

## ORIGINAL ARTICLE

# Effects of aryl substituents in *N*-acetyl- $\alpha$ -dehydroarylalanine naphthyl ester additive on the photoinduced refractive index change of poly(methyl methacrylate) film

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Aryl substituent effects on photoinduced refractive index changes were investigated with the use of poly(methyl methacrylate) (PMMA) films doped with (*Z*)-*N*-acetyl- $\alpha$ -dehydroarylalanine naphthyl esters (*Z*-1). Upon irradiation with Pyrex-filtered or unfiltered light from a high-pressure mercury lamp, (*Z*-1 underwent heterolytic cleavage of the ester C(=O)–O bond preferentially in both solution and PMMA film to afford arylmethylene-substituted (*Z*) oxazolone and naphthol derivatives as major products, irrespective of the aryl substituents introduced. Irradiation of (*Z*-1 in the film with the unfiltered light enabled much more rapid photochemical transformation into the oxazolones and the intense ultraviolet absorption shifted to longer wavelength relative to that of the starting naphthyl esters. Analysis of the aryl substituent effects confirmed that the PMMA/(*Z*-1 system, in which 1-naphthylmethylene-substituted oxazolone was formed along with 1-naphthol, enhanced the refractive index of this polymer film by as much as 0.020.

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## INTRODUCTION

Photochemistry has continued to contribute to the development of various types of optoelectronic materials such as optical fibers, microlenses, optical memories, switching devices, optical waveguides, liquid crystal display components and polymer light emitting diodes.<sup>1–3</sup> Recently, much attention has been devoted to the photochemical control of refractive indices for polymer films, owing to their potential in optical network technology.<sup>3</sup> Although there are extensive studies directed toward a photoinduced decrease in refractive indices for polymer films,<sup>4–19</sup> only a few attempts have been made to enhance the refractive index through photochemical transformations.<sup>12,20–25</sup> For example, Langer *et al.*<sup>21</sup> reported that irradiation of a polymer-bearing thiocyanate pendants enhanced the refractive index (*n*) of the polymer by 0.031. An additional increase in refractive index was observed upon treating the polymer with hydrazine (refractive index change,  $\Delta n = +0.035$ ). Murase *et al.*<sup>23</sup> also showed that photochemical and thermal treatments of poly(methyl methacrylate) (PMMA) film doped with 30 wt% of phenyl azide raised the index of this film by 0.016. In addition, the photo-Fries rearrangement in polymers bearing aromatic ester pendants was found to cause a large increase in refractive index for these polymer films ( $\Delta n = +0.03$ – $+0.07$ ).<sup>24,25</sup>

Very recently, Nishikubo and coworkers<sup>26</sup> found that photoacid-generating agent-induced decomposition of the bicyclo orthoester pendants in a polystyrene-based polymer film increased the refractive index of this film by 0.023. Although the refractive index changes described above seem to be of sufficient magnitude to use these polymers as optical materials, it is necessary to increase the stability of the polymer refractive index and also to accelerate the photochemical transformation responsible for the refractive index change of a given polymer film.

In the course of our systematic studies regarding the excited-state reactivities of *N*-acyl- $\alpha$ -dehydroarylalanines, it was found that (*Z*)-*N*-acetyl- $\alpha$ -dehydrophenylalanine aryl ester derivatives in the singlet excited state undergo heterolytic cleavage of the ester C(=O)–O bond to eventually form arylmethylene-substituted 5(*4H*) oxazolones and aryl alcohols by way of cyclization of an acylium ion intermediate.<sup>27</sup> In contrast to the photoisomerization of diarylnitron derivatives, the photoheterolysis of  $\alpha$ -dehydroarylalanine aryl esters gave arylmethylene-substituted (*Z*) oxazolones as one of the major products, the absorption of which was shifted to longer wavelength relative to that of the starting aryl esters. Thus, the novel photochemical transformation of these esters into oxazolones results in an

enhancement of  $\pi$ -conjugation, namely the linear polarizability of a given system, which allows us to predict that this transformation is accompanied by an increase in refractive index,  $n$ .

$$(n^2 - 1)/(n^2 + 2) = (4/3)\pi N\alpha \quad (1)$$

From the Lorentz-Lorenz equation (1), we see that if the number density of molecule ( $N$ ) remains constant during irradiation,  $n$  is determined by the linear polarizability of its molecule ( $\alpha$ ), which is closely related to the magnitude of  $\pi$ -conjugation. If we consider the significance of the relationship between  $\Delta n$  and the shift in a given absorption maximum, which is a measure of the alteration in  $\pi$ -conjugation, an investigation directed toward the elucidation of such a relationship would be of great value from a practical point of view. In a previous study, we found that there was good correlation between the  $\Delta n$  (caused by the irradiation of PMMA film doped with diarylnitronone additive) and the first absorption maximum wavelength of this additive.<sup>17</sup> Because this finding provides a good criterion for designing better optical materials, it is significant to generalize this correlation so as to be applicable to polymer films, the refractive indices of which are enhanced by the photochemical transformation of dopants. To confirm whether the above-mentioned correlation is applicable to other systems and then to obtain information for developing a new type of optical material, we synthesized (*Z*)-*N*-acyl- $\alpha$ -dehydroarylalanine naphthyl ester derivatives (*Z*)-**1a-f** (Scheme 1) and investigated aryl substituent effects on the refractive index change of PMMA films caused by the photochemical transformation of these naphthyl esters as dopants.

