

Kinetic Analysis of Solid-State Photodimerization Reaction of Photosensitive Monomers and a Polymer with Cinnamoyl Moieties

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ABSTRACT: This work focused on the different kinetic behaviors in photodimerization between a low-molecular-weight molecule and a macromolecule, and the relationship between photodimerization and photo free radical polymerization. We have synthesized two monomers, one (M_1) containing a cinnamoyl moiety and another (M_2) containing both a cinnamoyl moiety and an acrylate moiety. Their chemical structures were confirmed by FTIR and $^1\text{H-NMR}$ spectral analysis. Polymer (P_2) was obtained by free radical polymerization of acrylate moieties of M_2 . Real-time FTIR (RT-FTIR) was used to analyze the kinetic effects of photoreaction. The results strongly suggest that cinnamoyl moieties did not undergo free radical polymerization under exposure of ultraviolet (UV) light. Addition-

ally, the photodimerization of M_1 and P_2 has been confirmed by RT-FTIR spectra, UV absorption, and transmittance spectra; and photodimerization of M_1 was also confirmed by solid-state NMR spectra. The results show that this photoreaction of M_1 is much faster than that of M_2 and P_2 . Wide angle X-ray diffraction patterns have demonstrated their different molecular arrangements, which may be responsible for the difference in photodimerization reaction. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3569–3580, 2010

Key words: photochemistry; photodimerization; photopolymerization; solid-state reaction; cinnamic acid; kinetics

INTRODUCTION

Trans-cinnamic acid and its derivatives could undergo both reversible E–Z photoisomerization and irreversible photodimerization in the crystalline states (Scheme 1).¹ The crystalline-state photodimerizations of cinnamic acid to truxillic acid have been studied in detail by X-ray diffraction (XRD),^{2,3} atomic force microscopy,^{4,5} vibrational spectroscopy,^{6–8} and solid-state NMR.^{2,9} In 1964, to demonstrate the reaction behavior of cinnamic acid crystals, Schmidt and coworkers established the topochemical principle in which the reaction tends to occur with a minimum of atomic and molecular motion, and the solid-state packing of reactants ultimately determines the resulting products including their stereochemistry.¹⁰

As an important method for preparation and modification of polymers,^{11–15} the photodimerization of *trans*-cinnamic acid and its derivatives has been of continued interest since its initial reports. Polymers

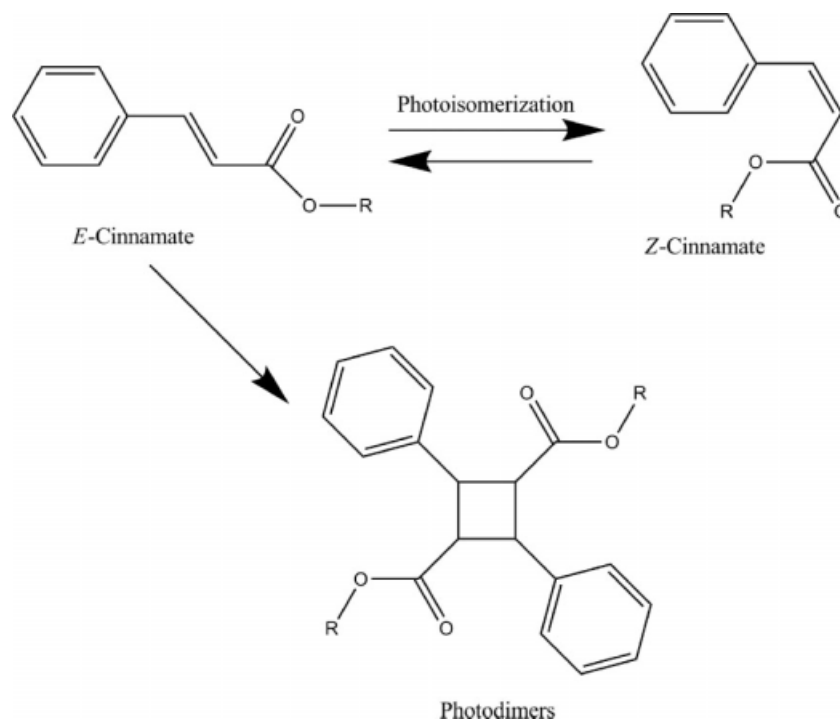
with cinnamoyl moieties have versatile potential applications including negative photoresist,¹⁶ holographic recording,¹⁷ photo-induced layer,^{18,19} and liquid crystalline polymers.^{20–23} Additionally, there is another study suggesting that a polymer blend with cinnamate side chains could serve as a reversible photoinduced shape memory material.²⁴

According to topochemistry, the efficiency of the photodimerization was strongly dependent on the structure of crystal forms²⁰; and the photodimerization seems unfavorable to polymers, which when incorporating with cinnamoyl side chains are spatially isotropic, and may undergo random crosslinking reactions by photoaddition.^{14,19} However, previous literatures have reported that photodimerization is the major photoprocess in films of poly(vinyl cinnamate) and its derivatives^{13,25–28} and occurs both inter- and intramolecularly.¹⁵

In this article, two novel monomers (M_1 and M_2) and a polymer (P_2) were synthesized of which molecular structures could be divided into two parts: the rigid one, helping the formation of crystal, and the flexible one, tending to arrange randomly. We elaborate on differences of the kinetics of photodimerization and molecular arrangement between low-molecular-weight molecules (M_1 and M_2) and macromolecule (P_2) and also state the relationship between photoreaction of acrylate moieties and

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Scheme 1 The photochemical reactions, E-Z photoisomerization, and (2 + 2) photodimerization of cinnamoyl derivatives.

cinnamoyl moieties of M_2 . Moreover, real-time FTIR (RT-FTIR), which permits *in situ* monitoring of the chemical processes via mimicking the disappearance of the characteristic bands of the reactive monomer, was utilized to monitor the change of C=C under the exposure of unpolarized ultraviolet (UV) light.

EXPERIMENTAL

Materials

Methyl 4-hydroxycinnamate (98%) was purchased from Wuhan Yuancheng Technology Development. 1-Bromohexane (98%) and 6-chloro-1-hexanol (98%) were purchased from Nankai University Fine Chemical Laboratories and, *p*-hydroxybenzoic acid (98%) was purchased from Zouping Mingxing Chemical. *N,N'*-dicyclohexylcarbodiimide (DCC, 99%) and 4-dimethylaminopyridine (DMAP, 98%) were purchased from Beijing Sanshengtengda Technology. Other reagents and all organic solvents were purchased from Beijing Chemical Reagent (China). The solvents used were either of analytical grade or bulk solvents distilled before use. 2,2'-Azobisisobutyronitrile (AIBN) was freshly recrystallized from methanol.

Synthesis of monomers (Scheme 2)

Synthetic routes for the target monomers are shown in Scheme 2. Compounds 1, 2, and 3 were synthesized

