

# Polyethers Containing Coumarin Dimer Components in the Main Chain. II. Reversible Photocleavage and Photopolymerization

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**ABSTRACT:** Polyethers, containing coumarin dimer components in the main chain, were irradiated successively in 1,4-dioxane with 254 and 350 nm (or 300 nm) light to investigate their reversible photoreaction properties. The coumarin dimer components cleave symmetrically under 254 nm (photocleavage) to original dioxycoumarins. Irradiating the cleaved sample with 350 nm (or 300 nm) leads to polymerization of the dioxycoumarins via dimerization of the telechelic coumarin chromophores ( $\lambda_{\text{max}} = 320$  nm). The absorbances at 320 nm of the sample solution were used to trace the photoreactions. For both **5** and **6**, the maximum absorbance (ABS) and  $\Delta$ ABS increase with the number of cycles (one photocleavage followed with one photopolymerization). However, the degenerates (percent decrease of absorbance per cycle) of **5** (ca. 50%) are much greater than those of **6** with 4-methyl substitution (ca. 29%), which has been explained by the formation of coumarin dimer components which are difficult to cleave under 254 nm. Moreover, photocleavage (254 nm) is much faster than is photopolymerization (350 nm) for both **5** and **6** due to the high-energy intensity of 254 nm light. Addition of the photosensitizer, benzophenone, enhances the photopolymerization rate with the photocleavage rate remaining almost unchanged. 4-Methyl substitution in **6** results in an increased rate for both reactions which can be attributable to its electron-releasing property. Photopolymerization under 300 nm light is more effective than under 350 nm, suggesting that the absorbing efficiency under 300 nm should be greater since it overlaps with the absorption of coumarin chromophores (320 nm). © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1759–1768, 1997

**Key words:** polyether; coumarin dimer; photocleavage; dioxycoumarin; photopolymerization

## INTRODUCTION

Photosensitive polymers are often used in the fields of printing, inks,<sup>1,2</sup> and coatings.<sup>3</sup> Especially in electronics, the development of photosensitive polymers made the technology of the integrated

circuit (IC), the large-scale integrated circuit (LSI), and the very large scale integrated circuit (VLSI) so important that it caused the revolution in the field of calculators and many electronic machines. As a result, many laboratories still continue exploring the field of photosensitive polymers.

At present, photosensitive polymers are defined as those with photosensitive groups in the main or pedant chains, which polymerize (or crosslink) or cleave after irradiation with UV light (or electron beam) depending on whether it

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is of a negative or positive type.<sup>3</sup> In general, for the negative type, there are three kinds of photosensitive groups used widely, i.e., azide groups,<sup>4</sup> cinnamate groups,<sup>5</sup> and diazo groups.<sup>6</sup> Also, their solubility in a developer is greater for light-unexposed than for exposed areas, leading to the formation of patterns by removal of unexposed zones. Four-center-type photopolymerization and [2 + 2] photopolymerization in the solid state were studied in detail by Hasegawa.<sup>7-9</sup> Right now, many researchers are still trying to synthesize new and useful photosensitive polymers and to investigate their potential applications.

Coumarin, 2-chromenone, exists in trace amounts in many plants, particularly in some kind of fruits as a component in aromatic flavors.<sup>10</sup> In 1902, Ciamician and Silber found that coumarin dimerized on photoirradiation ( $\lambda_{\max} > 300$  nm) in ethanol or in an aqueous medium.<sup>11</sup> Since then, the photocyclodimerization of coumarin has received much attention among organic chemists and has been studied extensively by several groups from both the synthetic and mechanistic points of view.<sup>12-18</sup> Coumarin yields four types of dimers on photoirradiation, of which the product ratio is influenced predominantly by the multiplicity in the [2 + 2] photochemical reactions. The structures of these dimers are *anti* head-to-head, *anti* head-to-tail, *syn* head-to-head, and *syn* head-to-tail types. Moreover, Krauch and co-workers reported the cycloreversion (photocleavage) of an *anti* head-to-head coumarin dimer in dioxane into the starting coumarin upon photoirradiation with wavelengths shorter than 300 nm.<sup>14</sup>

Similarly, *o*-acetyllumbiferone derived from umbelliferone (7-hydroxycoumarin) readily photodimerizes to form an *anti* head-to-head *o*-acetyllumbiferone dimer in a dichloromethane solution.<sup>19</sup> Dicumarins have also been synthesized from the condensation of diacid chlorides with umbelliferone or 4-methylumbelliferone and their photopolymerization behavior under 350 nm has been studied in detail.<sup>20,21</sup> Moreover, 7-acryloyloxy-4-methylcoumarin has also been prepared from umbelliferone and copolymerized with *N*-(1-phenylethyl)acrylamide.<sup>22</sup> Under photoirradiation with UV light having  $\lambda_{\max} = 350$  nm, the copolymer crosslinks readily by cyclodimerization of pendant coumarin components. However, the coumarin dimer chromophores cycloreverse to the original coumarin chromophores under 254 nm light. This indicates that the photoreaction re-

versibility of coumarin chromophores is not influenced by its substitution at the 7-position.

Thymine bases with a long alkyl chain convert to photodimers upon irradiation with UV light near  $\lambda_{\max} = 288$  nm, which is known to have a lethal effect in biological systems.<sup>23</sup> However, the photodimerization is a reversible reaction and the photodimers are cleaved to starting thymines efficiently upon irradiation at 240 nm. This reversible and thermally stable photochromic system of thymine has been applied to a reversible photorecording system.<sup>24,25</sup> The polymers containing thymine bases have high resolution and high sensitivity when used as negative, positive, and chemical amplification photoresists for microlithography.<sup>26-29</sup> We have synthesized coumarins with a long alkyl chain by the condensation of umbelliferone with alkanoyl chlorides, and their reversible photocyclodimerization behaviors have been investigated in detail after dispersing in poly(vinyl acetate).<sup>30</sup> Reversible photocleavage and photocrosslinking of copolymers derived from 7-acryloyloxy-4-methylcoumarin and acrylates have been investigated in the film state.<sup>31</sup>

In this work, reversible photocleavage (254 nm) and photopolymerization (300 or 350 nm) of polyethers containing coumarin dimer components were investigated in 1,4-dioxane, especially the influence of the composition, irradiation wavelength, and photosensitizer, benzophenone.

