Articles

Photoinduced Polymerization of Bisimides as Models for New Soluble Side-Chain-Substituted Negative-Type Photosensitive Polyimides

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In this paper, we study the photoinduced polymerization of bisimide models for our new soluble side-chain-substituted negative-type photosensitive polyimides (PSPI) in order to better understand the polymerization behavior of the latter. These model compounds were cross-linked by UV irradiation in the solid state and in *N*-methyl-2-pyrrolidinone (NMP) solution. Variations in the molecular structure of the photosensitive moieties were explored to change the photosensitivity of models and of polymers. The kinetics of photopolymerization of these bisimide models was investigated by using infrared and UV techniques. The cinnamate and furylacrylate derivatives were found mainly to photodimerize, whereas the two others, acrylate and methacrylate derivatives, photopolymerize. Reaction orders of 1.5 and 2.0 were verified in the case of models but could not be determined for the polymers, due to the restriction of mobility of the photosensitive side groups on the polymer chains (solid-state irradiation) and also because the cross-linked polymer was no longer soluble in NMP and precipitated as it was formed.

Introduction

In recent years, much attention has been devoted to the development of UV-sensitive organic materials as a result of the increasing demands on the miniaturization, higher electrical performance, and reduction of the cost of production of electronics components.[1] Aromatic polyimides have been widely used for microelectronics applications. They are among the best thermally stable polymers and have many other desirable properties that are useful in this industry.[1−5] A certain number of photosensitive polyimides (PSPI) are now commercialized, but most of them belong, in fact, to the family of PSPI precursors. They must be converted into polyimides after irradiation and developing, which generally causes considerable shrinkage (up to 50%).[6] To overcome this problem, we recently reported[7] the synthesis and characterization of new, negative-type photosensitive polyimides, having a soluble, fully imidized polyimide backbones with photoreactive groups attached as substituents, as well as the solubility of these polymers before and after UV irradiation in solution and as freshly cast films at room temperature. Thus, after UV irradiation at room temperature, PSPI ester films were immediately immersed in NMP at 30 °C and washed in water for 1 min. The insoluble fraction was dried under vacuum. The shrinkage of the film after this postbaking was in the range of 20%, the value depending only on the structure of the photoreactive group, because these PSPI ester systems consist of fully imidized, nondegradable polyimides.[8−10] PSPI esters form a gel in NMP solution when exposed to UV.

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Scheme 1. Synthesis of Model Bisimides

$R_1 = H, R_2 = $ ⬡ **1** $R_1 = H, R_2 = H$ **4**

$R_1 = H, R_2 = $ (furan) **2** $R_1 = C H_3, R_2 = H$ **3**
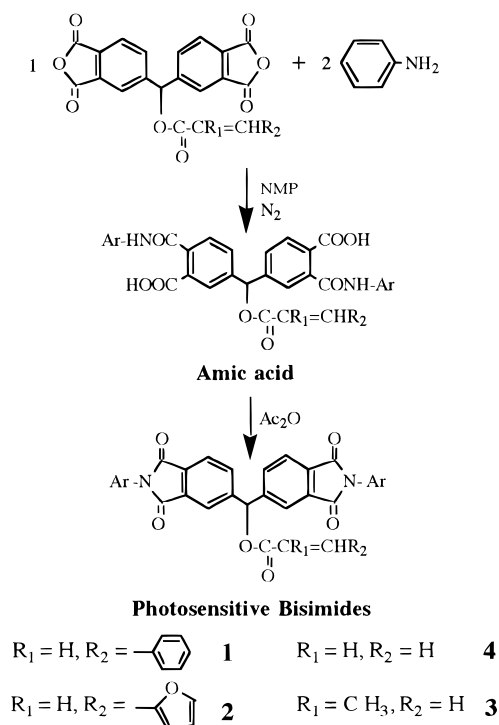
The essential aim of this work was to get some further insight into the chemistry involved in the transformation occurring under UV irradiation of these novel PSPI materials. To this end, we have combined results from UV and IR spectroscopy of the bisimide models to characterize these cross-linked polyimides. The photochemical studies are performed in both solid and liquid states, and the relationship between the molecular structure of the photoreactive groups and the photochemical reactions is discussed.

Experimental Section

Reactants. The starting material 3,3′,4,4′-benzhydrol tetracarboxylic dianhydride (BHTDA) was kindly provided by CEMOTA and purified by Soxhlet extraction with diethyl ether before use. The aromatic diamines oxydianiline (ODA) and methylene dianiline (MDA) were obtained from Merck and were used as received. All of the other reagents and solvents are commercially available and were used after appropriate purification in the normal manner.