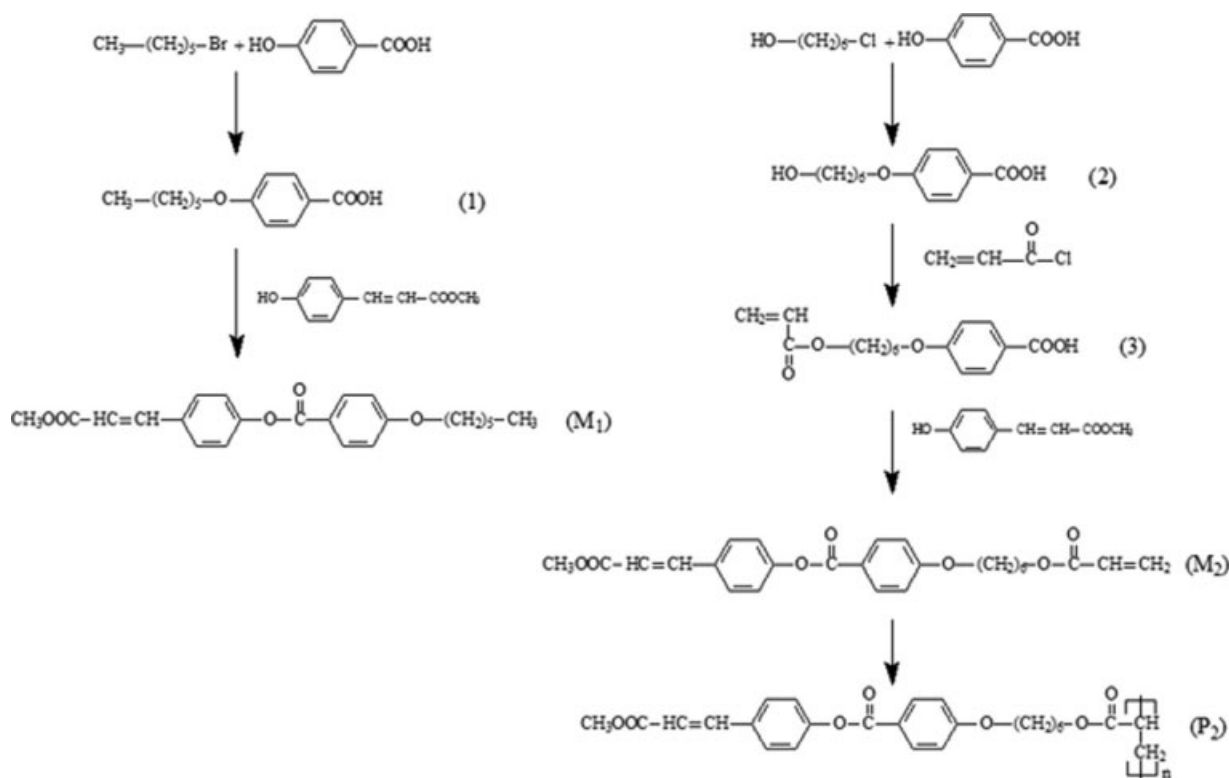
according to procedures similar to those described in the literature.^{29–32}

4-(Hexyloxy)benzoic acid (1)

Yield: 13.8 g (50%). FTIR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 2935, 2861 cm^{-1} (CH_2); 1729 cm^{-1} (C=O in Ar-COO-); 1604, 1511 cm^{-1} (C-C in Ar); 1262, 1206 cm^{-1} (COC). $^1\text{H-NMR}$ (CDCl_3 , δ in ppm): 0.89–0.91 (t, 3H, CH_3 , $J = 6.6$), 1.33–1.80 (m, 8H, CH_2), 4.00–4.02 (t, 2H, CH_2OPh , $J = 6.31$ Hz), 6.91–6.93 (d, 2H, Ar-H, $J = 8.42$ Hz), 8.04–8.06 (d, 2H, Ar-H, $J = 8.41$ Hz), 12.56 (s, 1H, COOH).

(E)-4-(3-methoxy-3-oxoprop-1-enyl)phenyl 4-(hexyloxy)benzoate (M_1)

4-(Hexyloxy) benzoic acid (3.51 g, 15.0 mmol) and methyl 4-hydroxycinnamate (2.22 g, 12.5 mmol) were dissolved in dry CH_2Cl_2 (50 mL) at 30°C. *N,N'*-Dicyclohexylcarbodiimide (DCC; 4.64 g, 22.5 mmol) and 4-DMAP (0.27 g, 2.3 mmol) were dissolved in methylene dichloride (30 mL) and then added to the solution. The reaction mixture was stirred for 2 days at 30°C. A solid, *N,N'*-dicyclohexyl urea, was precipitated and filtered off. The resulting solution was washed with water, dried with anhydrous MgSO_4 , and evaporated to dryness. The crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 1 : 5). Yield: 3.73 g (75%). $T_m = 109^\circ\text{C}$. FTIR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 2932, 2859 cm^{-1}

Scheme 2 Synthetic routes of M_1 , M_2 , and P_2 .

(CH_2); 1730 cm^{-1} ($\text{C}=\text{O}$ in $\text{Ar}-\text{COO}-$); 1710 cm^{-1} ($\text{C}=\text{O}$ in $-\text{C}=\text{C}-\text{COO}-$); 1637 cm^{-1} ($\text{C}=\text{C}$); 1604 , 1512 cm^{-1} ($\text{C}-\text{C}$ in Ar); 1259 , 1208 cm^{-1} (COC). $^1\text{H-NMR}$ (CDCl_3 , δ in ppm): 0.89 – 0.91 (t, 3H, CH_3 , $J = 6.3$), 1.34 – 1.82 (m, 8H, CH_2), 3.80 (s, 3H, CH_3O), 4.02 – 4.04 (t, 2H, CH_2OPh , $J = 6.31$ Hz), 6.91 – 6.93 (d, 2H, $\text{Ar}-\text{H}$, $J = 8.42$ Hz), 8.04 – 8.06 (d, 2H, $\text{Ar}-\text{H}$, $J = 8.41$ Hz), 12.56 (s, 1H, COOH), 6.40 – 6.42 (d, 1H, $\text{CH}=\text{CH}$, $J = 16.2$ Hz), 6.95 – 6.97 (d, 2H, $\text{Ar}-\text{H}$, $J = 8.4$ Hz), 7.22 – 7.25 (t, 2H, $\text{Ar}-\text{H}$, $J = 8.1$ Hz), 7.57 – 7.58 (d, 2H, $\text{Ar}-\text{H}$, $J = 8.4$ Hz), 7.68 – 7.70 (d, 1H, $\text{CH}=\text{CH}$, $J = 16.2$ Hz), 8.11 – 8.13 (d, 2H, $\text{Ar}-\text{H}$, $J = 8.4$ Hz).

4-(6-Hydroxyhexyloxy)benzoic acid (2)

Yield: 18.5 g (62%). $T_m = 137$ – 138°C . FTIR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 3337 cm^{-1} (OH); 2947 , 2861 cm^{-1} (CH_2); 1670 cm^{-1} ($\text{C}=\text{O}$ in $\text{Ar}-\text{COO}-$); 1603 , 1511 cm^{-1} ($\text{C}-\text{C}$ in Ar); 1283 , 1254 cm^{-1} (COC); 2639 , 2532 (COOH). $^1\text{H-NMR}$ ($\text{DMSO}-d_6$, δ in ppm): 1.35 – 1.74 (m, 8H, CH_2), 2.51 (s, 1H, OH), 3.39 – 3.41 (t, 2H, OCH_2CH_2 , $J = 6.01$ Hz), 4.03 – 4.05 (t, 2H, CH_2OPh , $J = 6.03$ Hz), 6.99 – 7.01 (d, 2H, $\text{Ar}-\text{H}$, $J = 8.42$ Hz), 7.87 – 7.89 (t, 2H, $\text{Ar}-\text{H}$, $J = 8.41$ Hz), 12.56 (s, 1H, COOH).

4-(6-Acryloyloxyhexyloxy)benzoic acid (3)

Yield: 4.8 g (72%). FTIR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 2937 , 2856 cm^{-1} (CH_2); 1728 cm^{-1} ($\text{C}=\text{O}$ in $-\text{C}=\text{C}-\text{COO}-$);

1688 cm^{-1} ($\text{C}=\text{O}$ in $\text{Ar}-\text{COO}-$); 1631 cm^{-1} ($\text{C}=\text{C}$); 1606 , 1514 cm^{-1} ($\text{C}-\text{C}$ in Ar); 1254 , 1197 cm^{-1} (COC); 2673 , 2564 (COOH). $^1\text{H-NMR}$ (CDCl_3 , δ in ppm): 1.46 – 1.84 (m, 8H, CH_2), 4.02 – 4.04 (t, 2H, CH_2OPh , $J = 6.31$ Hz), 4.16 – 4.19 (t, 2H, COOCH_2 , $J = 6.62$ Hz), 5.81 – 5.83 (d, 1H, $\text{CH}_2=\text{CH}$, $J = 10.82$ Hz), 6.10 – 6.15 (dd, 1H, $\text{CH}_2=\text{CH}$, $J = 10.38$ Hz), 6.39 – 6.42 (d, 1H, $\text{CH}_2=\text{CH}$, $J = 17.4$ Hz), 6.92 – 6.93 (d, 2H, $\text{Ar}-\text{H}$, $J = 8.42$ Hz), 8.05 – 8.06 (d, 2H, $\text{Ar}-\text{H}$, $J = 8.41$ Hz).

