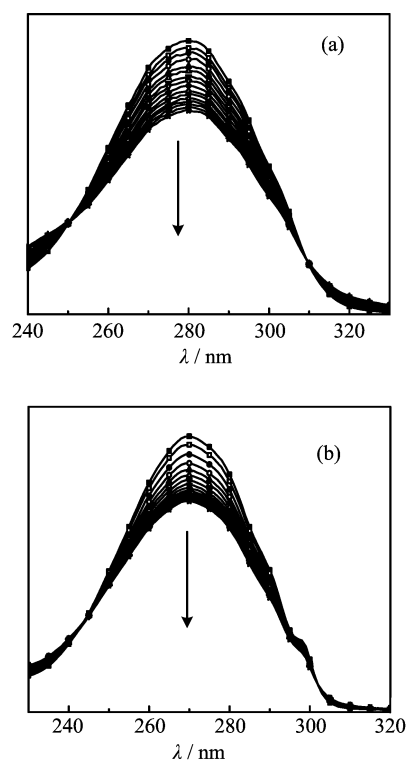Scheme 2 (a) *E*-4-(4-pentyl-cyclohexyl) phenol cinnamate and (b) *E*-cholesteryl cinnamate.

FIG. 1 Differential scanning calorimetry of (a) PCPC, (b) CC.

FIG. 2 The UV-Vis absorption of (a) PCPC and (b) CC after irradiation in solution at different E_t of 0.00, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75 J/cm^2 (up to down in arrow direction).

CC was synthesized according to the method reported in Ref.[37]. FTIR (KBr, $v_{\max}$ in cm^{-1}): 2945, 2847(CH$_2$), 1713(C=O in $-$C=C$-$COO$-$); 1637(C=C), 1496(C$-$C in Ar). Phase transition temperature (Fig.1(b)): 162 °C (crystal to cholesteryl), 209 °C (cholesteryl to isotropic liquid).

III. RESULTS AND DISCUSSION

A. Photoreactions of cinnamates in dilute solution

The UV-Vis absorption spectrum of PCPC in THF at a concentration of 0.02 g/L and the UV-Vis absorption spectrum of CC in *n*-hexane at a concentration of 0.03 g/L upon UV light irradiation at different E_t are shown in Fig.2. Both the maximal absorbencies is the contribution of the cinnamate unit [38, 39]. It can

be seen that the intensity of the absorption band apparently decreases with an increase in irradiation time. The change of UV-Vis absorption spectra is a convenient method to investigate the photoreaction of cinnamoyl moiety [15, 16]. It allows an estimation of photoproduct distribution. Firstly, the cinnamates is exposed and the absorbance after exposure is recorded. Secondly, the exposed compounds, which contains *E* isomer, *Z* isomer and photodimer, are analyzed to obtain concentration of photoproduct by high speed liquid chromatography (HPLC). Then, we can work out these molar extinction coefficient. The equation is:

$$A = \varepsilon_E[E] + \varepsilon_Z[Z] + \varepsilon_D[D] \qquad (1)$$

where A is the absorbencies after photoreaction, ε_E, ε_Z, ε_D are the molar extinction coefficients of the E/Z iso-

TABLE I *E*-cinnamates as low-mass model compounds by spectral analysis.

Substituent	λ_{max}[a]/nm	λ_{iso}[b]/nm	$\varepsilon/(10^4 L/(mol\ cm))$	
			E	*Z*
PCPC	280	251	3.25	1.67
CC	272	243	2.5	1.24

[a] Wavelength at the absorption maximum of *E*-isomer.
[b] Wavelength at an isosbestic point.
[c] Absorption coefficients of *E* and *Z* isomers at λ_{max} of the corresponding *E* isomer, respectively. The molar extinction coefficient of the *Z* isomer of cinnamates was calculated by means of HPLC analysis.

mer, photodimer, and $[E]$, $[Z]$, $[D]$ are the concentration of the E/Z isomer, photodimer. Then using absorbance at the maximal wavelength and an isosbestic point of the UV-Vis spectra, the fraction of photoproducts can be calculated according to the following equations:

$$f_E = \frac{\varepsilon_E}{\varepsilon_E - \varepsilon_Z} \left(\frac{A}{A^0} - \frac{\varepsilon_Z}{\varepsilon_E} \frac{A_{iso}}{A_{iso}^0} \right) \quad (2)$$

$$f_Z = \frac{\varepsilon_E}{\varepsilon_E - \varepsilon_Z} \left(\frac{A_{iso}}{A_{iso}^0} - \frac{A}{A^0} \right) \quad (3)$$

$$f_{dimer} = 1 - \frac{A_{iso}}{A_{iso}^0} \quad (4)$$

where A, A_{iso} are the absorbencies during photoreaction at the maximal wavelength of an isosbestic point; A^0, A_{iso}^0 are the corresponding absorbencies before irradiation; and ε_E, ε_Z are the molar extinction coefficients of the E/Z isomer. These data for spectral analysis are shown in Table I. The photoproduct distributions are summarized in Fig.3.