Synthesis of Model Imide Compounds (Scheme 1). *Synthesis of Bis(N-phenylphthalimid-3-yl)methylcinnamate (1).* The synthesis of **1** is given as a typical synthetic example.[11] An amine solution was prepared by dissolving 0.41 g (4.4 mmol) of aniline in NMP. BHTDA cinnamate ester (1.0 g, 2.2 mmol) was gradually added to the amine solution under a nitrogen atmosphere. The reaction mixture was stirred for 12 h at ambient temperature, to which was then added 2.0 mL of acetic anhydride as a dehydrating agent for chemical imidization. The solution was mechanically stirred for 24 h at room temperature. After the reaction was completed, the solution was poured into 50 mL of dry, ice-cold methanol. The precipitated product was washed with large amounts of distilled water to remove occluded acetic acid and purified by chromatography on a silica column (CHCl₃/hexane 1/1) followed by recrystallization from *n*-hexane/methylene chloride. The product was dried under high vacuum for 16 h to yield **1** as a white powder (yield 0.89 g, 67%).

(11) Berrada, M. Synthesis and Characterization of Thermostable photosensitive Polyimides for Applications in Microelectronics. Ph.D. Thesis, Pierre and Marie Curie University, 1992.

**Scheme 2. Synthesis of Soluble Photosensitive Polyimides**

$R_1 = H, R_2 = $ ⬡ **5** $R_1 = H, R_2 = H$ **8**

$R_1 = H, R_2 = $ (furan) **6** $R_1 = C H_3, R_2 = H$ **7**
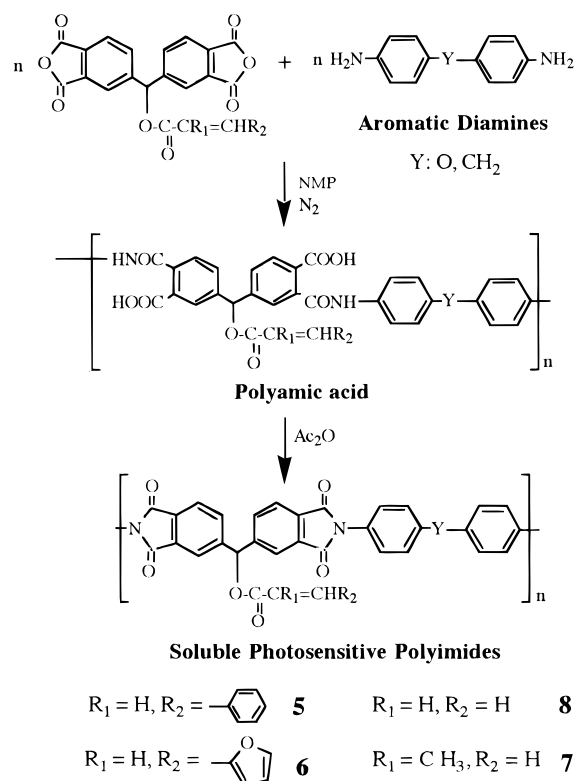
1: ¹H NMR (DMSO-d_6) δ 8−8.5 (m, 6H, ArH), 7.87 (d, 1H, vinyl), 7.5 (m, 15H, ArH), 7.35 (s, 1H, −CH−), 6.95 (d, 1H, vinyl); IR (KBr) ν 1779, 1722 (*s*, C=O imide, ester), 1635 (s, C=C) cm⁻¹. Anal. Calcd for $C_{38}H_{24}N_2O_6$: C, 75.49; H, 3.90; N, 4.63. Found: C, 75.37; H, 3.95; N, 4.61.

Synthesis of Soluble PSPI Esters (Scheme 2). *Synthesis of PSPI Cinnamate Ester (5).* The synthesis of PSPI cinnamate ester **5** is given as a typical example.[11] BHTDA cinnamate ester (2.0 g, 4.4 mmol) was added to a solution of 0.87 g (4.4 mmol) MDA or 0.88 g of ODA in NMP (70 wt %). The reaction mixture was stirred mechanically for 24 h at ambient temperature. Acetic anhydride (5.0 mL) was added to the amic acid solution. The solution was stirred overnight. After the reaction was completed, the solution was added dropwise to 100 mL of methanol to precipitate the photosensitive polyimide (PSPI) ester. The product was washed with large amounts of distilled water to remove occluded acetic acid. The isolated PSPI ester was in the form of a beige powder and was dried under high vacuum for 16 h at 40 °C to yield **5**. IR (KBr) ν 1779, 1722 (s, C=O imide, ester), 1635 (s, C=C) cm⁻¹. The inherent viscosity of this polymer was 0.80 dL/g in NMP ($C = 1$ g/dL) at 30 °C.

