

# Copolymers derived from 7-acryloyloxy-4-methylcoumarin and acrylates: 2. Reversible photocrosslinking and photocleavage

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Photosensitive copolyacrylates with pendant 4-methylcoumarin chromophores were derived from 7-acryloyloxy-4-methylcoumarin and various acrylates (methyl methacrylate: MMA, methyl acrylate: MA, ethyl acrylate: EA, butyl acrylate: BA). The pendant 4-methylcoumarins dimerize under irradiation with 300 nm or 350 nm light (photocrosslinking), and the dimers split into original 4-methylcoumarins under 254 nm light (photocleavage). The reversible photocrosslinking (300 nm or 350 nm) and photocleaving (254 nm) reactions of these copolymers were investigated in the film state by tracing their ultraviolet (u.v.) absorption at 310 nm (maximum absorption of 4-methylcoumarin chromophore). These photochemical reactions are mainly affected by the copolymer composition, wavelength of irradiation light, and photosensitizer. For copolyacrylates with glass transition temperature ( $T_g$ ) higher than room temperature, photocrosslinking rate is mainly determined by the content of 4-methylcoumarin chromophore. However, for those with  $T_g$  near or lower than room temperature, the rate is mainly influenced by the chain segmental mobility. The irradiation of 300 nm of u.v. is more efficient than 350 nm because the maximum absorption of 4-methylcoumarin chromophore is about 310 nm. The rate of photocrosslinking is increased in the presence of the triplet photosensitizer benzophenone. Copyright © 1996 Elsevier Science Ltd.

(Keywords: 7-acryloyloxy-4-methylcoumarin; copolyacrylates; reversible photocrosslinking)

## INTRODUCTION

Coumarin and its derivatives readily dimerize on photoirradiation with light longer than 300 nm to yield four types of dimer depending on the reaction conditions<sup>1–9</sup>. The dimer cycloreverses to the original coumarins when light with  $\lambda_{\max} = 254$  nm is employed as the energy source<sup>10</sup>. We have investigated the copolymerizability of 7-acryloyloxy-4-methylcoumarin with acrylates and photocrosslinking behaviours of the resulting copolyacrylates<sup>11</sup>.

Thymine bases with long alkyl chain convert to photodimers upon irradiation with ultraviolet (u.v.) light near the  $\lambda_{\max} = 288$  nm, which is known to have a lethal effect in biological systems<sup>12</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>13,14</sup>. The polymers containing thymine bases have high resolution and high sensitivity when used as negative, positive, and chemical amplification photoresists for microlithography<sup>15–18</sup>. We have synthesized coumarins with long alkyl chain by condensation of umbelliferone with alkanoyl chlorides, and their reversible photocyclodimerization behaviours have been investigated in detail after dispersing in poly(vinyl acetate)<sup>19</sup>.

In this work, photoreactive copolymers were prepared from 7-acryloyloxy-4-methylcoumarin ( $M_1$ ) and four acrylates ( $M_2$ : MMA, MA, EA, BA) with different composition. Reversible photocrosslinking (300 nm or 350 nm) and photocleaving (254 nm) reactions of these copolymers in the film state were investigated in detail, especially the influence of composition, irradiation wavelength, and photosensitizer–benzophenone.

## EXPERIMENTAL

### Preparation of copolyacrylates P1–P4<sup>11</sup>

Copolymerization of 7-acryloyloxy-4-methylcoumarin ( $M_1$ ) with acrylates ( $M_2$ ) was conducted in DMF at 60°C using AIBN (azobisisobutyronitrile) as free radical initiator. For example, to a 50-ml two-necked flask were added 7-acryloyloxy-4-methylcoumarin (2.0 g, 8.7 mmol), MA (1.5 g, 17.4 mmol), and DMF (20 ml). The mixture was purged with nitrogen and heated slowly to 65°C under gentle stirring. A solution of AIBN (2 wt% of monomers) in DMF was injected by a syringe to the mixture under vigorous stirring. The mixture was allowed to react for 6 h under a nitrogen blanket. The copolymer (P2) was isolated by reprecipitation in a large amount of ethanol. Yield 77%, reduced viscosity  $\eta_{\text{red}} = 0.23$  dl g<sup>-1</sup> (0.3 g dl<sup>-1</sup> CHCl<sub>3</sub>, 30°C).