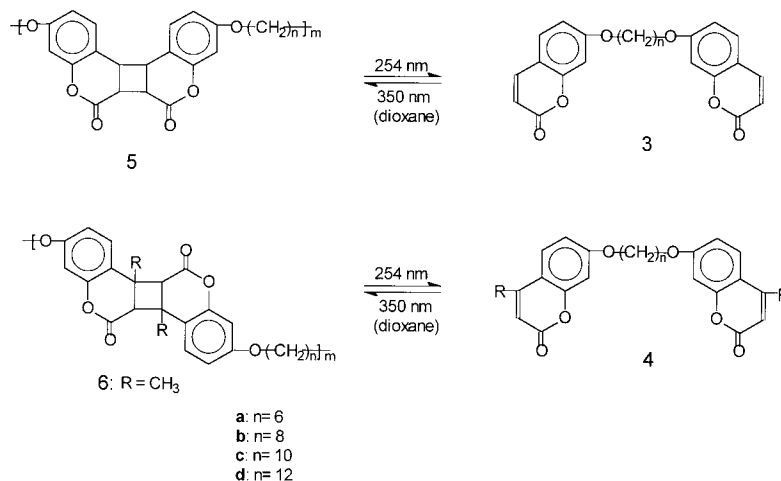
## EXPERIMENTAL

### Preparation of Polyethers 5 and 6<sup>32</sup>

Photopolymerization of 7,7'-(polymethylenedioxy) dicoumarins in dichloromethane results in polyethers **5** and **6** with reduced viscosities between 0.05 and 0.23 dL/g.<sup>32</sup> The configurations of the polyethers were characterized by <sup>1</sup>H-NMR spectra. For unsubstituted (in cyclobutane ring) polyethers **5**, the coumarin dimer linkages are of *syn* and *anti* head-to-head structure. However, they are *syn* and *anti* head-to-tail for methyl-substituted polyethers **6**.

### Repeated Photocleavage and Photopolymerization of 5 and 6 (Scheme 1)

The solutions used for photocleavage (254 nm) and photopolymerization (300 or 350 nm) were prepared by dissolving polyethers in 1,4-dioxane



Scheme 1

( $3 \times 10^{-5} M$  repeating unit). After purging with dried nitrogen, it was sealed into a quartz UV cell and then put into a photochemical chamber reactor, Model RPR-100, from Rayonet, equipped with 16 UV lamps. The photocleavage, a symmetric split of cyclobutane of coumarin dimer linkage, was first conducted by irradiating with 254 nm light. Then, after exchanging with 300 or 350 nm UV lamps, the cleaved sample was then photopolymerized through dimerization of telechelic coumarin chromophores. The photoreactions were traced by recording the absorbance at 320 nm, which is the maximum absorption of coumarin groups, using a UV-visible spectrophotometer, Model UV-160A, from Shimadzu. The photocleavage and photopolymerization cycle was repeated several times to investigate their reversibility. In addition, the photoreactions were conducted both in the presence and absence of benzophenone to elucidate the role of the photosensitizer.

## RESULTS AND DISCUSSION

In solution, coumarin readily dimerizes to the coumarin dimer in high yield under photoirradiation with a UV light of  $\lambda_{\max} > 300$  nm, especially in the presence of the photosensitizer benzophenone.<sup>1</sup> 4-Methylcoumarin also exhibits photodimerization reactivity similar to that of coumarin and both have been employed in the photocrosslinking reaction.<sup>33,34</sup> Upon irradiation with a shorter UV light ( $\lambda_{\max} = 254$  nm), the coumarin dimer cycloreverses to the original coumarins. Photoreactive copolymers containing 4-methylcoumarin groups

were prepared from 7-acryloyloxy-4-methylcoumarin and *N*-(1-phenylethyl)acrylamide.<sup>22</sup> They also showed reversible photocrosslinking through reversible photodimerization of pendant 4-methylcoumarin chromophores. However, upon irradiation with 254 nm light, not only photocleavage but also photodimerization occurs and the reaction reaches equilibrium.

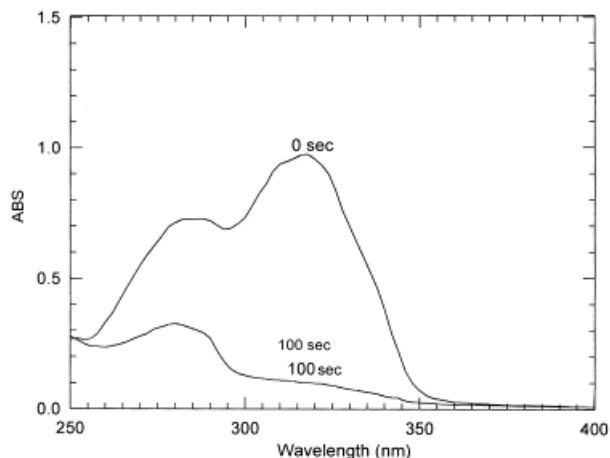
The photodimerization of coumarin chromophores results in a decrease of absorbance at  $\lambda_{\max} = 320$  nm, which increases again by symmetric splitting of the photodimer. In this work, UV lights with  $\lambda_{\max} = 350$  nm (or 300 nm) and  $\lambda_{\max} = 254$  nm were used for the photodimerization and photocleavage reaction, respectively. Within a Rayonet photochemical chamber reactor equipped with 16 UV lamps, the intensity readings at the reaction site are 7.05 mJ/cm<sup>2</sup> s (350 nm), 6.17 mJ/cm<sup>2</sup> s (300 nm), and 10.28 mJ/cm<sup>2</sup> s (254 nm), as measured with UV meters. Systems with benzophenone are compared with those without it to investigate the role of the photosensitizer.