(E)-4-(3-methoxy-3-oxoprop-1-enyl)phenyl 4-(6-(acryloyloxy)hexyloxy)benzoate (M_2)

4-(6-Acryloyloxyhexyloxy) benzoic acid (4.47 g, 15.0 mmol) and methyl 4-hydroxycinnamate (2.22 g, 12.5 mmol) were dissolved in dry methylene dichloride (50 mL) at 30°C . N,N' -DCC (4.64 g, 22.5 mmol) and 4-DMAP (0.27 g, 2.3 mmol) were dissolved in CH_2Cl_2 (30 mL) and then added to the solution. The reaction mixture was stirred for 2 days at 30°C . A solid, N,N' -dicyclohexyl urea, was precipitated and filtered off. The resulting solution was washed with water, dried with anhydrous MgSO_4 , and evaporated to dryness. The crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 1 : 5). Yield: 4.2 g (62%). $T_m = 71.8^\circ\text{C}$. FTIR (KBr, $\nu_{\text{max}}/\text{cm}^{-1}$): 2946 , 2869 cm^{-1} (CH_2); 1728 cm^{-1} ($\text{C}=\text{O}$ in $\text{Ar}-\text{COO}-$); 1637 cm^{-1} ($\text{C}=\text{C}$); 1604 , 1509 cm^{-1} ($\text{C}-\text{C}$ in Ar); 1264 , 1201 cm^{-1} (COC).

$^1\text{H-NMR}$ (CDCl_3 , δ in ppm): 1.46–1.83 (m, 8H, CH_2), 3.80 (s, 3H, CH_3O), 4.03–4.04 (t, 2H, CH_2OPh , $J = 6.01$ Hz), 4.16–4.18 (t, 2H, COOCH_2 , $J = 6.65$ Hz), 5.80–5.82 (d, 1H, $\text{CH}_2=\text{CH}$, $J = 10.22$ Hz), 6.09–6.14 (dd, 1H, $\text{CH}_2=\text{CH}$, $J = 10.38$ Hz), 6.38–6.40 (d, 1H, $\text{CH}_2=\text{CH}$, $J = 9.65$ Hz), 6.41–6.42 (d, 1H, $\text{CH}=\text{CH}$, $J = 8.46$ Hz), 6.95–6.96 (d, 2H, Ar–H, $J = 8.48$ Hz), 7.22–7.25 (t, 2H, Ar–H, $J = 7.81$ Hz), 7.56–7.58 (d, 2H, Ar–H, $J = 8.48$ Hz), 7.68–7.70 (d, 1H, $\text{CH}=\text{CH}$, $J = 15.65$ Hz), 8.11–8.13 (d, 2H, Ar–H, $J = 8.41$ Hz).

Synthesis of the homopolymer (P_2) (Scheme 2)

Radical polymerization of M_2 was carried out in 10 wt % solution in the following procedure. The monomer (1.0 g) and AIBN (10 mg) as a polymerization initiator, which was beforehand recrystallized from methanol, were dissolved in 10 mL of dried benzene. The solution was placed in an ampoule and was heated at 60°C for 24 h. The resultant solution was poured into methanol to separate the crude polymer, which was purified by reprecipitation from methanol for several times. Finally, the polymer was dried in vacuum at room temperature. Yield: 81%. $M_w (\times 10^{-4})$: 1.8; M_w/M_n : 1.86; T_g : 53°C .

Sample preparation

The samples, M_1 and M_2 , were recrystallized from methylene dichloride. Crystals of 100–500 μm were sieved, and approximately 10 mg was evenly distributed in a thin layer of microcrystalline powder. A thin film of the polymer (P_2) with a thickness of 60 nm was obtained on a piece of quartz or KBr substrate by spin-coating of their 1.5 wt % solutions in methylene dichloride.

Irradiation experiment

The samples were put in the focus of a 200 W high-pressure mercury lamp for the irradiation experiments. The irradiance at the place where the samples were put was measured with a UV light radiometer (Photoelectric Instrument Factory, Beijing Normal University, China).

Measurements

FTIR spectra were recorded on a Nicolet 5700 (USA) FTIR spectrophotometer. Samples were thoroughly mixed with KBr and pressed into pellet form. For each sample, 32 scans at 2 cm^{-1} were collected in the absorption mode.

RT-FTIR spectra were also taken on that Nicolet 5700 FTIR spectrophotometer. Omnic series software was utilized for data acquisition and Oringin-Pro 8.0 software was used for data processing and

graph drawing. RT-FTIR instrument was modified to provide nitrogen environment in a sealed glass reactor cell equipped with quartz windows. Samples were placed in the aforementioned FTIR spectrometer chamber and exposed to UV light through the quartz windows with the aid of an optical fiber cable. Subsequently, the reduction in the IR absorbance of double bonds at specific wavenumbers was monitored to determine the reaction rate. The conversion of the carbon double bond at a given time was calculated according to the following equation:

$$\alpha_w(t) = \frac{(A_w)_{t_0} - (A_w)_t}{(A_w)_{t_0}} \quad (1)$$

where w is wavenumbers; $\alpha_w(t)$ is the conversion of the bond at w wavenumbers; $(A_w)_{t_0}$ is the area of the bond of the functional group before irradiation by UV light; and $(A_w)_t$ is the area of that bond when the sample is irradiated for t time. In this study, we calculate $\alpha_{1637}(t)$ of M_1 and P_2 , and $\alpha_{980}(t)$ and $\alpha_{840}(t)$ of M_2 .

$^1\text{H-NMR}$ spectra were obtained on a Bruker AV600 (Darmstadt, Germany) NMR spectrometer and chemical shifts were reported in ppm with tetramethylsilane as an internal standard.

Solid-state $^{13}\text{C-NMR}$ spectra were obtained using a 4 mm triple resonance magic angle spinning probe from Varian, and data were recorded using a Bruker AV300 (Darmstadt, Germany) NMR spectrometer. Resonance frequencies were 75.46 MHz.

The thermal properties of the polymers were analyzed at a heating rate of $10^\circ\text{C min}^{-1}$ with a NETZSCH DSC 204 F1 differential scanning calorimeter (Germany).

The molecular masses and their distributions were determined by gel permeation chromatography (GPC; Waters515-241GPC system, America) at a flow rate of 1.0 mL min^{-1} using tetrahydrofuran as an eluent on the basis of calibration with polystyrene standards.

Wide angle X-ray diffraction (WAXD) patterns were gained at room temperature on XRD RU-200 (Ragaku, Japan) diffractometer with a CuK α radiation source (wavelength 0.154 nm). Samples were exposed at a scan rate of $2\theta = 10^\circ\text{min}^{-1}$ between $2\theta = 5^\circ$ – 40° .

The UV–visible absorption and transmittance spectrum was taken on a Hitachi U-3010 (Japan) UV–visible spectrophotometer with 0.1 nm resolution. Because of solubility differences, samples of M_1 with different exposure time were dissolved in CHCl_3 at identical concentration of 50 μM . The sample of P_2 was prepared by spin-coating on a piece of quartz.