Compounds **6−8** were prepared by following the same procedure as described for **5**. All of the procedures were carried out under dry nitrogen gas or argon or in a vacuum to avoid ambient moisture because of the hydrolytic instability of the anhydride groups. The photosensitive products were shielded from direct sunlight during preparation and purification stages to minimize the photopolymerization process.

Preparation of Polyimide and Bisimide Films. Sample films for irradiation experiments were prepared by casting onto KBr plates (sample for IR) concentrated solutions of PSPI and bisimide models, respectively, from NMP and methylene chloride (DCM) (bisimide models are not film forming). The solutions were first filtered under pressure using a Teflon filter having pores of 1.0 μm and the films were dried at 40 °C in a vacuum to remove the solvent. The thickness of the films was around 20−30 μm.

Measurements of UV, IR Spectra, and Photo-Cross-Linking Reaction. A 125 W mercury lamp, giving strong emissions at 365, 405, and 436 nm was used. The distance
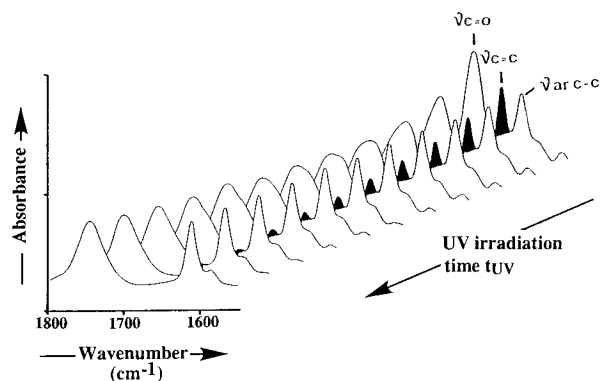
Figure 1. Change of IR spectrum of photosensitive bisimide models upon UV irradiation.
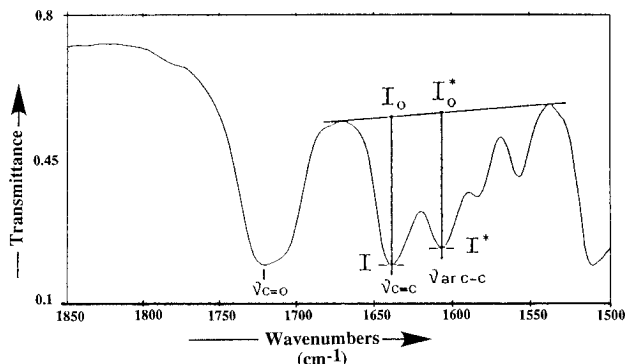
Figure 2. Determination of the number of photosensitive units unreacted in the film by IR.

from the lamp to the sample was 9 cm. The photochemical change of the films and solutions was subsequently investigated by using IR and UV spectroscopic techniques.

Kinetics of Photochemical Reactions

The infrared spectra of the photosensitive bisimide models before and after ultraviolet irradiation are shown in Figure 1. After UV irradiation conjugated double bonds (1635 cm^{-1}) decreased, and carbonyl groups of the ester of α,β-unsaturated carboxylic acid (1720 cm^{-1}) moved toward the shorter wavelength region and approached that of saturated carboxylic acids. This change suggests that the cross-linking occurs by the reaction of the C=C moiety. These systems change from being weakly, to being heavily cross-linked during irradiation. The absorption band at 1635 cm^{-1} disappeared after long irradiation time.

Assuming that the photochemical change in PSPI is caused by the dimerization reaction according to Scheme 3, the change in the number of reacted photosensitive groups with light of energy dE is proportional to the square of the number of photosensitive groups:

$$\mathrm{d}x/\mathrm{d}E = K_1(a - x)^2 \tag{1}$$

where x is the number of reacted photosensitive groups and a is the number of photosensitive groups at initiation. K_1 is a factor directly proportional to the quantum yield. The quantum yield is assumed to be constant, and

$$\mathrm{d}E = K_2\,\mathrm{d}t \tag{2}$$

where K_2 is a constant and t is the irradiation time. Integration of the equation obtained from eqs 1 and 2

gives

$$1/(a - x) - 1/a = K_1 K_2 t \tag{3}$$

if $C = a - x$, $C_0 = a$, and $k = K_1 K_2$, then

$$1/C - 1/C_0 = kt \tag{4}$$

On the other hand, if we consider the photochemical change in PSPI to be a polymerization reaction according to Scheme 3, the change in the number of reacted photosensitive groups with light of energy dE is proportional to the 1.5 power of the number of photosensitive groups:

$$\mathrm{d}x/\mathrm{d}E = K_1(a - x)^{1.5} \tag{5}$$

Integrating eqs 5 and 2, we obtain

$$1/C^{1/2} - 1/C_0^{1/2} = kt \tag{6}$$

where k is the rate constant and $C = E/E^*$ the instantaneous concentration of C=C bonds remaining in the irradiated film which is determined from the IR spectrum (Figure 2). E is the molecular extinction coefficient determined by the absorbance ratio of the vinyl band at 1635 cm^{-1} before and after irradiation, and E^* is the molecular extinction value relative to the aromatic band which is used as reference (see Figure 2):

$$E(\nu_{\mathrm{C=C}}) = \ln I_0/I$$

$$E^*(\nu_{\mathrm{(ar)C-C}}) = \ln I_0^*/I^*$$

C is a function of the light intensity of the UV lamp, the film thickness, and the viscosity of the solution.

Results and Discussion

Synthesis and Characterization of Photosensitive Bisimides. The bisimides containing photosensitive groups are highlighted in Scheme 1. The two-step synthesis of bisimide esters is used as a reaction model for the preparation of PSPI esters.[8] The bisimide is prepared by reacting benzhydrol tetracarboxylic dianhydride ester (BHTDA) derivatives with aniline in NMP solution under a dry nitrogen atmosphere to avoid the hydrolysis of anhydride groups. After complete reaction, the amic acid is chemically imidized using acetic anhydride as the dehydrating agent. The characterization of these bisimides was achieved by NMR and infrared spectroscopies and elemental analysis. The infrared spectra showed the presence of imide C=O at 1780 cm^{-1}, imide C–N at 1380 cm^{-1}, and vinyl C=C at 1635 cm^{-1}.

Synthesis and Characterization of Soluble Photosensitive Polyimide. A new family of negative photosensitive polyimides has been prepared by the condensation of dianhydrides carrying a photoreactive group and aromatic diamines. The viscosity increases gradually by the polycondensation reaction shown in Scheme 2, and viscous solutions suitable for thick coatings were obtained. The characterization of the resulting polymers was realized with the help of bisimide models. The amide absorption peak at 1650 cm^{-1} served as a criterion for the degree of imidization, and complete cyclization to imide was achieved under the above-described chemical condition. Using bisimide as

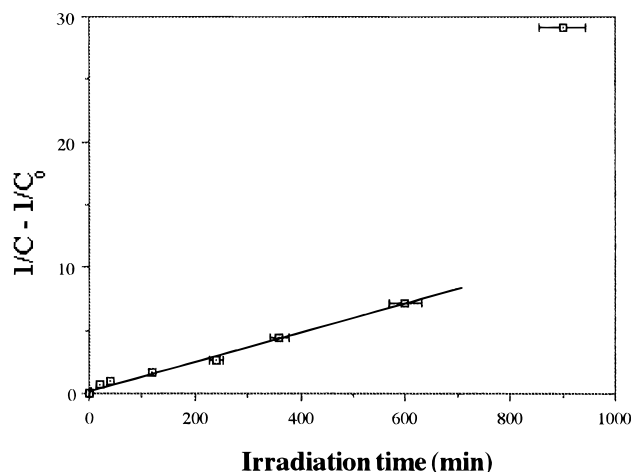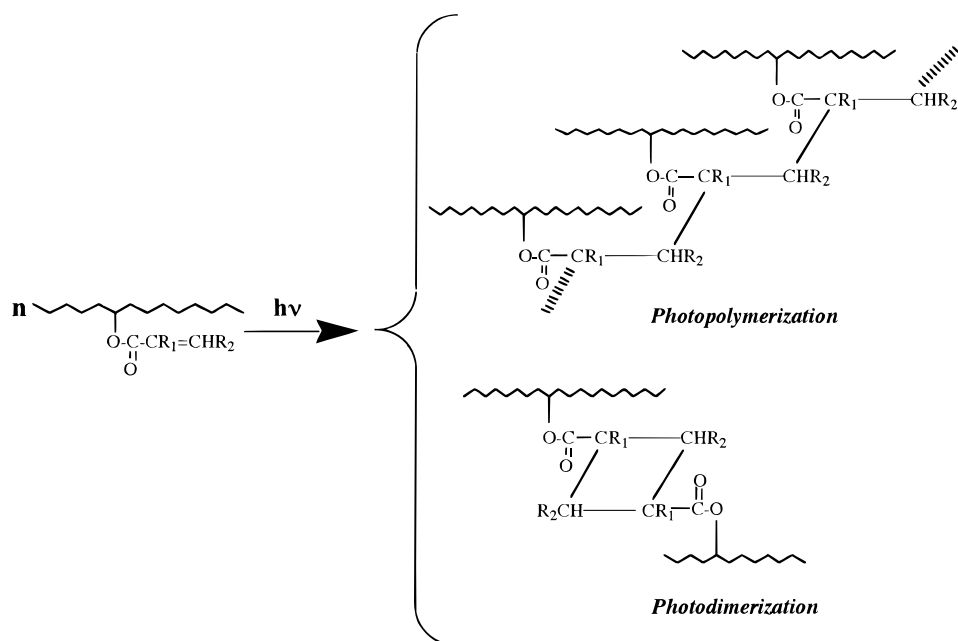**Scheme 3. Chemical Principle for Polyimide Relief Patterns**