As shown in Figure 1, the UV spectrum of polyether **6b** from 7,7'-(octamethylenedioxy)di-4-methylcoumarin shows two absorptions at 280 and 320 nm. The bands at 280 and 320 nm can be, respectively, attributed to the B band ( $\pi - \pi^*$ ) and the R band ( $n - \pi^*$ ) absorptions caused by 4-methylcoumarin chromophores.<sup>35</sup> Upon irradiation with 254 nm light, the coumarin dimer groups are symmetrically split to the original 4-methylcoumarin (photocleavage) as shown in Scheme 1. Followed by irradiating with 350 nm (or 300 nm) light, the absorption at 320 nm de-

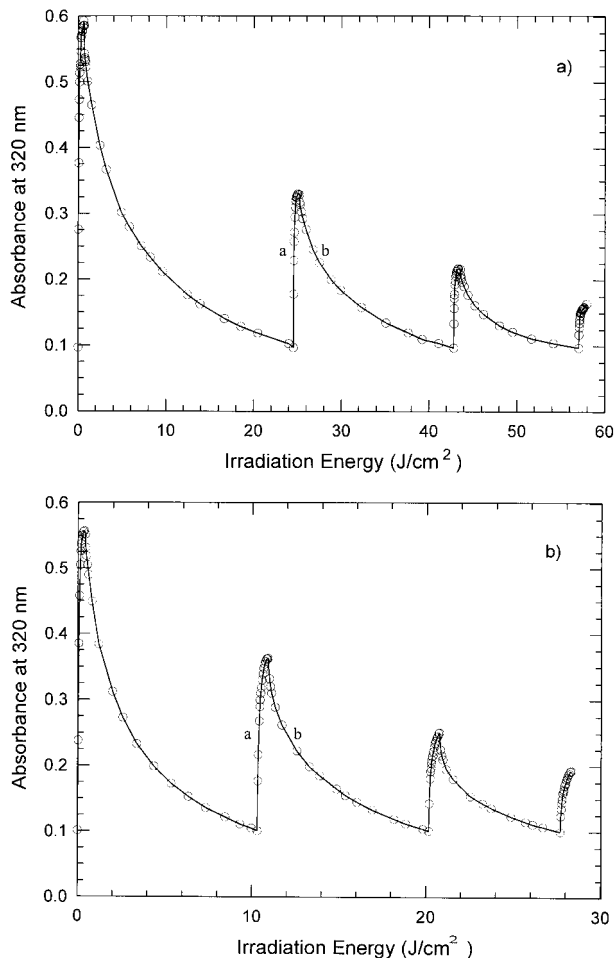
creases gradually to an equilibrium value (Fig. 2) due to the dimerization of pendant 4-methylcoumarin chromophores (photopolymerization). Using these characteristics, reversible photoreactions of the polyethers (**5**, **6**) can be traced by recording their absorption variation at 320 nm.

### Photoreactions of **5b** and **5d** Without Benzophenone

For convenience of comparison, one photocleavage followed by one photopolymerization is defined as one cycle. The maximum absorbance (Max. ABS: the greatest absorbance at the beginning of photopolymerization),  $\Delta$ ABS (absorbance decrease during one photopolymerization), photocleavage energy and photopolymerization energy (energy required for unit absorbance change), and degenerate (percent decrease of the maximum absorbance for the successive cycle) are summarized in Tables I and II. Figure 2(a) illustrates the absorbance variation of **5b** in 1,4-dioxane during successive photocleavage (254 nm) and photopolymerization (350 nm) cycles. For the initial cycle, the absorbance at 315 nm increases abruptly from 0.097 to 0.593 upon photocleavage, followed by a smooth decrease to the original 0.097 upon photopolymerization. For the second cycle, the maximum absorbance increased from 0.097 to only 0.330 compared to 0.593 of the first cycle, suggesting that some of the cyclobutane rings formed during the first cycle (photopolymerization) cannot be cleaved by 254 nm light. This seems to be due to the formation of stable isomers of coumarin



**Figure 1** UV spectral change of **6b** in 1,4-dioxane ( $3 \times 10^{-5} M$ ) under irradiation with 254 nm light.



**Figure 2** Absorbance change at 320 nm of **5b** in 1,4-dioxane ( $3 \times 10^{-5} M$ ) under repeated irradiation with (path a) 254 nm and (path b) 350 nm light. (a) Without benzophenone; (b) with equivalent benzophenone.

dimer components that are difficult to be split by light. On photopolymerization, the absorbance returns to the original 0.097 again, indicating that the lactone rings disappear completely to form cyclobutane groups in the main chain. The following cycles show similar behaviors, i.e., the maximum ABS and  $\Delta$ ABS decrease with the number of cycles. The degenerates remain around 50% for two to four cycles, suggesting formation of half-isomers difficult to cleave during previous photopolymerization.

The energies required for photocleavage and photopolymerization to cause a unit absorbance change are estimated from the irradiation energy and  $\Delta$ ABS (irradiation energy/ $\Delta$ ABS). As shown in Table I, the photocleavage energies ( $1.24$ – $14.9 J/cm^2$ ) are very low compared to those