B. Kinetics of cinnamates in dilute solution

Because the photochemistry of cinnamates in dilute solution involves only one photoreaction upon irradiation in the UVB region of the electromagnetic spectrum, the reversible E to Z photoisomerization [40, 41], it is easy to test whether UV-Vis spectral analysis is suitable to study the kinetic behaviors of cinnamoyl moiety photoreaction. This photoreaction (Scheme 3) is a typical opposite reaction. We suppose that it is a first order opposite reaction, so the relationship between reaction time and photoproduct concentration can be calculated according to the following equation:

$$t = \ln \frac{c_{A,0} - c_{A,e}}{K_1 + K_{-1}} - \ln \frac{c_A - c_{A,e}}{K_1 + K_{-1}} \quad (5)$$

where t is the reaction time, $c_{A,0}$ is the initial concentration of E isomer, $c_{A,e}$ is the equilibrium concentration of E isomer, c_A is the concentration when the time is
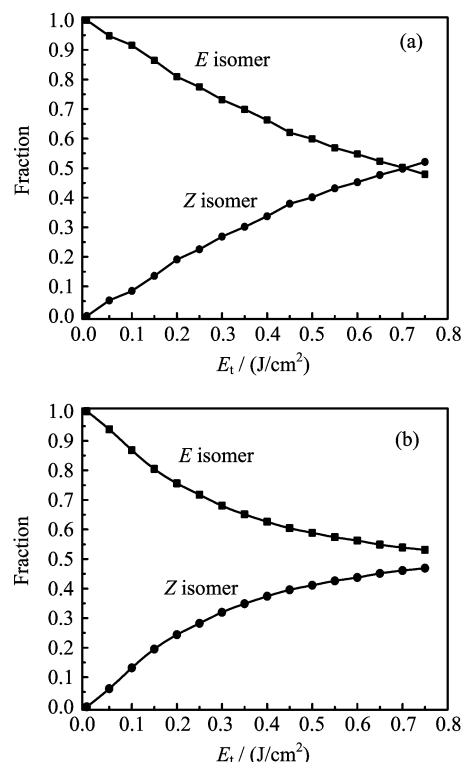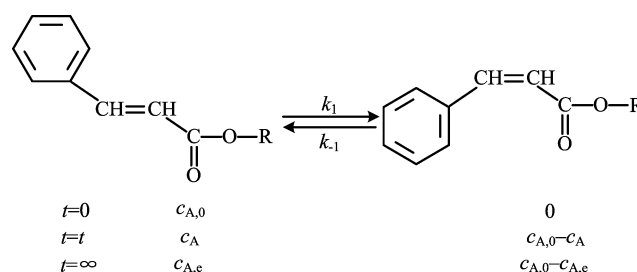
FIG. 3 The photoproduct distributions of (a) PCPC and (b) CC after irradiation different at E_t in solution.

Scheme 3 The kinetic behaviors of cinnamoyl moiety photoreaction.

t, K_1 is the reaction rate of E to Z photoisomerization and K_{-1} is the reaction rate of Z to E photoisomerization. Non-linear curve fit is used and the equation is:

$$y = a - b\ln(x + c) \quad (6)$$

$$a = \ln \frac{c_{A,0} - c_{A,e}}{K_1 + K_{-1}} \quad (7)$$

$$b = \frac{1}{K_1 + K_{-1}} \quad (8)$$

obviously, in Eq.(6), y is t. Figure 4 gives the plots of time versus the concentration of E isomer. Then Eq.(5) is used to curve fit iterated 100 times. It shows an excellent fit to first order (PCPC: $R^2=0.9991$, CC: $R^2=0.9996$). Besides R^2, it is another proof (Table II)
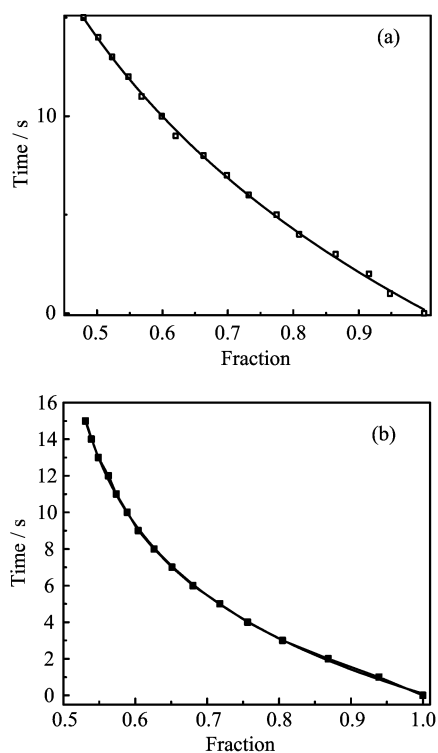
FIG. 4 Time versus the fraction of E isomer after irradiation in solution and curve fit iterated 100 times. (a) PCPC and (b) CC.