### Reversible photocrosslinking of the copolymers (Scheme 1)

The films used for photocrosslinking (300 nm and

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350 nm) and photocleavage (254 nm) were prepared by casting a solution of the copolyacrylates P1–P4 on the outside wall of a quartz u.v. cell. For example, a clear solution was formulated by dissolving ca. 50 mg pf P1 in 5 ml chloroform. The cell, after casting and evaporation of the solvent, was then put into a photochemical reactor, model RPR-100 from Rayonet, containing 16 u.v. lamps. The photocrosslinking of P1, through dimerization of pendant 4-methylcoumarin chromophores, was first conducted by irradiating with 350 nm (or 300 nm) light. Then, after exchanging to 254 nm u.v. lamps, it was photocleaved symmetrically at 4-methylcoumarin dimer to the original P1. Photoreaction was traced by recording the absorbance change at 310 nm, which is the maximum absorption of 4-methylcoumarin groups, using a u.v.–visible spectrophotometer, model UV-160A from Shimadzu. The photocrosslinking and photocleavage cycles were repeated several times to investigate their reversibility. In addition, photoreactions were conducted both in the presence and absence of benzophenone to elucidate the role of the photosensitizer.

## RESULTS AND DISCUSSION

### Copolymers of 7-acryloyloxy-4-methylcoumarin ( $M_1$ ) and acrylates ( $M_2$ )

We have previously reported the synthesis and photoreaction kinetics of the photoreactive copolymer derived from 7-acryloyloxy-4-methylcoumarin ( $M_1$ ) and *N*-(1-phenylethyl)acrylamide ( $M_2$ )<sup>10</sup>. Their monomer reactivity ratios are  $r_1 = 1.22$ ,  $r_2 = 0.11$ , and  $r_1 = 1.28$ ,  $r_2 = 0.16$  as estimated by the Fineman–Ross and Kelen–Tudos methods, respectively. Poly(ethyleneimine) with coumarinyl pendant groups has been prepared by Chuo *et al.* and its photocrosslinking properties investigated by u.v. spectral change<sup>20</sup>. In this work 7-acryloyloxy-4-methylcoumarin ( $M_1$ ) is first polymerized with four acrylate monomers (MMA, MA, EA, and BA) to prepare photoreactive copolyacrylates with 4-methylcoumarin pendant chromophores.

7-Acryloyloxy-4-methylcoumarin ( $M_1$ ) readily copolymerizes with these acrylate monomers<sup>11</sup>. The copolymer yields are greater than 75% and their reduced viscosities ( $\eta_{red}$ ) are in the range of 0.21–0.26 dl g<sup>-1</sup>. Furthermore, mol% of 7-acryloyloxy-4-methylcoumarin ( $M_1$ ) in the copolymers P2–P4 are greater than those in the feed, indicating that  $M_1$  is more easily incorporated into the copolymers than MA, EA, and BA. On the contrary, for copolymer P1, the mol% of  $M_1$  is less than that in the feed, indicating that the reactivity of MMA is greater than  $M_1$ . The copolymerizability of  $M_1$  with the acrylates has been investigated in detail<sup>11</sup>. The copolymers used in the photoreaction are prepared by the same procedures, except the feed compositions vary.

### Reversible photocrosslinking and photocleavage

In solution, coumarin readily dimerizes to coumarin dimer in high yield under photoirradiation with u.v. light of  $\lambda_{max} > 300$  nm, especially in the presence of 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>21</sup>. Upon irradiation

with shorter wavelength u.v. light ( $\lambda_{max} = 245$  nm), coumarin dimer cycloreverses to coumarins. Photoreactive copolymers containing 4-methylcoumarin groups have been prepared from 7-acryloyloxy-4-methylcoumarin and *N*-(1-phenylethyl)acrylamide<sup>10</sup>. They also show 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  $\lambda_{max} = 310$  nm, which increases again by symmetric splitting of the photodimer. In this work, u.v. 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 u.v. lamps, their intensity readings at the reaction site are 7.05 mJ cm<sup>-2</sup> s<sup>-1</sup> (350 nm), 6.17 mJ cm<sup>-2</sup> s<sup>-1</sup> (300 nm), and 10.28 mJ cm<sup>-2</sup> s<sup>-1</sup> (254 nm), respectively, as measured with u.v. meters. Systems with benzophenone were compared with those without benzophenone to investigate the role of the photosensitizer.