**Table I Photocleavage (254 nm) and Photopolymerization (350 nm) of 5b and 5d in 1,4-Dioxane**

|                                                            | <b>5b</b>                     |                  |                  |                  | <b>5d</b>        |                  |                  |                  |
|------------------------------------------------------------|-------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|                                                            | Cycles                        |                  |                  |                  |                  |                  |                  |                  |
|                                                            | 1                             | 2                | 3                | 4                | 1                | 2                | 3                | 4                |
| Max. ABS <sup>b</sup>                                      | 0.593<br>(0.557) <sup>c</sup> | 0.33<br>(0.363)  | 0.217<br>(0.251) | 0.164<br>(0.193) | 0.584<br>(0.703) | 0.347<br>(0.143) | 0.219<br>(0.233) | 0.136<br>(0.169) |
| $\Delta$ ABS <sup>d</sup>                                  | 0.496<br>(0.456)              | 0.233<br>(0.262) | 0.119<br>(0.150) | 0.062<br>(0.092) | 0.492<br>(0.601) | 0.255<br>(0.311) | 0.127<br>(0.131) | 0.044<br>(0.067) |
| Degenerate (%) <sup>e</sup>                                | —                             | 53.0<br>(41.9)   | 48.5<br>(42.7)   | 48.3<br>(38.7)   | —                | 48.2<br>(48.2)   | 50.2<br>(57.7)   | 65.4<br>(50.0)   |
| Photocleavage energy<br>(J/cm <sup>2</sup> ) <sup>f</sup>  | 1.24<br>(0.79)                | 2.20<br>(2.35)   | 4.74<br>(4.10)   | 14.9<br>(6.69)   | 0.83<br>(0.39)   | 1.81<br>(2.47)   | 4.85<br>(4.76)   | 14.0<br>(16.1)   |
| Polymerization energy<br>(J/cm <sup>2</sup> ) <sup>f</sup> | 48.3<br>(21.8)                | 75.6<br>(35.3)   | 114.9<br>(46.2)  | —<br>—           | 46.9<br>(18.1)   | 71.6<br>(34.4)   | 103.9<br>(48.4)  | —<br>—           |

<sup>a</sup> One photocleavage (254 nm) followed with a photopolymerization (350 nm) is defined as one cycle.

<sup>b</sup> Max. ABS: maximum absorbance within one cycle.

<sup>c</sup> The values in the parentheses are for those with benzophenone ( $3 \times 10^{-5} M$ ).

<sup>d</sup> Absorbance difference between the maximum ABS and minimum ABS within one cycle.

<sup>e</sup> Degenerate:  $D_{n+1} = \{1 - [(\text{Max. ABS})_{n+1}/(\text{Max. ABS})_n]\} \times 100\%$ ;  $n$ : cycle.

<sup>f</sup> The energy required to cause unit absorbance change at 315 nm during photocleavage or photopolymerization, i.e., irradiation energy/ $\Delta$ ABS.

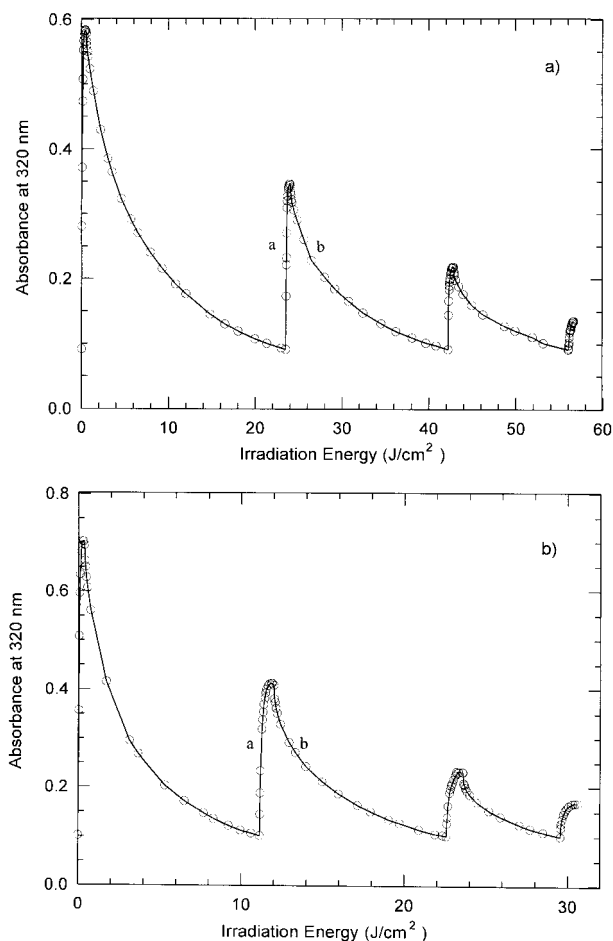
**Table II Photocleavage (254 nm) and Photopolymerization (350 nm) of 6b and 6d in 1,4-Dioxane**

|                                                            | <b>6b</b>                     |                  |                  |                  | <b>6d</b>        |                  |                  |                  |
|------------------------------------------------------------|-------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|                                                            | Cycles                        |                  |                  |                  |                  |                  |                  |                  |
|                                                            | 1                             | 2                | 3                | 4                | 1                | 2                | 3                | 4                |
| Max. ABS <sup>b</sup>                                      | 1.339<br>(1.089) <sup>c</sup> | 0.958<br>(0.771) | 0.713<br>(0.498) | 0.535<br>(0.335) | 0.731<br>(0.782) | 0.551<br>(0.408) | 0.419<br>(0.219) | 0.316<br>(0.150) |
| $\Delta$ ABS <sup>d</sup>                                  | 1.244<br>(1.004)              | 0.863<br>(0.686) | 0.618<br>(0.413) | 0.440<br>(0.249) | 0.640<br>(0.686) | 0.460<br>(0.312) | 0.328<br>(0.123) | 0.225<br>(0.054) |
| Degenerate (%) <sup>e</sup>                                | —                             | 30.5<br>(32.3)   | 28.4<br>(39.3)   | 28.2<br>(40.0)   | —                | 28.4<br>(54.5)   | 28.6<br>(60.6)   | 31.2<br>(56.1)   |
| Photocleavage energy<br>(J/cm <sup>2</sup> ) <sup>f</sup>  | 0.37<br>(0.61)                | 0.59<br>(1.12)   | 0.91<br>(1.86)   | 1.34<br>(2.47)   | 0.64<br>(1.91)   | 1.00<br>(3.95)   | 1.64<br>(8.34)   | 2.96<br>(18.1)   |
| Polymerization energy<br>(J/cm <sup>2</sup> ) <sup>f</sup> | 11.4<br>(12.1)                | 13.6<br>(17.6)   | 19.1<br>(24.4)   | —<br>(29.3)      | 17.2<br>(19.2)   | 24.7<br>(29.5)   | 36.3<br>(42.7)   | —<br>—           |