Figure 3. Second-order kinetic plot for the model bisimide cinnamate derivative **1**.

the model compound, the reactions between aromatic diamine and photosensitive ester or between acetic anhydride and photosensitive ester were found not to occur simultaneously with the chemical imidization, at room temperature and without triethylamine as the acid acceptor.[11] The ¹H NMR spectrum for **5** shows signals for the cinnamoyloxy group at 6.95 (vinyl proton), 7.87 (vinyl proton), and 7.40 (aromatic proton). Signals for the polymer backbone are at 7.7−8.5 (aromatic proton). This report considers several aspects of the photoreactive model compounds and polymers. The details of synthesis and characterization of dianhydride compounds and polymers are treated elsewhere.[7]

Photochemistry of PSPI. The incorporation of our photoreactive units into the polyimide chain endows the latter with a significant photochemical cross-linking ability which results in the change of solubility upon irradiation. To elucidate the mechanism of the photo-cross-linking reactions of these new soluble negative-type PSPI, we used bisimides as the model compounds of PSPI and studied their photoinduced reactions.

Bisimide Cinnamate Ester in the Solid State. The IR spectral absorbance near 1635 cm⁻¹ of the
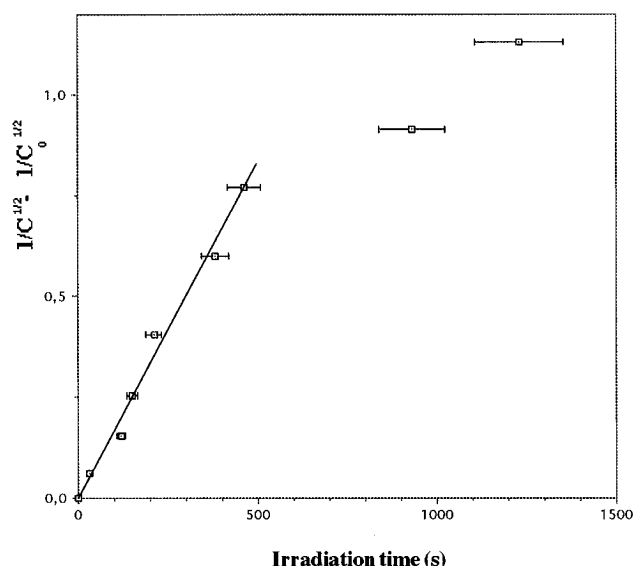
Figure 4. 1.5-order kinetic plot for the model bisimide methacrylate derivative **3**.

photosensitive bisimide cinnamate ester decreased upon UV irradiation.

Figure 3 shows the second-order kinetic plot for the model bisimide cinnamate ester **1**. The straight line obtained attests to the fact that in the case of this cinnamate derivative, photodimerization occurs (see Scheme 4) which is well-known in the literature.[12] An irradiation of 600 min corresponds to 80% conversion of cinnamate groups. Our studies showed that the rate equation (eq 4) could fit the experimental data only up to 80% conversion. Near the end of the reaction, side reactions (photo-Fries rearrangements, polymerization) could affect the kinetic data significantly.
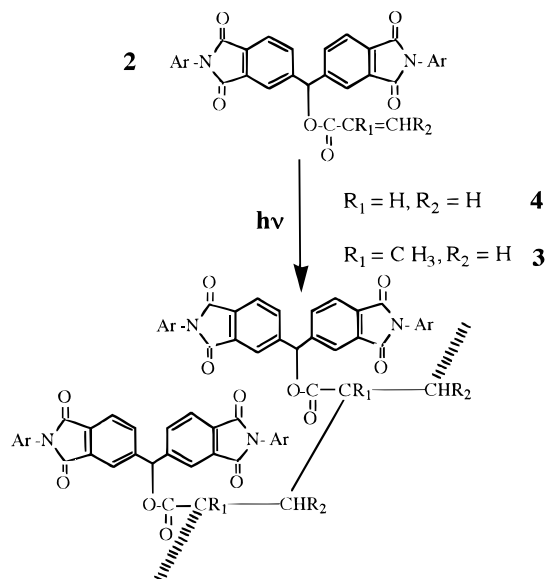
Bisimide Methacrylate Ester in the Solid State. Figure 4 shows the 1.5-order kinetic plot for the model bisimide methacrylate ester **3**. The linearity of this plot