### Influence of composition

As shown in Figure 1, the u.v. spectrum of homopolymer PM<sub>1</sub> from 7-acryloyloxy-4-methylcoumarin ( $M_1$ ) shows two absorptions at 275 nm and 310 nm. The band at 275 nm can be attributed to K band absorption caused by the double bonds of lactone rings in 4-methylcoumarin chromophores, while the band at 310 nm is B band absorption caused by phenyl groups<sup>22</sup>. Upon irradiation with 350 nm (or 300 nm) light, the absorption at 310 nm decreases gradually to an equilibrium value (Figure 2) due to the dimerization of pendant 4-methylcoumarin chromophores (photocrosslinking). Followed by irradiating with 254 nm light, the dimers are symmetrically split to the original 4-methylcoumarin (photocleavage) as shown in Scheme 1. Using these characteristics, the reversible photoreaction of the copolyacrylates (P1–P4) can be traced by recording their absorption variation at 310 nm.

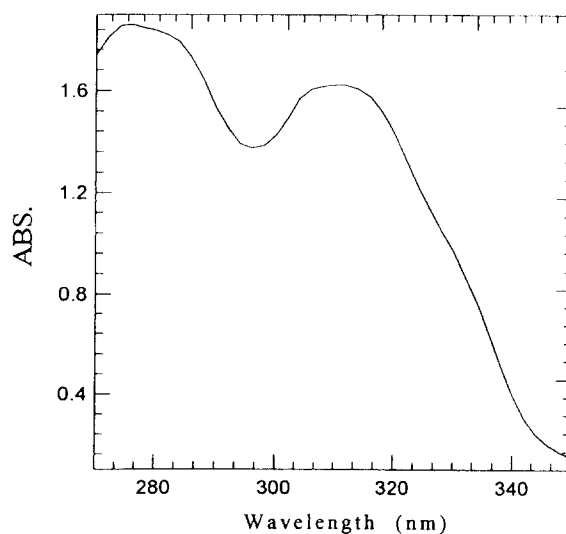


Figure 1 U.v. spectrum of PM<sub>1</sub> in the film state

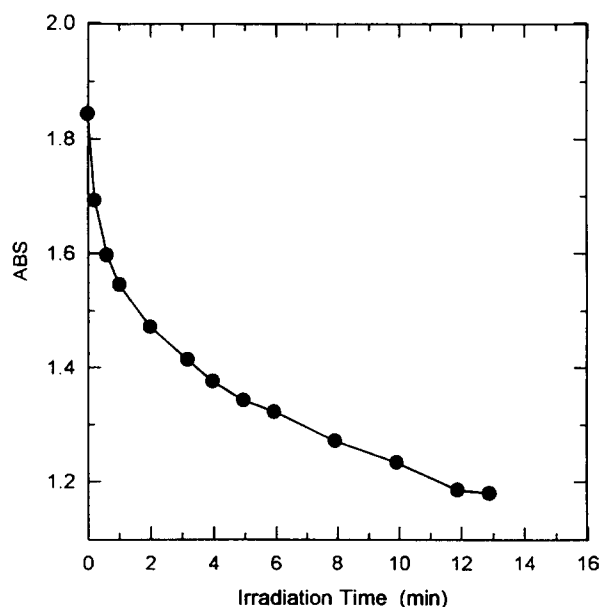
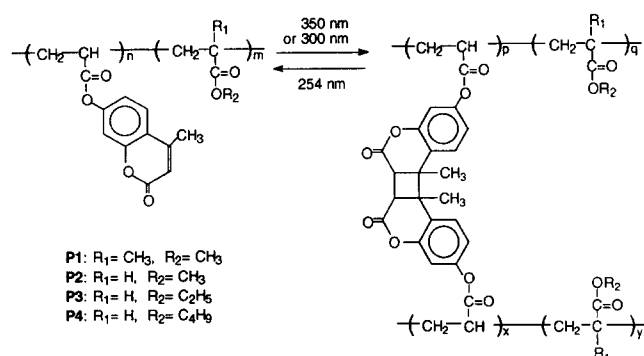


Figure 2 Absorbance variation (at 310 nm) of P4 with 66.7% BA, irradiated with 350 nm u.v. light in the film state