<sup>a-f</sup> See footnotes a–f to Table I.

of photopolymerization ( $48.3\text{--}114.9\text{ J/cm}^2$ ), indicating that photocleavage under  $254\text{ nm}$  is much faster than is photopolymerization ( $350\text{ nm}$ ). This should be attributable to the higher energy of the  $254\text{ nm}$  light ( $10.28\text{ mJ/cm}^2\text{ s}$ ) than that of the  $350\text{ nm}$  light ( $7.05\text{ mJ/cm}^2\text{ s}$ ). However, both energies increase with the number of cycles, i.e., from  $1.24$  and  $48.3\text{ J/cm}^2$  to  $14.9$  and  $114.9\text{ J/cm}^2$  for photocleavage and photopolymerization, respectively. This means that both rates diminish with the number of cycles. Clearly, this is caused by the decrease in concentration of photoreactive cyclobutane and lactone rings, since the coumarin dimer components which are difficult to cleave accumulate with the number of cycles.

Polyethers **5d** exhibit very similar behaviors as to those of **5b** as shown in Table I and Figure 3(a). The maximum ABS and  $\Delta$ ABS decrease



**Figure 3** Absorbance change at  $320\text{ nm}$  of **5d** in 1,4-dioxane ( $3 \times 10^{-5}M$ ) under repeated irradiation with (path a)  $254\text{ nm}$  and (path b)  $350\text{ nm}$  light. (a) Without benzophenone; (b) with equivalent benzophenone.

from  $0.584$  and  $0.492$  to  $0.136$  and  $0.044$ , respectively, within cycles one to four. Also, the degenerates increase slightly from  $48.2$  to  $65.4\%$ . The photocleavage ( $0.83\text{--}14.0\text{ J/cm}^2$ ) and photopolymerization energies ( $46.9\text{--}103.9\text{ J/cm}^2$ ) are comparable to those of **5b** and both increase with the number of cycles due to the same reason mentioned above.

### Photoreactions of **5b** and **5d** in the Presence of Benzophenone

It is well known that photosensitizers are an effective energy transfer intermediate in photochemical reaction systems. Therefore, it is interesting to investigate the influence of a photosensitizer on our system from both academic and practical viewpoints. In this work, benzophenone was employed as a triplet photosensitizer and the concentration was  $3 \times 10^{-5}M$ , which is equal to that of a repeating unit of polyethers.

For **5b** and **5d**, addition of benzophenone exhibits little influence on the maximum ABS,  $\Delta$ ABS, degenerate, and photocleavage energy, as can be seen from the values in the parentheses of Table I. However, the photopolymerization energy decreases significantly upon the addition of benzophenone as shown in Figure 2(b) and Figure 3(b). For example, for **5b** and **5d** without benzophenone, the energies in the first cycle are  $48.3$  and  $46.9\text{ J/cm}^2$  compared to  $21.8$  and  $18.1\text{ J/cm}^2$  in the presence of benzophenone, respectively. The following cycles show the same trend, indicating that benzophenone enhances the photopolymerization rate significantly. However, its presence exhibits little influence on the photocleavage rate because the photocleavage energies remain almost unchanged except that for **5b** in the fourth cycle ( $6.69\text{ J/cm}^2$  compared to  $14.9\text{ J/cm}^2$ ). This result can be explained by the greater energy-transfer efficiency of benzophenone under  $350\text{ nm}$  than under  $2504\text{ nm}$  light.

### Photoreactions of **6b** and **6d** Without Benzophenone

The structures of polyethers **6** are head-to-tail in comparison to the head-to-head structures of polyethers **5**.<sup>32</sup> Moreover, polyethers **6** possess methyl substituents in the cyclobutane rings. These methyl groups should play a role in determining the reactivity of the photoreaction. As shown in

**Table II Photocleavage (254 nm) and Photopolymerization (350 nm) of 6b and 6d in 1,4-Dioxane**

|                                                            | <b>6b</b>                     |                  |                  |                  | <b>6d</b>        |                  |                  |                  |
|------------------------------------------------------------|-------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|                                                            | Cycles                        |                  |                  |                  |                  |                  |                  |                  |
|                                                            | 1                             | 2                | 3                | 4                | 1                | 2                | 3                | 4                |
| Max. ABS <sup>b</sup>                                      | 1.339<br>(1.089) <sup>c</sup> | 0.958<br>(0.771) | 0.713<br>(0.498) | 0.535<br>(0.335) | 0.731<br>(0.782) | 0.551<br>(0.408) | 0.419<br>(0.219) | 0.316<br>(0.150) |
| $\Delta$ ABS <sup>d</sup>                                  | 1.244<br>(1.004)              | 0.863<br>(0.686) | 0.618<br>(0.413) | 0.440<br>(0.249) | 0.640<br>(0.686) | 0.460<br>(0.312) | 0.328<br>(0.123) | 0.225<br>(0.054) |
| Degenerate (%) <sup>e</sup>                                | —                             | 30.5<br>(32.3)   | 28.4<br>(39.3)   | 28.2<br>(40.0)   | —                | 28.4<br>(54.5)   | 28.6<br>(60.6)   | 31.2<br>(56.1)   |
| Photocleavage energy<br>(J/cm <sup>2</sup> ) <sup>f</sup>  | 0.37<br>(0.61)                | 0.59<br>(1.12)   | 0.91<br>(1.86)   | 1.34<br>(2.47)   | 0.64<br>(1.91)   | 1.00<br>(3.95)   | 1.64<br>(8.34)   | 2.96<br>(18.1)   |
| Polymerization energy<br>(J/cm <sup>2</sup> ) <sup>f</sup> | 11.4<br>(12.1)                | 13.6<br>(17.6)   | 19.1<br>(24.4)   | —<br>(29.3)      | 17.2<br>(19.2)   | 24.7<br>(29.5)   | 36.3<br>(42.7)   | —<br>—           |

<sup>a–f</sup> See footnotes a–f to Table I.