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Scheme 4. Photodimerization of Bisimide Models

$R_1 = H$, $R_2 = $ ⟨phenyl⟩   **1**

$R_1 = H$, $R_2 = $ ⟨furyl⟩   **2**
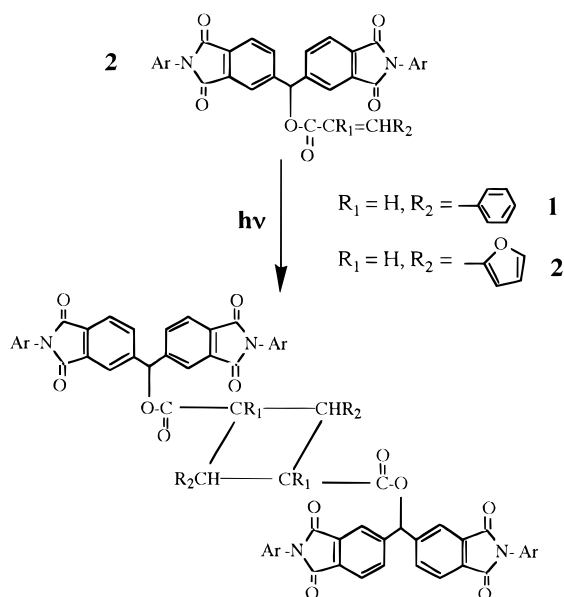
Scheme 5. Photopolymerization of Bisimide Models

$R_1 = H$, $R_2 = H$ **4**

$R_1 = CH_3$, $R_2 = H$ **3**

Figure 5. Changes of the ultraviolet spectrum of bisimide furylacrylate derivative **2** in chloroform upon UV irradiation.

Figure 6. Second-order kinetic plot for the model bisimide furylacrylate derivative **2**.

is considered to be the result of photopolymerization (see Scheme 5). In this case a conversion of 80% was obtained after 300 s of irradiation.

Bisimide Furylacrylate Ester in Solution. The ultraviolet spectrum of bisimide furylacrylate derivative **2** has a peak at about 310 nm, extending to about 400 nm in solution in chloroform. This model compound shows photosensitivity. The mechanism of its photochemical reaction is the same as that of the cinnamate derivative; the chemical structures of the two photosensitive groups are very similar.

The UV spectral absorbance near 310 nm decreased rapidly upon irradiation with the mercury lamp as shown in Figure 5. UV−visible spectral studies of bisimide model solutions suggest that aryl furylacrylate chromophores tend to aggregate significantly. The predominant photoreaction that takes place both in the film and in solution is 2+2 cycloaddition leading to cyclobutane formation. We do not observe any new absorption tailing beyond 300−350 nm, which could be
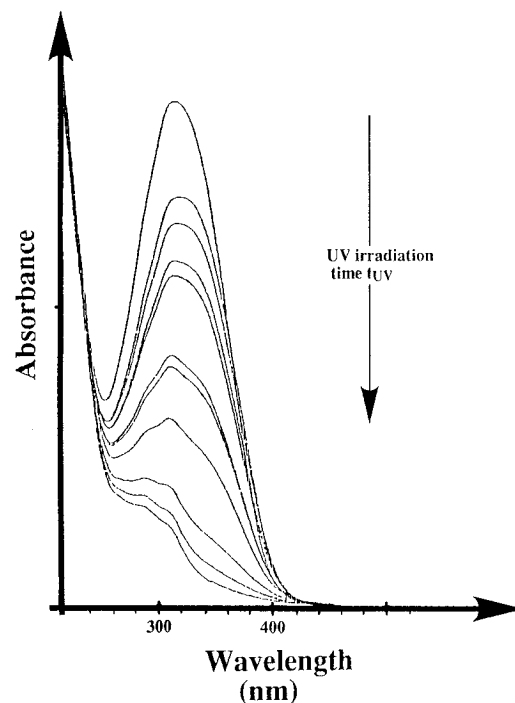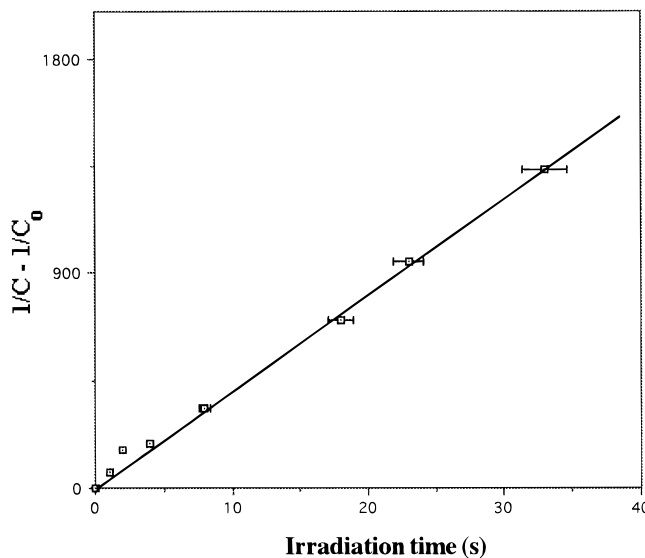
attributed to photo-Fries rearrangement products.[13] Fries product formation is essentially eliminated by irradiation at 365 nm where only aggregates are excited.[14]