Scheme 1

For convenience of comparison, the maximum absorbance (max. ABS; the greatest absorbance at the beginning of photocrosslinking),  $\Delta$ ABS (absorbance decrease during one photocrosslinking), required energy (energy required for unit absorbance change), and degenerate (percent decrease of the maximum absorbance for the successive cycle) are summarized in Tables 1–6. Figure 3 depicts the absorption variation of PM<sub>1</sub> in the film state during photocrosslinking (350 nm) and photocleavage (254 nm) cycles. For initial cycle, the

absorbance at 310 nm decreases smoothly from about 1.62 to 0.79 upon photocrosslinking, then it increases abruptly to 1.25 upon photocleavage. The required energy remains almost constant with cycles (Table 1: ca. 26 J cm<sup>-2</sup>). Maximum absorbance cannot restore to its original 1.63 due to the fact that under 254 nm both photocleavage and photocrosslinking are under progress and come to an equilibrium<sup>10</sup>. From the second cycle on, the maximum absorbance and  $\Delta$ ABS decreases slightly with cycles from 1.25 to 1.19 and from 0.46 to 0.40, respectively.

As shown in Table 1, homopolymer PM<sub>1</sub> and copolyacrylate P1 with 73.9% MMA exhibit different photoreaction characteristics. The required energy for P1 (28.1–42.4 J cm<sup>-2</sup>) are greater than those for PM<sub>1</sub> (26.1–26.8 J cm<sup>-2</sup>) regardless of the difference in *T*<sub>g</sub>s (122.1°C for PM<sub>1</sub>, 112.1°C for P1), indicating that the concentration of photoreactive pendant 4-methylcoumarin plays a major role in determining the reactivity in systems with *T*<sub>g</sub> above room temperature. Other characteristics such as max. ABS,  $\Delta$ ABS, and degenerate percent show a similar trend. However, from the fact that the degenerate of P1 from the second cycle on (3.0–4.9%) are greater than those of PM<sub>1</sub> (1.6–3.3%), clearly PM<sub>1</sub> exhibits better reversibility than P1.

By comparing the results of PM<sub>1</sub> and P4 under 350 nm (Tables 1–3), it is clear that an increase in BA content renders a significant decrease in the required energy. The required energy is about 26 J cm<sup>-2</sup> for homopolymer PM<sub>1</sub>, and the values fall to 12.4–18 J cm<sup>-2</sup> and 7.5–8.3 J cm<sup>-2</sup> as BA contents increase to 38.9% and 66.7%, respectively. The *T*<sub>g</sub>s of PM<sub>1</sub>, P4 with 38.9% BA, and P4 with 66.7% BA are 122.1°C, 39.6°C, and 2.1°C, respectively<sup>11</sup>. The required energy decreases with increased BA content, suggesting that the photocrosslinking rate is mainly determined by the chain mobility of the copolyacrylates. Clearly, under photochemical chamber at about 36°C, the segmental chain motion is the easiest for P4 with 66.7% BA (*T*<sub>g</sub> = 2.1°C), followed by P4 with 38.9% BA (*T*<sub>g</sub> = 39.6°C) and PM<sub>1</sub> (122.1°C).

For P3 the influence of composition is similar to that of PM<sub>1</sub>/P1. As shown in Table 4, the required energies are 3.4–5.4 J cm<sup>-2</sup> and 12.9–18.6 J cm<sup>-2</sup> for 91.1% EA (*T*<sub>g</sub> = 13.9°C) and 98.7% EA (–17.6°C), respectively. That means the photocrosslinking rate depends mainly on the content of photoreactive 4-methylcoumarin and not on the *T*<sub>g</sub>s (since both *T*<sub>g</sub>s are lower than operating temperature). However, they both degenerate

Table 1 Reversible photocrosslinking (350 nm) and photocleavage (254 nm) of PM<sub>1</sub> and P1 in the film state

| Cycle <sup>a</sup>                                 | PM <sub>1</sub> |      |      |      | P1 (73.9% MMA) |      |      |      |
|--|-----------------|------|------|------|----------------|------|------|------|
|  | 1               | 2    | 3    | 4    | 1              | 2    | 3    | 4    |
| Max. ABS <sup>b</sup>                              | 1.62            | 1.25 | 1.23 | 1.19 | 1.91           | 1.67 | 1.62 | 1.54 |
| $\Delta$ ABS                                       | 0.83            | 0.46 | 0.44 | 0.40 | 0.72           | 0.48 | 0.44 | 0.38 |
| Degenerate (%) <sup>c</sup>                        | 22.0            | 1.6  | 3.3  | –    | 12.6           | 3.0  | 4.9  | –    |
| Required energy (J cm <sup>-2</sup> ) <sup>d</sup> |                 | 26.1 | 26.2 | 26.8 |                | 42.4 | 28.1 | 29.8 |