Table II and Figures 4(a) and 5(a), for **6b** and **6d**, both maximum ABS and  $\Delta$ ABS decrease with the number of cycles, which is very similar to polyethers **5**. However, the degenerates are around 29% regardless of number of cycles and is much lower than those of **5b** and **5d** (ca. 50%). This implies the formation of ca. 29% coumarin dimer components (at previous photopolymerization) that are difficult to cleave under 254 nm. Moreover, photocleavage and photopolymerization energies gradually increase with the number of cycles for both **6b** and **6d**, indicating that both rates decrease with the number of cycles due to the decrease in the concentration of photoreactive cyclobutane and lactone rings. It is also found that, for each cycle, the photopolymerization energy (11.4–19.1 J/cm<sup>2</sup> and 17.2–36.3 J/cm<sup>2</sup> for **6b** and **6d**, respectively) is much greater than is the photocleavage energy (0.37–1.34 J/cm<sup>2</sup> and 0.64–2.96 J/cm<sup>2</sup>), suggesting that the photocleavage reaction is much faster than is photopolymerization, which is attributable to the higher energy of the 254 nm light as mentioned above.

Furthermore, both energies of **6b** (photocleavage: 0.37–1.34 J/cm<sup>2</sup>; photopolymerization: 11.4–19.1 J/cm<sup>2</sup>) are much lower than those of **5b** (photocleavage: 1.24–14.9 J/cm<sup>2</sup>; photopolymerization: 48.3–114.9 J/cm<sup>2</sup>). The result is presumably due to 4-methyl substitution in the cyclo-

butane rings and coumarin chromophores, i.e., methyl groups enhance both photocleavage and photopolymerization rates through an electron-releasing process. Polyether **6d** also exhibits similar trends in comparison with polyether **5d**.

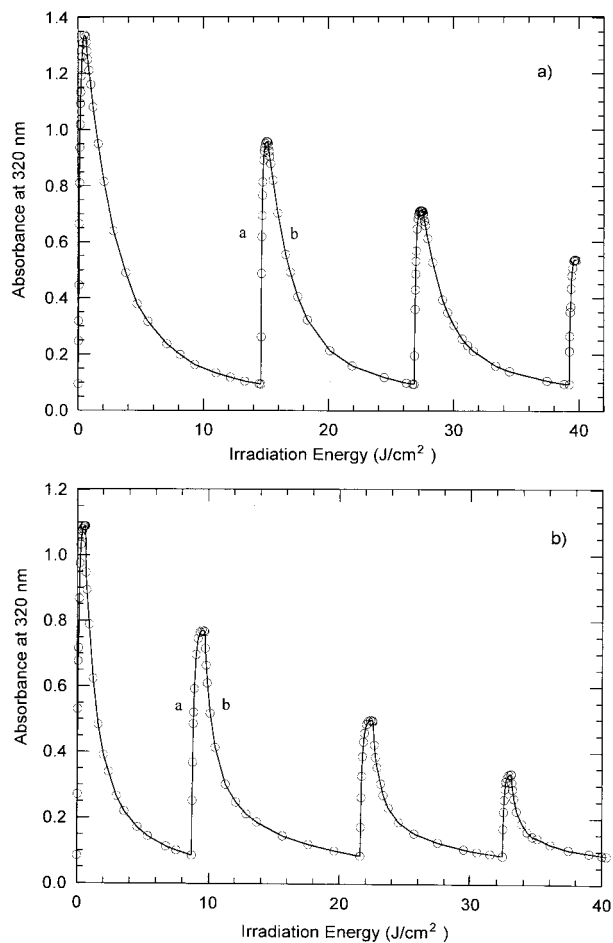
#### Photoreactions of 6b and 6d in the Presence of Benzophenone

As shown in Table II and Figures 4 and 5, addition of benzophenone exhibits a significant influence on the degenerates, photocleavage, and photopolymerization. For **6b**, the degenerates are increased slightly from 28.2–30.5% to 32–40%, and for **6d**, they are increased from 28.4–31.2% to 54.5–60.6%. In the presence of benzophenone, the ratio of coumarin dimer components that are difficult to cleave under 254 nm is increased. Furthermore, contrary to **5b** and **5d**, both photocleavage and photopolymerization energies are greater than those without benzophenone. For example, cleavage and polymerization energies of **6b** increase from 0.37–1.34 and 11.4–19.1 J/cm<sup>2</sup> to 0.61–2.47 and 12.1–29.3 J/cm<sup>2</sup>, respectively (Table II). Those for **6d** increase from 0.64–2.96 and 17.2–36.3 J/cm<sup>2</sup> to 1.91–18.1 and 19.2–42.7 J/cm<sup>2</sup>, respectively. In the presence of the triplet sensitizer, benzophenone, photodimerization of coumarin results exclusively in an *anti* head-to-