Figure 6 (extracted from Figure 5) shows the second-order kinetic plot for the model bisimide furylacrylate derivative. The linearity of this plot is in good agreement with the formation of photodimers. The apparent rate constant ($k = 39.3$ L mol^{-1} s^{-1}) was determined from Figure 6. Irradiation for 23 s produces a conversion of 60% of the photoreactive groups.

We have found that the principal photochemical reaction upon irradiation of solutions and of cast films

(13) Creed, D.; Griffin, A. C.; Gross, J. R. D.; Vekataram, K. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 59.
(14) Singh, S.; Creed, D.; Hoyle, C. E. *Polym. Prepr. (ACS)* **1993**, *34*, 743.
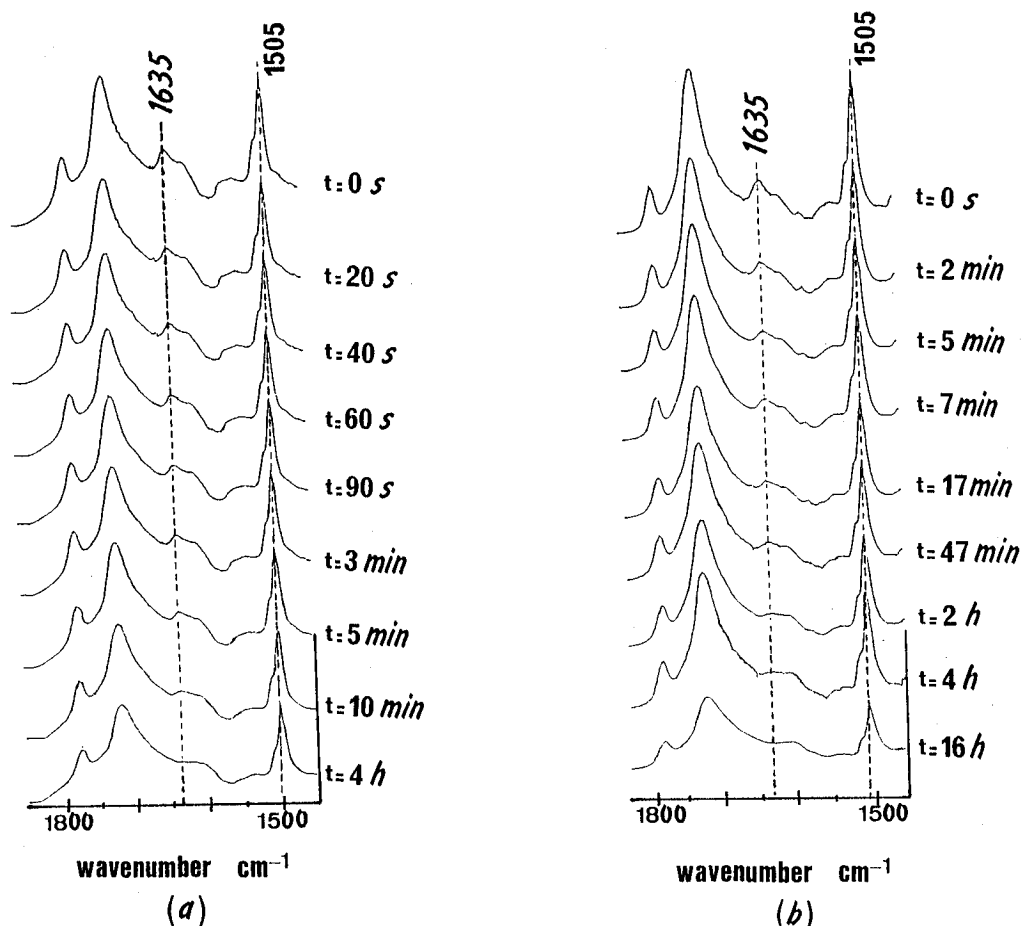
Figure 7. Change of IR spectrum of photosensitive polyimides: furylacrylate (a) and cinnamate (b) upon UV irradiation.