<sup>a</sup> One photocrosslinking (350 nm or 300 nm) followed with a photocleavage (254 nm) is defined as one cycle

<sup>b</sup> ABS: Absorbance of the sample in the film state

<sup>c</sup> Degenerate (%):  $D_n = \{ -[(\text{Max. ABS})_{n+1}/(\text{Max. ABS})_n] \} \times 100\%$ ; *n*: number of the cycle

<sup>d</sup> The energy required to cause unit absorbance change at 310 nm during photocrosslinking, i.e. irradiation energy/ $\Delta$ ABS

**Table 2** Reversible photocrosslinking (350 nm) and photocleavage (254 nm) of P4 (M<sub>1</sub> = 61.1%, BA = 38.9%) in the film state

| Cycle <sup>a</sup>                                 | 350 nm/254 nm |      |      |      | 300 nm/254 nm |      |      |      |
|--|---------------|------|------|------|---------------|------|------|------|
|  | 1             | 2    | 3    | 4    | 1             | 2    | 3    | 4    |
| Max. ABS <sup>b</sup>                              | 1.84          | 1.54 | 1.48 | 1.45 | 1.76          | 1.41 | 1.38 | 1.33 |
| ΔABS   | 0.66          | 0.36 | 0.30 | 0.22 | 0.70          | 0.34 | 0.30 | 0.26 |
| Degenerate (%) <sup>c</sup>                        | 16.3          | 3.9  | 2.0  |      | 19.9          | 2.1  | 3.6  |      |
| Required energy (J cm <sup>-2</sup> ) <sup>d</sup> |               | 18.0 | 12.9 | 12.4 |               | 2.5  | 2.6  | 2.7  |

<sup>a</sup> One photocrosslinking (350 nm or 300 nm) followed with a photocleavage (254 nm) is defined as one cycle<sup>b</sup> ABS: Absorbance of the sample in the film state<sup>c</sup> Degenerate (%):  $D_n = \{1 - [(\text{Max. ABS})_{n+1}/(\text{Max. ABS})_n]\} \times 100\%$ ;  $n$ : number of the cycle<sup>d</sup> The energy required to cause unit absorbance change at 310 nm during photocrosslinking, i.e. irradiation energy/ΔABS**Table 3** Reversible photocrosslinking (350 nm) and photocleavage (254 nm) of P4 (M<sub>1</sub> = 33.3%, BA = 66.7%) in the film state

| Cycle <sup>a</sup>                                 | 350 nm/254 nm |      |      |      | 300 nm/254 nm |      |      |      |      |
|--|---------------|------|------|------|---------------|------|------|------|------|
|  | 1             | 2    | 3    | 4    | 1             | 2    | 3    | 4    | 5    |
| Max. ABS <sup>b</sup>                              | 1.83          | 1.47 | 1.47 | 1.46 | 2.17          | 1.73 | 1.68 | 1.58 | 1.53 |
| ΔABS   | 0.73          | 0.38 | 0.39 | 0.37 | 1.19          | 0.75 | 0.70 | 0.59 | 0.55 |
| Degenerate (%) <sup>c</sup>                        | 19.7          | 0    | 0.7  |      | 20.3          | 2.9  | 6.0  | 3.2  |      |
| Required energy (J cm <sup>-2</sup> ) <sup>d</sup> |               | 8.3  | 8.1  | 7.5  |               | 1.4  | 1.6  | 1.9  | 2.0  |