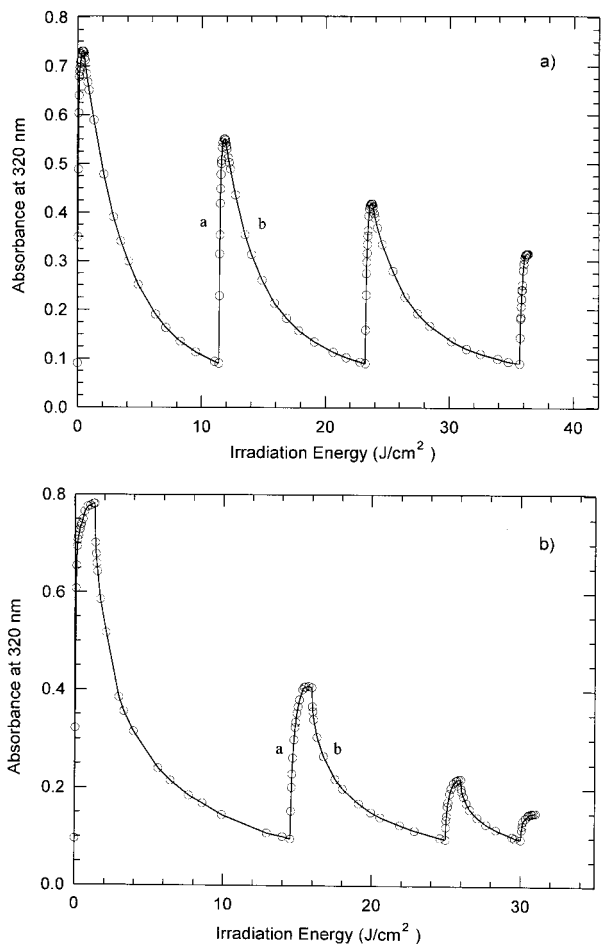
head coumarin dimer in both polar and nonpolar solvents.<sup>13</sup> The structures of polyethers **5** are also head-to-head.<sup>32</sup> However, the structures of polyethers **6** are mainly head-to-tail due to 4-methyl substitution. It is evident that benzophenone is not only unable to enhance the photoreaction of polyether **6** containing 4-methyl groups, but also increases the photocleavage and photopolymerization energies by absorbing the light.

### Influence of Wavelength in Photopolymerization

The **6b** solution is first irradiated with 254 nm, then it is photopolymerized under 300 or 350 nm after separating into two quartz cells. As shown in Table III, the photocleavage energy ( $0.53 \text{ J/cm}^2$ ) is much lower than is photopolymerization



**Figure 4** Absorbance change at 320 nm of **6b** in 1,4-dioxane ( $3 \times 10^{-5} M$ ) under repeated irradiation with (path a) 254 nm and (path b) 350 nm light. (a) Without benzophenone; (b) with equivalent benzophenone.



**Figure 5** Absorbance change at 320 nm of **6d** in 1,4-dioxane ( $3 \times 10^{-5} M$ ) under repeated irradiation with (path a) 254 nm and (path b) 350 nm light. (a) Without benzophenone; (b) with equivalent benzophenone.

( $5.29 \text{ J/cm}^2$  under 300 nm and  $8.41 \text{ J/cm}^2$  under 350 nm). Under both wavelengths (350 and 300 nm), photopolymerization rates are much lower than that of photocleavage under 254 nm. Moreover, from the fact that the required energy is greater for 350 nm, clearly, **6b** photopolymerizes faster under 300 nm than under 350 nm. This should be attributable to the enhanced absorbing efficiency under 300 nm since it overlaps partially with the absorption of photoreactive coumarin chromophores ( $\lambda_{\text{max}} = 320 \text{ nm}$ ). However, using 300 nm light as the photopolymerization energy source, the degenerate is very high (80%) as shown in Table IV and Figure 6. This can be explained by the formation of a higher ratio of coumarin dimer components that are difficult to cleave during photopolymerization under 300 nm



**Table III Influence of Irradiation Wavelength on Photoreaction of 6b in 1,4-Dioxane<sup>a</sup>**

|                                                              | Photocleavage<br>254 nm | Photopolymerization |        |
|--------------------------------------------------------------|-------------------------|---------------------|--------|
|                                                              |                         | 300 nm              | 350 nm |
| $\Delta$ ABS <sup>b</sup>                                    | 0.974                   | 0.968               | 0.976  |
| Irradiation energy (J/cm <sup>2</sup> ) <sup>c</sup>         | 0.516                   | 5.12                | 8.21   |
| Photocleavage energy (J/cm <sup>2</sup> ) <sup>b</sup>       | 0.53                    | —                   | —      |
| Photopolymerization energy (J/cm <sup>2</sup> ) <sup>b</sup> | —                       | 5.29                | 8.41   |

<sup>a</sup> The solution of **6b** in 1,4-dioxane ( $3 \times 10^{-5} M$ ) was first irradiated with 254 nm light, then irradiated with 300 nm or 350 nm light.

<sup>b</sup> The definitions are the same as those in Tables I and II.

<sup>c</sup> Accumulated irradiation energy during one photocleavage or photopolymerization.

light. Unfortunately, the structures of these coumarin dimer isomers have not been elucidated so far, but their identifications are in progress.

## CONCLUSION

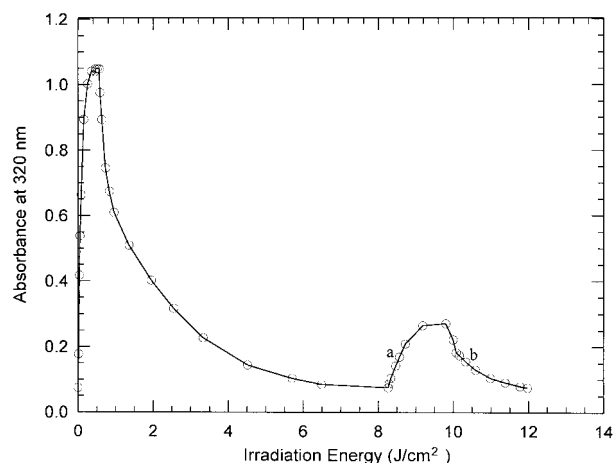
Polyethers containing coumarin dimer components in the main chain were irradiated repeatedly with 254 and 350 nm (or 300 nm) light to investigate their reversible photoreaction properties. For polyethers **5** and **6**, the maximum absorbance (ABS) and  $\Delta$ ABS increase with the number of cycles. However, the degenerates of **5** (ca. 50%) are much greater than of **6** with 4-methyl substitution (ca. 29%), which has been explained by the formation of a corresponding percent of coumarin dimer components difficult to

photocleave (254 nm) during photopolymerization. Moreover, photocleavage (254 nm) is much faster than is photopolymerization (350 nm) for both **5** and **6** due to the greater energy of 254 nm light. Addition of a triplet photosensitizer (benzophenone) enhances the photopolymerization rate with the photocleavage rate remaining almost unchanged. 4-Methyl substitution in **6** results in an increased rate for both reactions which can be attributable to its electron-releasing property. Photopolymerization is faster under 300 nm light than under 350 nm, suggesting that absorption under 300 nm should be more efficient since it overlaps partially with the absorption of coumarin chromophores ( $\lambda_{\max} = 320$  nm).