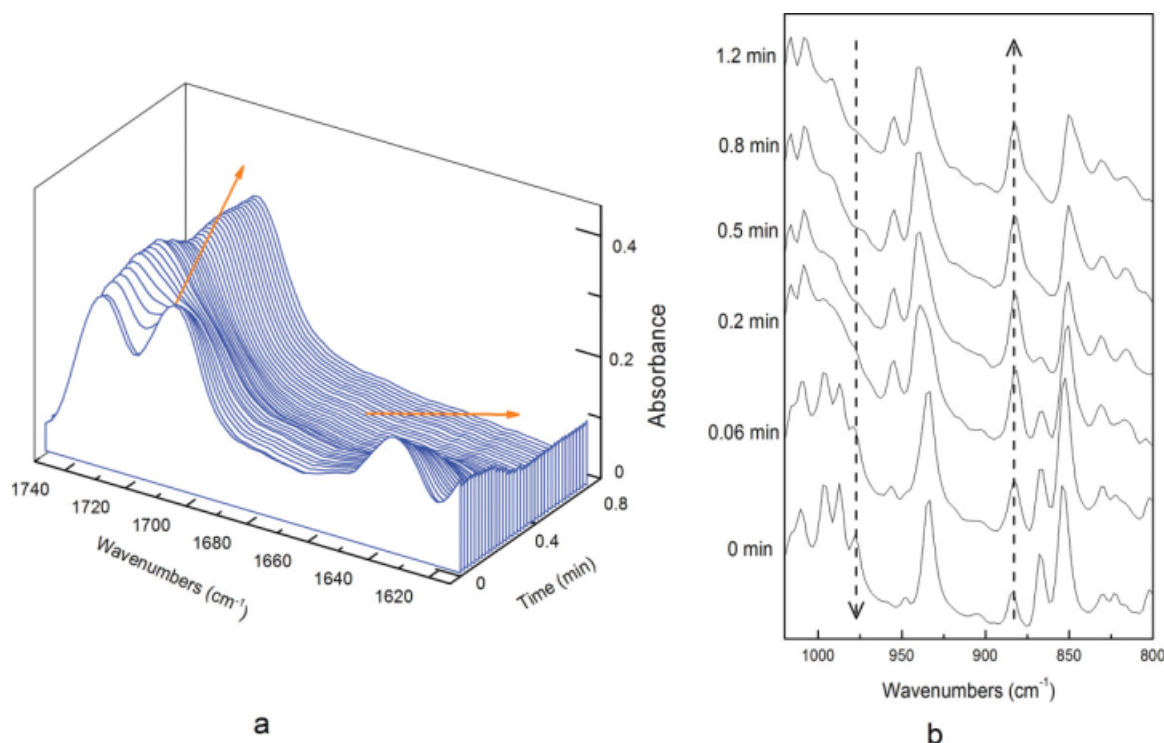


Figure 1 RT-FTIR spectra of M₁ irradiated with irradiance of UV light at 40 mW/cm². [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Photoreaction of monomers and the polymer

Figures 1–3 illustrates FTIR spectra of M₁, M₂, and P₂ collected by RT-FTIR, subjected to irradiation of unpolarized UV light. All observed vibrational bands in the spectra can be assigned in accordance with the results reported previously.^{13,14,29} For all of them, 1637, 980, and 880 cm⁻¹ correspond to the vinylene C=C stretching vibration, *trans*-, and *cis*-vinylene C-H deformation in the cinnamoyl moiety, respectively. The increase in exposure time leads to evident decrease in the intensities of the bands at 1637 and 980 cm⁻¹, and a small raise at 880 cm⁻¹. The intensity drop in 1637 cm⁻¹ might result from the loss of C=C caused by photodimerization for M₁ and P₂, and by both photodimerization and polymerization for M₂; while the drop in 980 cm⁻¹ could be attributed to the consumption of the *trans*-vinylene linkage in the cinnamoyl moiety because of *trans*-*cis* photoisomerization and photodimerization; and raise in 880 cm⁻¹ indicates the increase in the number of *cis*-vinylene that resulted from photoisomerization.

Besides that, in Figure 1(a), the bands at 1730 and 1710 cm⁻¹ correspond to the C=O stretching vibration in the 4-(hexyloxy) benzoic ester unit and in the cinnamoyl moiety of M₁, respectively. As the exposure time increases, the intensity of the band at 1710 cm⁻¹ decreases, and its position shifts to higher

wavenumbers, which could be attributed to two possible factors: the loss of π -conjugation resulted from photodimerization and the *trans*-*cis* photoisomerization of the cinnamoyl moieties. However, the position shift of the conjugated C=O stretching band resulting from *trans*-*cis* photoisomerization is small,¹³ and in fact cannot be observed in Figure 1(a) because of extensive overlapping of the band at 1710 cm⁻¹ with the one at 1730 cm⁻¹. What is actually discerned is that the band at 1730 cm⁻¹ increases and shifts to higher wavenumbers. Meanwhile, the band at 880 cm⁻¹ increases slightly and at 1637 cm⁻¹ decreases sharply. These results support that the intensity drop and the position shift of the conjugated C=O stretching band originate principally from the photodimerization of the cinnamoyl moieties and in part from the *trans*-*cis* photoisomerization of the cinnamoyl moieties.

For M₂ (Fig. 2), the band at 1728 cm⁻¹ is an overlapped band that corresponds to the C=O in stretching vibration in the 4-(hexyloxy) benzoic ester unit, in cinnamoyl moiety, and in acrylate moiety; and the band at 840 cm⁻¹ corresponds to vinyl C-H deformation in acrylate moiety. There is also a slight position shift of the band at 1728 cm⁻¹, and a small increase in the band at the new position indicating the change of C=O from conjugated before the UV exposure into unconjugated. The reduced intensity at 840 cm⁻¹ demonstrates the loss of vinyl in acrylate moieties.

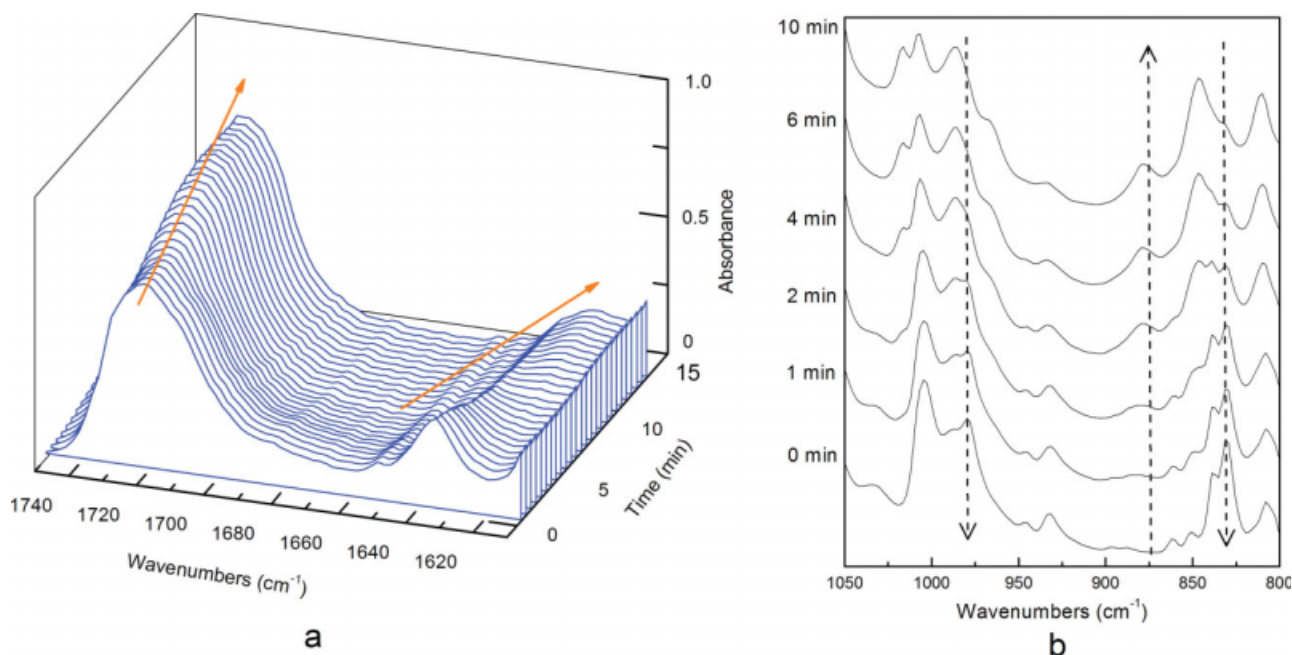


Figure 2 RT-FTIR spectra of M_2 irradiated with irradiance of UV light at $80 \text{ mW}/\text{cm}^2$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

UV absorption and transmittance spectra could also demonstrate the photo reaction of cinnamoyl moieties.^{9,13,19} Figure 4 shows UV absorption spectra of M_1 and transmittance spectra of P_2 . Figure 4(a) shows a strong and broad band centered at 285 nm, which is extensively overlapped with the other two bands discerned as shoulder peaks that are centered at 275 and 303 nm, respectively. These absorption bands could not be resolved quantitatively because of their large overlaps. The absorption maximum at 285 nm relating to *trans*-cinnamoyl moieties decreases from 2.1 to 0.9 under UV exposure for 2 min. At the same time, the absorption maximum shifts to 275 nm. The spectral changes are indicative of the disappearance of *trans*-cinnamoyl moieties and the formation of a cyclobutane ring.