<sup>a</sup> One photocrosslinking (350 nm or 300 nm) followed with a photocleavage (254 nm) is defined as one cycle<sup>b</sup> ABS: Absorbance of the sample in the film state<sup>c</sup> Degenerate (%):  $D_n = \{1 - [(\text{Max. ABS})_{n+1}/(\text{Max. ABS})_n]\} \times 100\%$ ;  $n$ : number of the cycle<sup>d</sup> The energy required to cause unit absorbance change at 310 nm during photocrosslinking, i.e. irradiation energy/ΔABS**Table 4** Reversible photocrosslinking (300 nm) and photocleavage (254 nm) of P3 in the film state

| Cycle <sup>a</sup>                                 | 91.1% EA |      |      | 98.7% EA |      |      |
|--|----------|------|------|----------|------|------|
|  | 1        | 2    | 3    | 1        | 2    | 3    |
| Max. ABS <sup>b</sup>                              | 1.17     | 0.92 | 0.88 | 1.46     | 1.05 | 0.96 |
| ΔABS   | 0.35     | 0.11 | 0.06 | 0.57     | 0.18 | 0.10 |
| Degenerate (%) <sup>c</sup>                        | 21.4     | 4.3  |      | 28.1     | 8.6  |      |
| Required energy (J cm <sup>-2</sup> ) <sup>d</sup> |          | 5.4  | 3.4  |          | 18.6 | 12.9 |

<sup>a</sup> One photocrosslinking (300 nm) followed with a photocleavage (254 nm) is defined as one cycle<sup>b</sup> ABS: Absorbance of the sample in the film state<sup>c</sup> Degenerate (%):  $D_n = \{1 - [(\text{Max. ABS})_{n+1}/(\text{Max. ABS})_n]\} \times 100\%$ ;  $n$ : number of the cycle<sup>d</sup> The energy required to cause unit absorbance change at 310 nm during photocrosslinking, i.e. irradiation energy/ΔABS**Table 5** Reversible photocrosslinking (350 nm) and photocleavage (254 nm) of P2 (M<sub>1</sub> = 11.2%, MA = 88.8%) in the film state

| Cycle <sup>a</sup>                                 | 350 nm/254 nm               |                |                |                | 300 nm/254 nm |      |      |      |
|--|-----------------------------|----------------|----------------|----------------|---------------|------|------|------|
|  | 1                           | 2              | 3              | 4              | 1             | 2    | 3    | 4    |
| Max. ABS <sup>b</sup>                              | 1.69<br>(1.79) <sup>c</sup> | 1.58<br>(1.49) | 1.56<br>(1.46) | 1.55<br>(1.43) | 1.50          | 1.29 | 1.26 | 1.24 |
| ΔABS   | 0.37<br>(0.62)              | 0.26<br>(0.31) | 0.25<br>(0.27) | 0.23<br>(0.25) | 0.52          | 0.31 | 0.30 | 0.29 |
| Degenerate (%) <sup>c</sup>                        | 6.5<br>(16.8)               | 1.3<br>(2.0)   | 0.6<br>(2.1)   | (-)            | 14.0          | 2.3  | 1.6  |      |
| Required energy (J cm <sup>-2</sup> ) <sup>d</sup> |                             | 24.2<br>(12.0) | 16.9<br>(10.8) | 16.3<br>(12.2) |               | 5.0  | 4.4  | 4.6  |

<sup>a</sup> One photocrosslinking (350 nm or 300 nm) followed with a photocleavage (254 nm) is defined as one cycle<sup>b</sup> ABS: Absorbance of the sample in the film state<sup>c</sup> Degenerate (%):  $D_n = \{1 - [(\text{Max. ABS})_{n+1}/(\text{Max. ABS})_n]\} \times 100\%$ ;  $n$ : number of the cycle<sup>d</sup> The energy required to cause unit absorbance change at 310 nm during photocrosslinking, i.e. irradiation energy/ΔABS<sup>e</sup> The values in the parentheses are for those with benzophenone ([benzophenone]/[4-methylcoumarin] = 0.91)

**Table 6** Reversible photocrosslinking (350 nm) and photocleavage (254 nm) of P4 ( $M_1 = 33.3\%$ , BA = 66.7%) in the film state