FIG. 5 The UV-Vis absorption of (a) PCPC and (b) CC after irradiation in solid state at different E_t.

TABLE II Comparisons between $c_{A,e}$ worked out through a, b and $c_{A,e}$ obtained for c in Eqs. (6)−(8).

Compound	$c_{A,e}$/(mg/L)	
	Through a, b	For c
PCPC	1.74	1.85
CC	4.78	4.86

TABLE III Kinetic constants of the photoisomerization in dilute solution.

Compound	K_1/s^{-1}	K_{-1}/s^{-1}	$c_{A,e}/c_{A,0}$
PCPC	0.0560	0.0127	0.185
CC	0.0867	0.0763	0.486

showing the excellent fit to first order that when we obtain a and b by curve fit, we can work out $c_{A,e}$, and we compare $c_{A,e}$ to c which is $c_{A,e}$ obtained by curve fit. Table III shows the kinetic constants of these photoreactions.

C. Photoreactions of cinnamates in mesomorphic state

The solid samples after irradiation are dissolved in corresponding solvents. The UV-Vis absorption spectrum of PCPC in THF at a concentration of 0.02 g/L and the UV-Vis absorption spectrum of CC in n-hexane at a concentration of 0.03 g/L upon UV light irradiation at different E_t is shown in Fig.5. The photoproduct distributions are summarized in Fig.6. Both of the compounds photoreaction in solid state only involves irreversible photodimerization which we think is due to the steric hindrance of the regular crystal structure. Because of the regular crystal structure, there are not
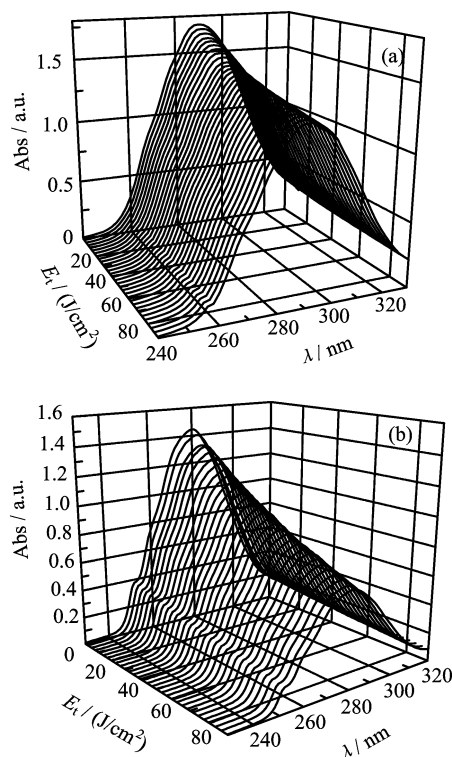
enough space for the reverting.