As regards P_2 , the transmittance minimum (absorption maximum) is at about 275 nm as shown in Figure 4(b), a lower position than that of M_2 , because electron in solid state cannot be excited as easily as in solution. The peak at 275 nm disappears and shifts to lower wavelength with increase in time, which indicates the photodimerization of cinnamoyl moieties.

Solid-state NMR spectra could further confirm the photodimerization. Figure 5 shows solid-state ^{13}C -NMR spectra for M_1 and the [2 + 2] photodimerization product. Figure 5(a) is the parent M_1 , before irradiation; and Figure 5(b) is the solid-state ^{13}C -NMR spectrum of the [2 + 2] photodimerization product, which was irradiated for 2 min with the irradiance of 80 mW cm^{-2} to get an ultimate

conversion. The complete assignments of the carbon sites are given in Table I (numbering from Scheme 3).

A decrease of the vinylic carbon signal (C4) is observed with a concomitant increase of the cyclobutane carbon signals. Three cyclobutane carbon signals are observed, one of which is overlapped with C1 at 51.2 ppm, whereas only two are expected—two carbons adjacent to the phenyl rings and two carbons adjacent to the ester groups. Bertmer et al.⁹ ascribed these three signals to solid-state packing

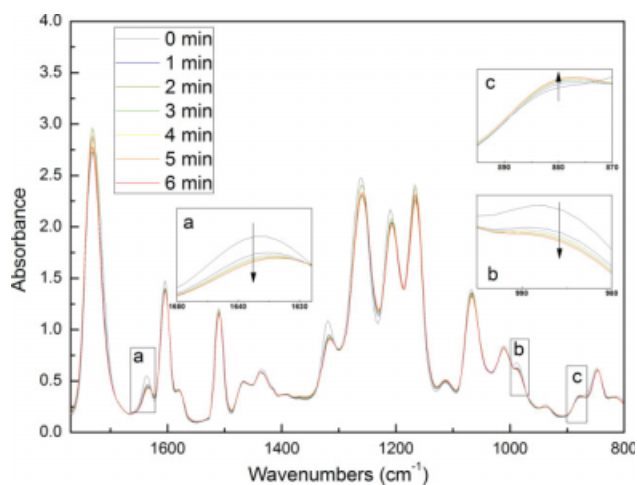


Figure 3 RT-FTIR spectra of P_2 irradiated with irradiance of UV light at $80 \text{ mW}/\text{cm}^2$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

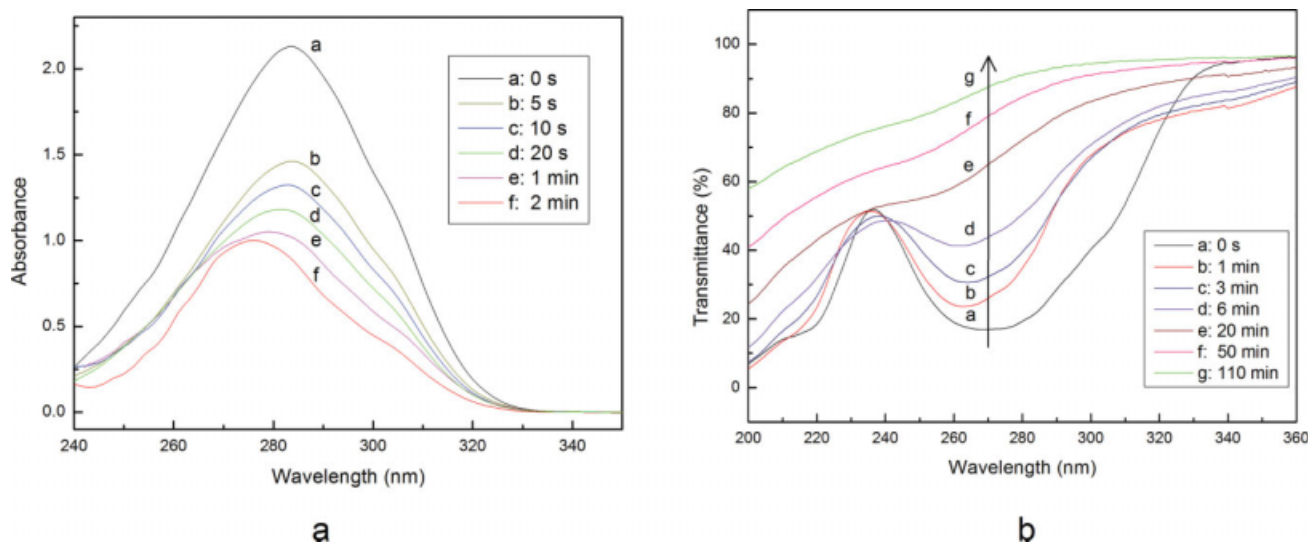


Figure 4 UV spectra change of M_1 and P_2 irradiated with unpolarized UV light. (a) UV absorption spectra of M_1 ; (b) UV transmittance spectra of P_2 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

effects, such as distortions of the cyclobutane ring and dihedral angle “twists” of the phenyl rings and ester groups with respect to an idealized solution-phase structure. Additionally, the chemical shifts of the neighboring carbons, for example, the ipso (non-protonated aromatic) carbon (C5, C'5) and the carboxylic carbon (C2, C'2) show a small shift between reactant and product because of different inductive effects of the neighboring groups (vinylene vs. cyclobutane). However, the vinylenic carbon signals do not disappear in Figure 5(b). The residue vinylenic could be attributed to two possible reasons: (i) residue parent M_1 that did not react; (ii) *cis*-isomers including those photoisomerized from *trans*-isomers.

Effects of photoinitiator and the irradiance of UV light on photodimerization

Figure 6 shows the change of double carbon bond conversion $\alpha_{1637}(t)$ versus time in the cinnamoyl moieties of M_1 with and without radical photoinitiator (Irgacure 651) under the irradiance of UV light at 40 mW cm^{-2} . $\alpha_{1637}(t)$ decreases when photoinitiators exist indicating that the photoinitiator disturbed, rather than improved, the photo reaction of the cinnamoyl moieties. The result demonstrates that photodimerization, the photo reaction of $C=C$ in the cinnamoyl moieties, is different from photo-initiated free radical polymerization. And also,

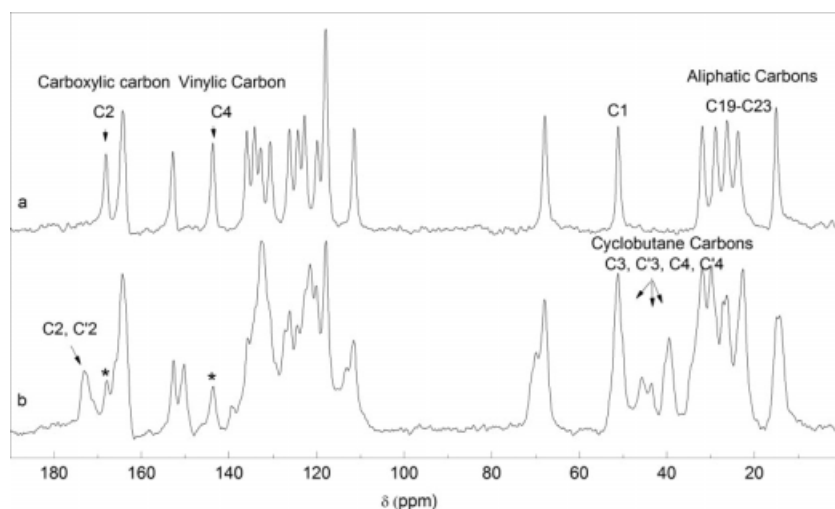


Figure 5 ^{13}C CPMAS spectra of M_1 with (a) no irradiation; (b) irradiation for 2 min. * indicates residual M_1 without UV irradiation.