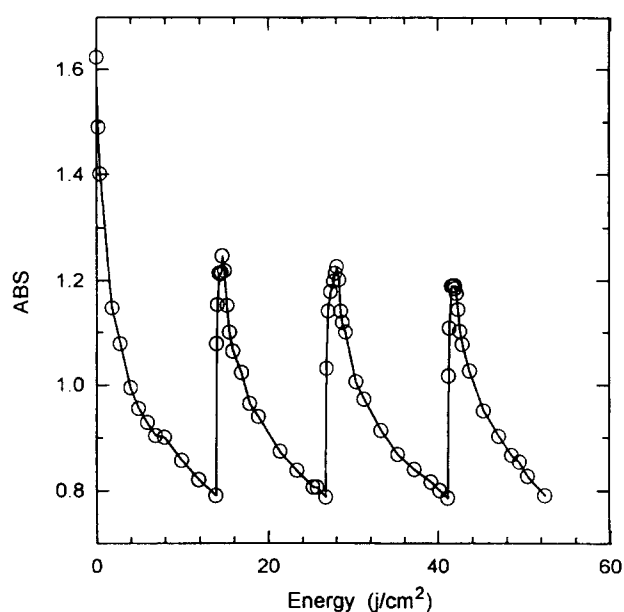
| Cycle <sup>a</sup>                                 | [Benzophenone]/[M <sub>1</sub> ] = 0.33 |      |      |      | [Benzophenone]/[M <sub>1</sub> ] = 4.2 |      |      |      |
|--|---|------|------|------|--|------|------|------|
|  | 1                                       | 2    | 3    | 4    | 1                                      | 2    | 3    | 4    |
| Max. ABS <sup>b</sup>                              | 1.85                                    | 1.31 | 1.26 | 1.23 | 1.56                                   | 0.89 | 0.90 | 0.91 |
| ΔABS   | 0.83                                    | 0.30 | 0.23 | 0.21 | 1.03                                   | 0.35 | 0.35 | 0.35 |
| Degenerate (%) <sup>c</sup>                        | 29.2                                    | 3.8  | 2.4  | –    | 42.9                                   | –1.1 | –1.1 | –    |
| Required energy (J cm <sup>-2</sup> ) <sup>d</sup> |   | 4.4  | 5.2  | 5.7  |  | 18.8 | 22.8 | 33.7 |

<sup>a</sup> One photocrosslinking (350 nm or 300 nm) followed with a photocleavage (254 nm) is defined as one cycle

<sup>b</sup> ABS: Absorbance of the sample in the film state

<sup>c</sup> Degenerate (%):  $D_n = \{1 - (\text{Max. ABS})_{n+1}/(\text{Max. ABS})_n\} \times 100\%$ ;  $n$ : number of the cycle

<sup>d</sup> The energy required to cause unit absorbance change at 310 nm during photocrosslinking, i.e. irradiation energy/ΔABS



**Figure 3** Absorbance at 310 nm versus irradiation energy for PM<sub>1</sub> in the film state (photocrosslinking: 350 nm, photocleavage: 254 nm)

significantly and the ΔABS after the first cycle are very small (0.06–0.18) compared to other systems. A too dilute concentration of photoreactive 4-methylcoumarin may result in side reactions such as the formation of *anti* head-to-tail 4-methylcoumarin dimers which are difficult to photocleave under 254 nm.

#### Influence of wavelength

Absorption of photoenergy is an essential process in photoreaction. In our system, the maximum absorbance of the polymers is around 310 nm. It is therefore reasonable to predict that 300 nm light irradiation should be more efficient than 350 nm light. As shown in Table 2, for P4 with 38.9% BA the required energy is ca. 12.4–18.0 J cm<sup>-2</sup> under 350 nm light, whereas it is only 2.5–2.7 J cm<sup>-2</sup> under 300 nm light. Clearly, the photocrosslinking reaction is much faster under 300 nm light than under 350 nm light due to the difference in absorption efficiency. For P4 with higher BA content (66.7%), similar trends are observed. As shown in Table 3, the required energies are ca. 7.5–8.2 J cm<sup>-2</sup> and 1.4–2.0 J cm<sup>-2</sup> for 350 nm and 300 nm light irradiation, respectively. The reversibility under 350 nm is very good, i.e. the degenerate percents are 0% and 0.7% for the second and third cycles. However, it

degenerates much faster (2.9–6.0%) under 300 nm light. This can be explained by possible side reactions under higher energy light of 300 nm. For P2 with 88.8% MA, similar trends are also observed as shown in Table 5. The required energies are 16.3–24.2 J cm<sup>-2</sup> and 4.4–5.0 J cm<sup>-2</sup> for 350 nm light and 300 nm light, respectively. The degenerate percents are only 0.6–1.3% and 1.6–2.3% for the second and third cycles, indicating that photo-reaction reversibility of P2 is quite good under both 300 nm and 350 nm light.