Table 1. Apparent Rate Data of the Photochemical Reactions of Photosensitive Bisimides

bisimide models	$10^3 r_p$ (mol L^{-1} s^{-1})	conversion (%)
1	2	95
2	5	95
3	8	100
4	9.5	100

of the bisimide cinnamate and furylacrylate ester models is the 2+2 photocycloaddition (see Scheme 4). The photo-Fries rearrangements of the aryl cinnamate or furylacrylate chromophores is avoided by irradiation at 365 nm. Especially, we report that the irradiation of the bisimide models results in a continuous loss of the absorption of the photoreactive chromophores, and the simultaneous buildup of a band at 300 nm as shown in Figure 5. This band with a maximum around 300 nm is due to the saturation of the furylacrylate double bond including cyclobutane ring formation.

The apparent rate of the photochemical reaction, r_p, which shows a maximum rate of disappearance of the vinyl group, is given by

$$r_p = C_0(\alpha_{t1} - \alpha_{t2})/(t_2 - t_1) \tag{7}$$

where $\alpha = C/C_0$.

The experimental results in Table 1 indicate that the photopolymerizable derivatives are more sensitive to UV irradiation than the photodimerizable ones. The interesting point is how similar all the rates are despite the apparent difference in reaction mechanism (one photon dimerization versus acrylate polymerization).

Photosensitive Polyimide Ester in the Solid State. Photosensitive polyimides, furylacrylate ester and cinnamate ester, were irradiated in the solid state by mercury lamp for various irradiation times. Polyimide furylacrylate ester and polyimide cinnamate ester films were prepared in similar conditions. The corresponding changes in the IR spectra are shown in Figure 7.

According to Figure 7, there is a detectable difference in photosensitivity between the two systems, the absorbance near 1635 cm^{-1} decreases much more rapidly in polyimide furylacrylate than polyimide cinnamate attesting to the higher reactivity of the furylacrylic substituent group. This decrease corresponds to the photoinduced chemical reaction of the C=C moiety (see Scheme 3), which results in the formation of cross-linking. Thus, the insoluble fraction of film samples increases with increasing irradiation time. However, reaction orders of 2 and 1.5 can no longer be verified for the respective polymers. A possible interpretation of this phenomenon is the decrease of the frequency factor in the reaction of the high molecular weight polymers. In short, increase in molecular weight makes the photodimerization difficult. In the case of bisimide furylacrylate and bisimide cinnamate models of these polyimides, the internal closeness of the ethylenic double bonds in the solid state is high due to the symmetrical nature of the bisimide models, and this leads to an efficient chemical reaction which, according to Bort,[12] is mostly a dimerization reaction. When the molecular weight increases, the internal closeness of the ethylenic double bonds decreases due to a fall in overall

mobility of the chains, thereby decreasing the efficiency of the cross-linking reactions. This effect is well documented in the work of Green et al.[15]

Using poly(vinyl 2-furylacrylate) and poly(vinyl 2-cinnamate), Tsuda[16] had shown that both polymers undergo photodimerization, and the first is more sensitive than the second, which is in good agreement with our results. The photochemistry of our PSPI furylacrylate and cinnamate derivatives is not understood well, and we cannot confirm the reaction order. The behavior at room temperature is rather complicated, and may be due to improper alignment and restricted movement of the potentially reactive double bonds (topochemical control). We suppose that the local photochemical behavior of the polymers is essentially similar to that of the bisimide models.

Conclusion

Four bisimide models corresponding to our four new soluble negative-type photosensitive polyimides have been prepared. These bisimide models have been photo-cross-linked by UV irradiation in the solid state and in NMP solution. The mechanism of the reaction between photoreactive groups has been found to present two possibilities, namely, the photodimerization and photopolymerization reactions. The furylacrylate and cinnamate react preferentially on irradiation at 365 nm to form the cycloaddition products, while the others (methacrylate and acrylate) undergo photopolymerization. Reaction orders of 2 and 1.5 have been verified. The photoreaction of the corresponding polymers have presented complicated behavior because of the restriction of mobility and improper alignment of photosensitive groups on the polymer side chains. Their reaction order could not be determined. In all cases, the sensitivity to UV light has been found to decrease in the following order: acrylate, methacrylate, furylacrylate, and cinnamate.

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