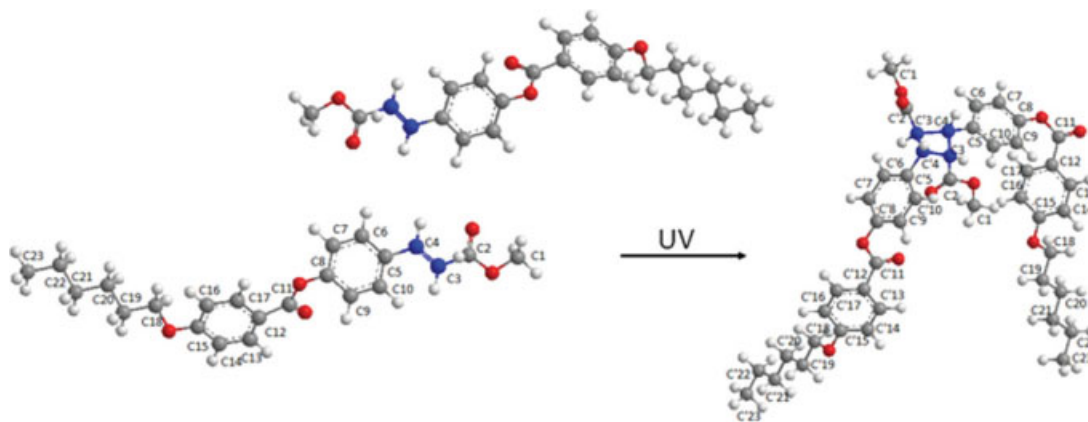
TABLE I
Resonance Assignment for M₁ and Product After UV Irradiation

Sample	Assignment	δ (ppm)	Sample	Assignment	δ (ppm)
M ₁	C1	51.2	Dimer	C1, C'1	51.2
	C2	168.0		C2, C'2	173.0
	C3	119.8		C3, C'3, C4, C'4	39.5–51.2
	C4	143.7		C5, C'5	139.4
	C5	135.9		C13, C17, C'13, C'17	132.3
	C6, C10	124.3–126.2		C6, C10, C'6, C'10	124.4–126.1
	C7, C9, C12	119.8–122.7		C7, C9, C12, C14, C16, C'7, C'9, C'12, C'14, C'16	111.5–121.4
	C8	152.7		C8, C'8	150.2–152.6
	C11, C15	164.1		C11, C'11, C15, C'15	164.2–167.9
	C13, C17	132.7–134.1		C18, C'18	67.9–69.9
	C14, C16	111.4–117.9		C19, C'19	29.8
	C18	67.9		C20, C'20	26.3–27.2
	C19	28.9		C21, C'21	31.9
	C20	26.3		C22, C'22	22.7
	C21	32.0		C23, C'23	14.2
	C22	23.9			
	C23	15.1			

trans-cinnamoyl moieties do not react in the way of free radical polymerization under the exposure of UV light, even if the molecules coexist with free radicals. As seen in Figure 6, when the exposure time is 1.5 min, the final conversions of the two curves are similar indicating that existence of photoinitiators delay the reaction but does not influence the final conversion of the sample. A possible reason is that photoinitiators absorbed part of UV light and thus decline the portion of UV light that trigger the reaction. Another possible reason is that the existence of photoinitiators disturbs the formation of crystal lattice. Based on these results, M₂ was believed to undergo polymerization of acrylate moieties and also photodimerization of cinnamoyl moieties at the same time under UV irradiation.

Figures 7(a) and 8(a) show the curves of conversion of double carbon bond $\alpha_{1637}(t)$ of M₁ and P₂ versus time with different irradiance of UV light, respectively, which indicates the conversion of photodimerization. It is obvious that the conversion of C=C in the cinnamoyl moieties increases with the raise in the irradiance. Also obvious is that the conversion of vinylene in the cinnamoyl moieties of M₁ is much faster than that of P₂. For example, under the exposure of UV light at 80 mW cm⁻², within 1 min, the conversion of M₁ has reached the ultimate value 90%. However, it takes about 15 min for the conversion of P₂ to be about 63%.

The caption of bottom axis is changed from exposure time to exposure energy, which equals that the irradiance of UV light multiplies exposure time. As



Scheme 3 Numbering scheme of M₁ and the photodimer. The grey, red, and white balls indicate carbon, oxygen, and hydrogen atoms. The blue ones are carbons in C=C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

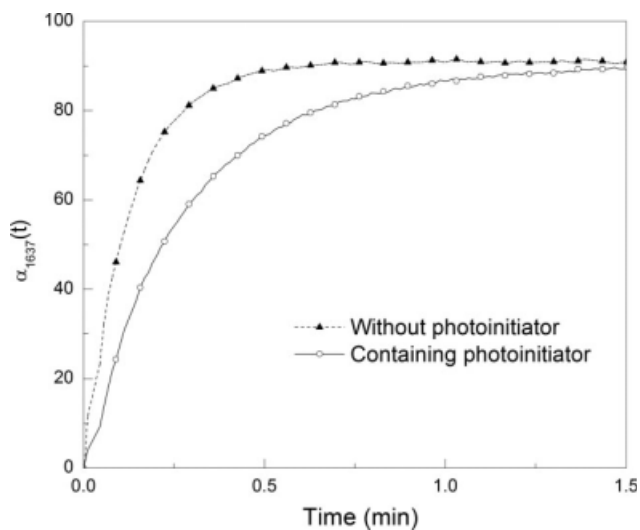


Figure 6 Effects of free radical photoinitiator on photoreaction of *trans*-cinnamoyl moieties.

seen in Figure 7(b), for M_1 , the five curves at different irradiance are close to each other, indicating that the conversion of photodimerization of M_1 is actually the function of photon energy (x), which could approximately fit the equation: $\alpha_{1637}(x) = 90 - 96^{-3x}$. However, in Figure 8(b), two conversion curves of P_2 at 20 and 40 mW cm^{-2} that are close to each other, conversion increase when light energy continues to rise. This result may be attributed to the molecular movements. The increase in the irradiance may speed up molecular movements, and thus make more of cinnamoyl moieties fitting for cycloaddition.

Figure 9 shows $\alpha_{840}(t)$ and $\alpha_{980}(t)$ of M_2 versus time, which are corresponding to the conversion of

vinyl in acrylate moieties and vinylene in cinnamoyl moieties, respectively. Evidently, both conversions increase with the raise in the irradiance. Like P_2 , the conversion of vinylene in the cinnamoyl moieties of M_2 is much slower than that of M_1 . However, the two vinylene conversions of M_2 and P_2 are not comparable, because the vinyl and vinylene of M_2 share the UV light, the actual UV light that vinylene of M_2 absorbed is less than that of P_2 did under the same irradiance.

As seen in Figure 10, curves of $\alpha_{840}(t)$ and $\alpha_{980}(t)$ of M_2 under the same irradiance are drawn together. When the irradiance is below 20 mW cm^{-2} , vinylene in the cinnamoyl moieties reacts little faster than vinyl in acrylate moieties. With increase in the irradiance, the conversion of vinyl increases faster than that of vinylene.