#### Influence of photosensitizer

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 academic and practical viewpoints. In this work, benzophenone was employed as the triplet photosensitizer and P4 as the model system.

As depicted in Table 5, for P2 with 88.8% MA addition of benzophenone ([benzophenone]/[4-methylcoumarin] = 0.91) decreases the required energy for photocrosslinking, i.e. 10.8–12.2 J cm<sup>-2</sup> compared to 16.3–24.2 J cm<sup>-2</sup> without benzophenone. For P4 with 66.7% BA, the influence of benzophenone is summarized in Table 6. When the addition quantity is 33% of that of 4-methylcoumarin, the required energies are ca. 4.4–5.7 J cm<sup>-2</sup> compared to 7.5–8.3 J cm<sup>-2</sup> without it (Table 3). This seems due to the enhanced crosslinking rate caused by benzophenone. Benzophenone is a triplet photosensitizer whose lifetime is 0.1–10 s, compared to 10<sup>-9</sup>–10<sup>-7</sup> s of singlet state. A longer lifetime in the excited state leads to a faster reaction rate by increasing the number of effective collisions.

However, the degenerate percent increases with the addition of benzophenone as shown in Table 5 and Table 6. For P2 with 88.8% MA, the degenerates in benzophenone-added sample (2.1–16.8%) are about twofold of those without it (0.6–6.5%). In general, addition of benzophenone results in a higher content of *anti* head-to-head 4-methylcoumarin dimer linkage because it is a triplet sensitizer<sup>23</sup>. Moreover, *anti*-isomer of coumarin dimer is more stable than *syn*-isomer and results in greater degenerate percent during photoreaction cycles. Similarly, for P4 with 66.7% BA at [benzophenone]/[M<sub>1</sub>] = 0.33, the degenerate percent (Table 6: 29.2%, 3.8%, 2.4%) are also greater than those without benzophenone (Table 3: 19.7%, 0%, 0.7%).

When the content of benzophenone is increased to be greater than that of photoreactive 4-methylcoumarin, the required energy is increased significantly. As shown in Table 6, the required energies are 18.8–33.7 J cm<sup>-2</sup> for the sample with [benzophenone]/[4-methylcoumarin] = 4.2, which is about four times the sample with the ratio 0.33. Clearly, although benzophenone enhances the photocrosslinking reaction, its dose in excess should be avoided. This abnormal depression in photocrosslinking reaction can be explained by the intrinsic absorbing ability of benzophenone around 350 nm. Moreover, too many benzophenone molecules may obstruct the collision between photoreactive 4-methylcoumarin chromophores and waste much of the irradiation energy. The degenerates are 42.9% for the first cycle followed with extraordinarily low -1.1% for both the second and third cycles. This peculiar phenomenon, unfortunately, has not been elucidated so far.

## CONCLUSION

Photoreactive copolyacrylates with pendant 4-methylcoumarin chromophores were prepared from 7-acryloyloxy-4-methylcoumarin and four acrylates (MMA, MA, EA, BA) by solution radical copolymerization. The copolyacrylates crosslink under irradiation with 300 nm or 350 nm light through dimerization of the pendant 4-methylcoumarin, and the dimers split into original 6-methylcoumarin (photocleavage) under 254 nm light. Their reversible photocrosslinking (300 nm or 350 nm) and photocleaving (254 nm) reaction were investigated in the film state by tracing their u.v. absorption at 310 nm (maximum absorption of 4-methylcoumarin chromophore). These photochemical reactions are mainly affected by the copolymer composition, wavelength of irradiation light, and photosensitizer. Copolyacrylate P1 (with 73.9% MMA,  $T_g = 112.1^\circ\text{C}$ ) photocrosslinks slower than homopolymer PM<sub>1</sub> ( $T_g = 122.1^\circ\text{C}$ ) due to lower content of photoreactive 4-methylcoumarin chromophores. For P4 with BA, the required energy decreases with increasing BA content, suggesting that relative ease of segmental chain mobility determines the reactivity. The irradiation of 300 nm u.v. light is more efficient than 350 nm because the maximum absorption of 4-methylcoumarin chromophores is around 310 nm. The rate of photocrosslinking increases

in the presence of benzophenone. However, excess dose results in significant depression of photocrosslinking.

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