**Table IV Photocleavage (254 nm) and Photopolymerization (300 nm) of 6b in 1,4-Dioxane**

|                                                              | Cycles <sup>a</sup> |       |
|--------------------------------------------------------------|---------------------|-------|
|                                                              | 1                   | 2     |
| Max. ABS <sup>b</sup>                                        | 1.049               | 0.272 |
| $\Delta$ ABS <sup>c</sup>                                    | 0.974               | 0.196 |
| Degenerate (%) <sup>d</sup>                                  | —                   | 80    |
| Photocleavage energy (J/cm <sup>2</sup> ) <sup>e</sup>       | 0.58                | 7.85  |
| Photopolymerization energy (J/cm <sup>2</sup> ) <sup>c</sup> | 7.90                | 11.09 |

<sup>a-e</sup> See footnotes a–e to Table I.



**Figure 6** Absorbance change at 320 nm of **6b** in 1,4-dioxane ( $3 \times 10^{-5} M$ ) under repeated irradiation with (path a) 254 nm and (path b) 300 nm light.

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## REFERENCES

1. S. P. Pappas, Ed., *UV Curing: Science and Technology*, Marketing Corp., Norwalk, CT, 1985, Vol. 2.
2. G. A. Senich and R. E. Florin, *J. Macromol. Sci. Rev. Macromol. Chem. C*, **24**, 239 (1986).
3. C. G. Roffey, *Photopolymerization of Surface Coating*, Wiley-Interscience, New York, 1982.
4. Kodak Co., U.S. Pat. 30963111 (1963).
5. F. I. Sonntag, R. Srinivasan, *Technical Paper 1st Technical Conference on Photopolymers*, SPE, 1967, p. 163.
6. W. E. Lee, J. G. Calvert, and E. W. Malmberg, *J. Am. Chem. Soc.*, **83**, (1928).
7. M. Hasegawa, *Adv. Polym. Sci.*, **42**, 1 (1982).
8. M. Hasegawa, *Chem. Rev.*, **83**, 507 (1983).
9. M. Hasegawa, *Comp. Polym. Sci.*, **5**, 217 (1989).
10. Sethna and Shah, *Chem. Rev.*, 1 (1945).
11. G. Ciamician and P. Silber, *Chem. Ber.*, **35**, 4128 (1902).
12. G. O. Schenk, I. von Wilucki, and C. H. Krauch, *Chem. Ber.*, **95**, 1409 (1962).
13. G. S. Hammond, C. A. Stout, and A. A. Lamola, *J. Am. Chem. Soc.*, **86**, 3103 (1964).
14. C. H. Krauch, S. Farid, and G. O. Schenk, *Chem. Ber.*, **99**, 625 (1966).
15. H. Morrison, H. Curtis, and T. McDowell, *J. Am. Chem. Soc.*, **88**, 5415 (1966).
16. R. Hoffman, P. Wells, and H. Morrison, *J. Org. Chem.*, **36**, 102 (1971).
17. N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings, Menlo Park, CA, 1978.
18. K. Muthuramu and V. Ramamurthy, *J. Org. Chem.*, **47**, 3976 (1982).
19. L. H. Leenders, E. Schouteden, and F. C. De Schryver, *J. Org. Chem.*, **38**, 957 (1973).
20. Y. Chen and R.-T. Hong, *J. Polym. Res.*, **1**(3), 185 (1994).
21. Y. Chen and R.-T. Hong, to appear.
22. Y. Chen and J.-D. Wu, *J. Polym. Sci. Part A Polym. Chem.*, **32**, 1867 (1994).
23. S. Y. Wang, Ed., *Photochemistry and Photobiology of Nucleic Acids*, Academic Press, New York, 1976, Vols. I and II.
24. Y. Inaki, Y. Wang, M. Kubo, and K. Takemoto, *J. Photopolym. Sci. Tech.*, **4**, 259 (1991).
25. Y. Inaki, *Polym. News*, **17**, 367 (1992).
26. Y. Inaki and K. Takemoto, in *Current Topics in Polymer Science*, R. M. Ottenbrite, L. A. Utracki, and S. Inoue, Eds., Hanser, Munich, 1987, Vol. 1, p. 79.
27. K. Takemoto and Y. Inaki, in *Functional Polymers and Monomers*, K. Takemoto, Y. Inaki, and R. M. Ottenbrite, Eds., Marcel Dekker, New York, 1987, p. 149.
28. Y. Inaki, M. J. Moghaddam, and K. Takemoto, in *Polymers in Microlithography*, E. Reichmans, S. MacDonald, and T. Iwayanagi, Eds., ACS Symposium Series 412, American Chemical Society, Washington, DC, 1989, p. 303.
29. H. Horito, Y. Inaki, and K. Takemoto, *J. Photopolym. Sci. Tech.*, **4**, 33 (1991).
30. Y. Chen and C.-F. Chou, *J. Polym. Sci. Part A Polym. Chem.*, **33**, 2705 (1995).
31. Y. Chen and J.-L. Geh, *Polymer*, **37**(20), 4481 (1996).
32. Y. Chen and C.-S. Jean, *J. Appl. Polym. Sci.* part I of this article, to appear.
33. G. A. Delzenne and U. L. Laridon, *Ind. Chim. Belg.*, 373 (1967).
34. Y. Chujo, K. Sada, and T. Saegusa, *Macromolecules*, **23**, 2693 (1990).
35. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 5th ed., Wiley, New York, 1991, Chap. 7.