Molecular arrangement analysis

Figure 11(a,b) show the powder WAXD patterns of M_1 without and after UV exposure at 80 mW cm^{-2} for 2 min. The irradiance and irradiation time was decided to obtain the ultimate conversion. The hexyloxy group of M_1 may disturb the formation of crystal, which was confirmed by the little portion of diffuse diffraction in Figure 11(a), indicating the existence of a little amorphous part. After exposed to UV light, the portion of diffuse diffraction increases, implying increase in the amorphous part. Figure 11(e) shows WAXD pattern of P_2 without UV irradiation, which indicates that P_2 is amorphous. According to topochemistry, solid-state packing of molecules is of great importance to the photodimerization.¹⁰ The regular arrangement of molecules, of

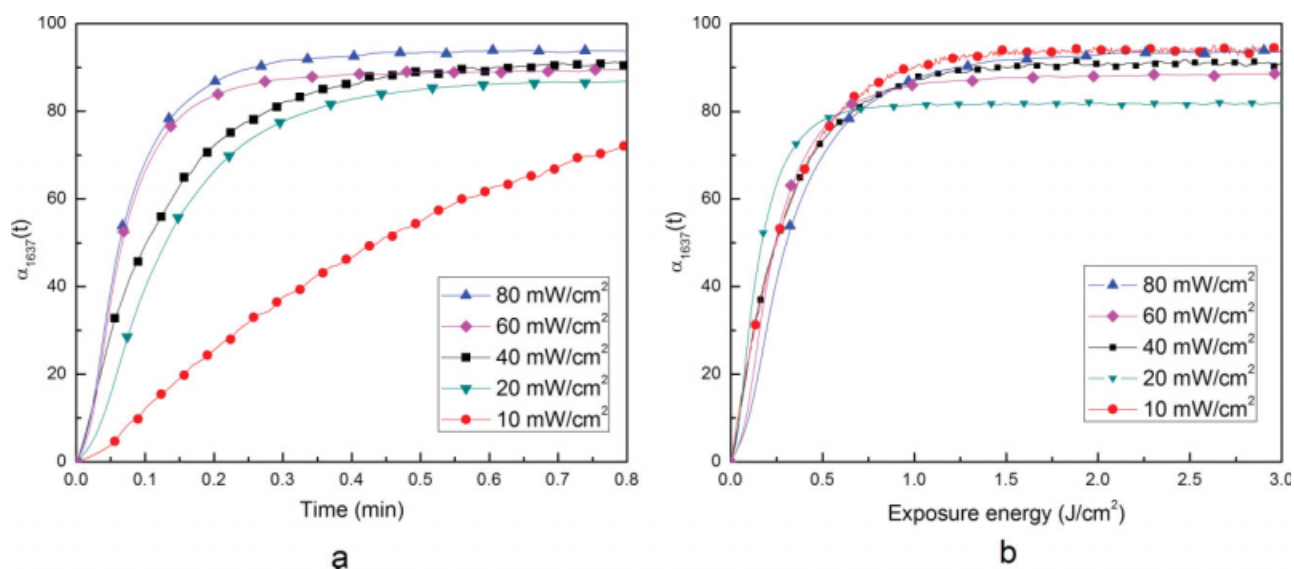


Figure 7 Conversion of photodimerization with various irradiance of UV light of M_1 versus (a) exposure time and (b) exposure energy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

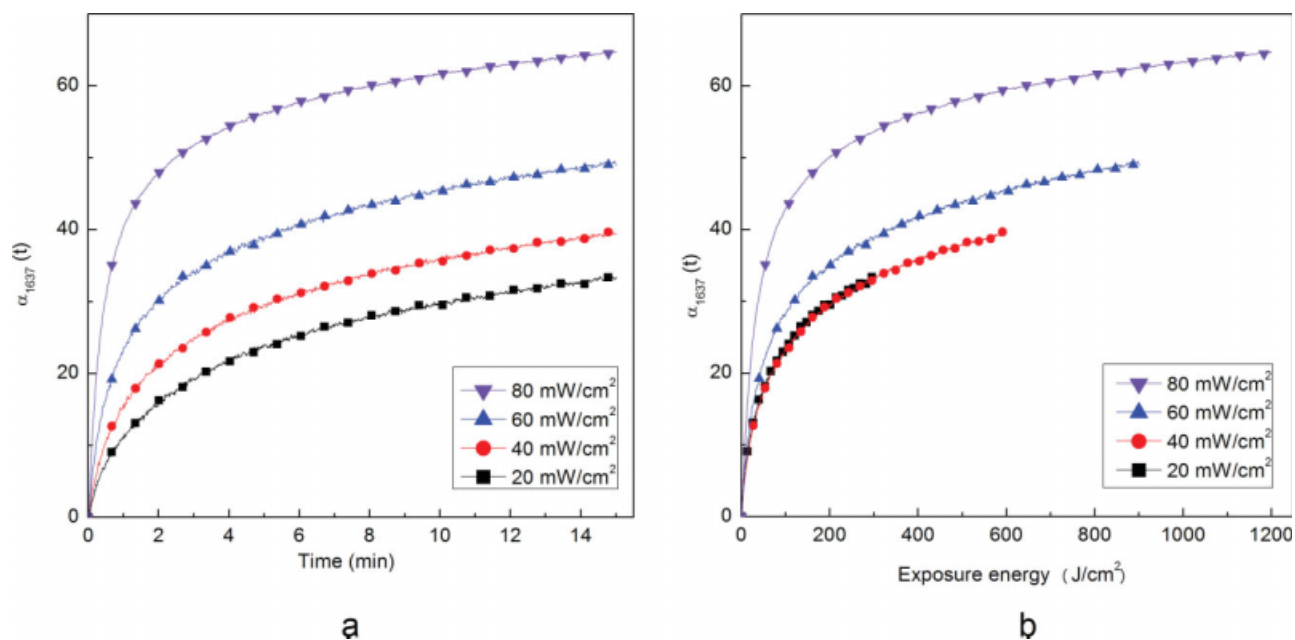


Figure 8 Conversion of photodimerization with various irradiance of UV light of P₂ versus (a) time and (b) exposure energy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

vinylene moieties close and parallel to each other, is necessary for photodimerization. Thus, the difference in molecules arrangements between M₂ and P₂ may be responsible for the different rate of photodimerization.

Figure 11(c,d) show the WAXD patterns of M₂ without and after UV exposure. To reach the ultimate C=C conversion, M₂ was irradiated under the UV exposure at 80 mW cm⁻² for 20 min. Compared with the structure of M₁, the molecule of M₂ contains an acrylate moiety and the hexyloxy, which

could disturb the formation of crystal further. Therefore, the area of diffuse diffraction is much bigger as shown in Figure 11(c), indicating the amorphous portion of M₂ is larger than that of M₁, which may explain why the photodimerization rate of M₂ is slower than that of M₁. Because of stereo hindrance of soft chain, the cinnamoyl moieties could not form crystal as regular as M₁, so some of vinylene groups may not be parallel or close enough to each other, and photodimerization of them was delayed. As the progress of reaction, they may be photo reactive due

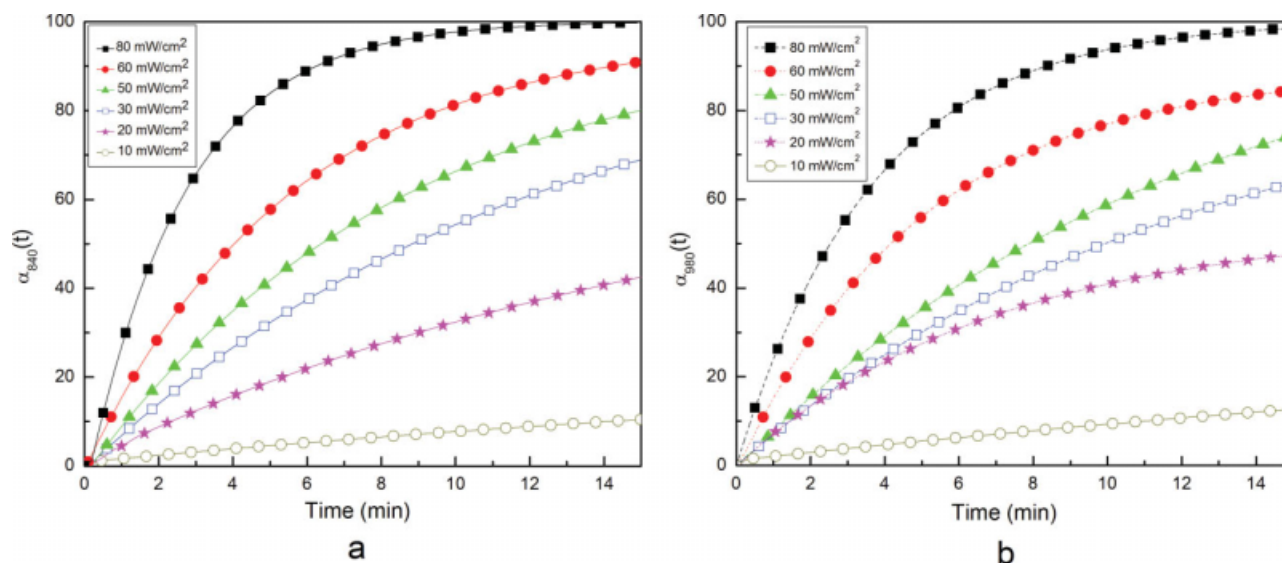


Figure 9 Conversion of C=C versus time with various irradiance of UV light of M₂. (a) Conversion of vinyl in acrylate moieties versus time of M₂; (b) Conversion in *trans*-vinylene in cinnamoyl moieties versus time of M₂. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