As mentioned above, the irradiating temperature of CC was 175 °C and the irradiating temperature of PCPC was 140 °C, both of which lie in the mesomorphic state. The samples after irradiation are dissolved in corresponding solvents. The UV-Vis absorption spectrum of PCPC in THF at a concentration of 0.02 g/L and the UV-Vis absorption spectrum of CC in n-hexane at a concentration of 0.03 g/L upon UV light irradiation at different time is shown in Fig.7. The photoproduct distributions are summarized in Fig.8. CC shows a complex reaction which can be divided into three parts as shown in Fig.8(b). At the first part, the photoreaction only involves irreversible photodimerization and the rate of photoreaction is slow. Owing to the steric hindrance of the cholesteric structure, there is no photoisomerization and the average distance between each layer of cholesteric state is beyond 4.2 Å, so few molecules can react with each other. At the second part, the rate of photoreaction becomes fast con-
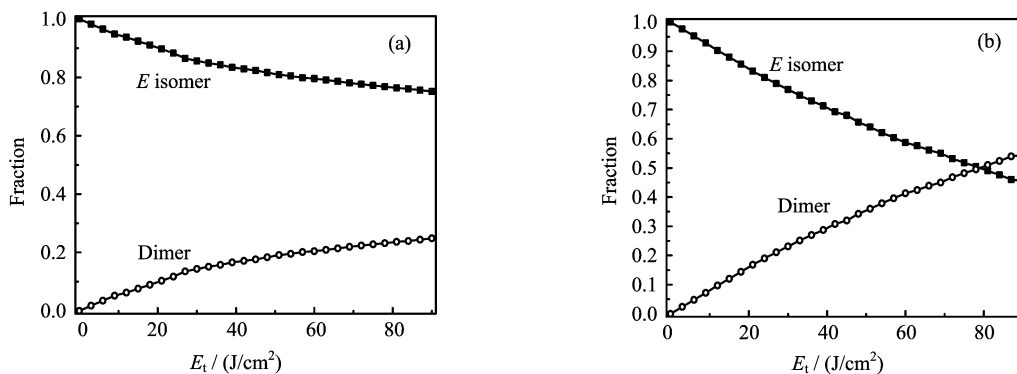
FIG. 6 The photoproduct distributions of (a) PCPC and (b) CC after irradiation in solid state.
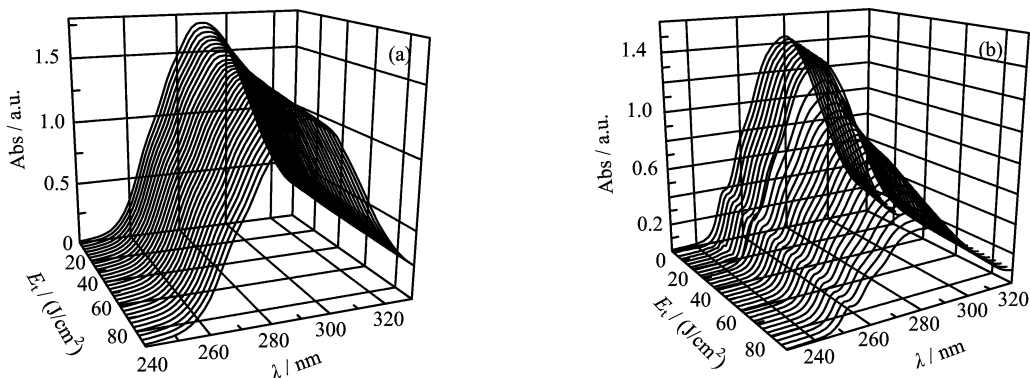

FIG. 7 The UV-Vis absorption of (a) PCPC and (b) CC after irradiation in mesomorphic state at different E_t.
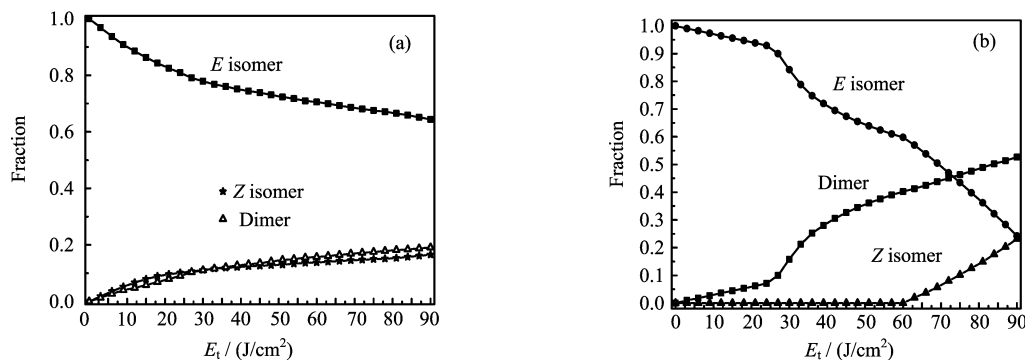

FIG. 8 The photoproduct distributions of (a) PCPC and (b) CC after irradiation in mesomorphic state.

spicuously. The reason for this may be that with the UV irradiation and photodimerization, the average distance between each layer of cholesteric state becomes smaller than 4.2 Å, and the number of photo-reactivity molecules becomes larger. At the third part, it involves two photoreactions, photodimerization, and photoisomerization. It is likely that with the photodimerization, cholesteric structure is destroyed, so the steric hindrance does not exist. PCPC shows a simple reaction as shown in Fig.8(a) compared with photochemistry of CC. It involves both photodimerization and photoisomerization. The reason may be that PCPC is in ne-

matic state and the mesomorphic structure is not as regular as CC in cholesteric state.

IV. CONCLUSION

In this work, a novel nematic crystal compound (PCPC) and a typically cholesteric liquid crystal (CC) were synthesized. The behaviors of two cinnamoyl moiety liquid crystal compounds in photoreaction of various states such as mesomorphic state and solution were studied by UV-Vis spectral analysis. The results of

solution photoreactions strongly suggest that UV-Vis spectral analysis can be used to study the kinetic behaviors of cinnamoyl moiety photoreaction and the kinetics fit to first order excellently. The photochemistry of PCPC in nematic state involves both photodimerization and photoisomerization, while CC shows a complex reaction which can be divided into three parts. These investigations have enabled us to present new data and interpretations regarding the [2+2] photocycloaddition reaction. What's more, it can also be used to analyze the photoreaction of the C=C bond which is expected to be applied to control the reflected band and color of cholesteric liquid crystals.

V. ACKNOWLEDGMENT

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