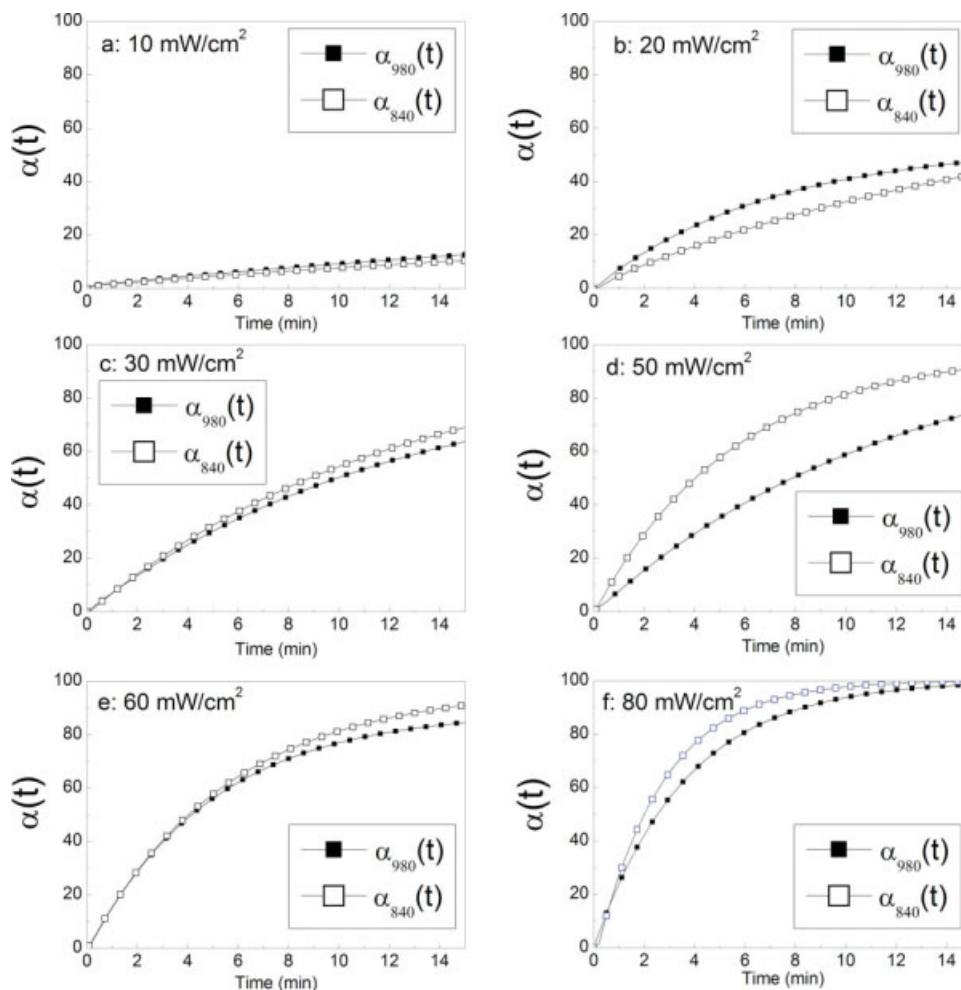


Figure 10 C=C conversion of M₂ versus time with various irradiance of UV light. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

to molecular movements. As seen in Figure 11(d), the curve of M₂ after UV irradiation shows no diffraction peak but a broad diffuse diffraction, indicating an amorphous state. Because both the vinyl in acrylate moieties and vinylene in cinnamoyl moieties could react under UV irradiation, molecules of M₂ grow into a network. The polymerization of acrylate moieties combines the soft chains of molecules together and thus destroys the crystalline lattice further. And, as proven above, the photodimerization could lead to the increase in amorphous part. Thus, finally, the molecules packing of M₂ would turn to be amorphous.

CONCLUSIONS

In this study, two novel monomers (M₁ and M₂) and a polymer (P₂) have been synthesized and their structures were confirmed. Each of the monomers contain a cinnamoyl moiety; M₂ also contains an acrylate moiety; and P₂ was obtained by free radical

polymerization of M₂. *Trans*-cinnamoyl moieties were proven not to undergo free radical polymerization. Difference in kinetic behaviors of photodimerization of M₁, M₂, and P₂ was confirmed, which may be attributed to their distinct molecular arrangements demonstrated by WAXD patterns. It demonstrates that photodimerization occurs faster in a regular molecular arrangement than in a random one. Meanwhile, the increase in irradiance of UV light apparently causes an increase in C=C conversion. Actually, the conversion of *trans*-vinylene in the cinnamoyl moiety of M₁ is the function of exposure energy. For P₂, under the same exposure energy, increase in irradiance also cause increase in conversion. That may be because of movements of molecular chains caused by extra energy which could make the positions of *trans*-cinnamoyl moieties fitting for photoreaction. M₂ could undergo photodimerization and free radical polymerization at the same time. With increase in irradiance, the conversion of vinyl in acrylate moieties increases faster than that of vinylene in cinnamoyl moieties. According to our

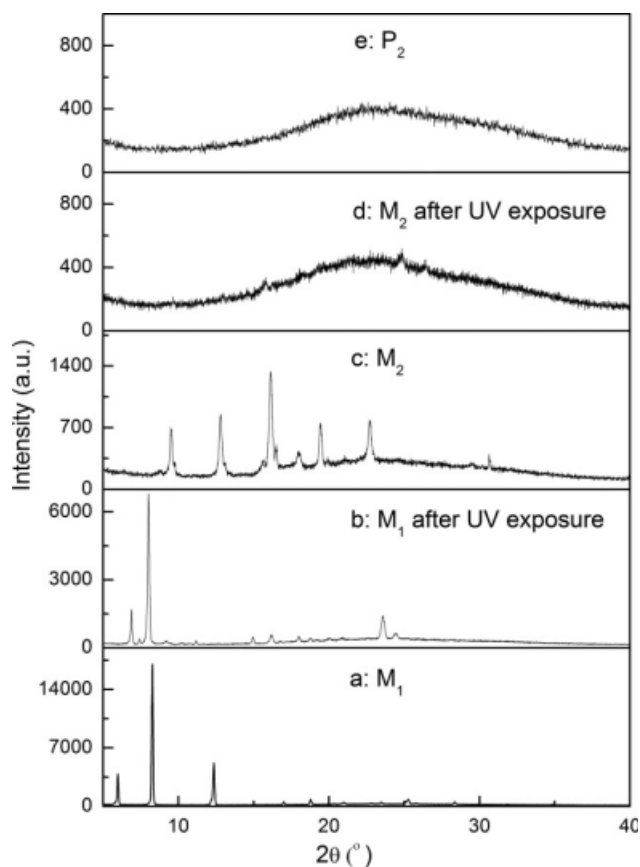


Figure 11 WAXD diffraction patterns of (a) M_1 without UV exposure; (b) M_1 after UV exposure at 80 mW/cm^2 for 2 min; (c) M_2 without UV exposure; (d) M_2 after UV exposure at 80 mW/cm^2 for 20 min; (e) P_2 without UV exposure.

study, the stringent steric arrangement may be not necessary for photodimerization, but of great importance to a faster photoreaction.

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