## EXPERIMENTAL PROCEDURE

### Materials and solvents

(*Z*)-4-Benzylidene-2-methyl-5(4*H*)-oxazolone and (*Z*)-2-methyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone were prepared by the Knoevenagel-type condensation ring-closure reactions of *N*-acetylglycine (0.085 mol) with benzaldehyde and 1-naphthaldehyde (0.10 mol) in acetic anhydride (100 ml) containing sodium acetate (0.070 mol) at 75–85 °C, respectively. Infrared (IR) and <sup>1</sup>H nuclear magnetic resonance (NMR) spectral data of these oxazolones were consistent with those of the corresponding oxazolones previously prepared.<sup>28,29</sup>

After (*Z*)-4-benzylidene-2-methyl-5(4*H*)-oxazolone or (*Z*)-2-methyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone (6.5 mmol) was dissolved in chloroform (25 ml) containing 1-naphthol, 4-methoxy-1-naphthol or 2-naphthol (7.2 mmol) and triethylamine (5.9 mmol), the resulting mixture was heated under reflux for 2–5 h and then concentrated to dryness under reduced pressure. The residual solid was purified by repeated reprecipitation from chloroform-hexane. Physical and spectroscopic properties of naphthyl (*Z*)-2-

acetylamino-3-phenyl-2-propenoate (**1a-c**) and naphthyl (*Z*)-2-acetylamino-3-(1-naphthyl)-2-propenoate (**1d-f**) are as follows.

**1a**, melting point (mp) 139.0–139.5 °C; IR (KBr, cm<sup>-1</sup>): 3213 (N–H), 1728 (OC=O), 1649 (NHC=O); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  2.40 (3H, s), 6.86 (1H, d,  $J=7.4$  Hz), 7.23 (1H, s), 7.28 (1H, dd,  $J=7.4, 8.0$  Hz), 7.32 (1H, dd,  $J=6.9, 8.0$  Hz), 7.41–7.50 (5H, m), 7.81 (1H, d,  $J=7.4$  Hz), 8.12 (1H, d,  $J=8.0$  Hz), 8.19 (2H, d,  $J=8.0$  Hz), 10.1 (1H, s); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  15.5, 108.1, 118.4, 122.0, 124.5, 124.6, 126.1, 126.5, 126.7, 127.4, 129.0 (2C), 131.1, 132.0 (2C), 132.7, 133.1, 134.5, 153.2, 166.8, 167.5; (found: C, 76.03; H, 5.24; N, 4.32%. Calcd for C<sub>21</sub>H<sub>17</sub>NO<sub>3</sub>: C, 76.12; H, 5.17; N, 4.23%).

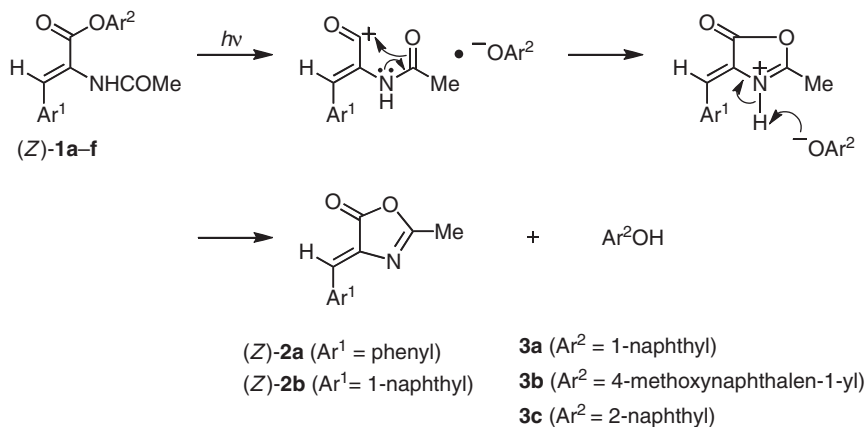
**1b**, mp 147.5–148.5 °C; IR (KBr, cm<sup>-1</sup>): 3211 (N–H), 1732 (OC=O), 1649 (NHC=O); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  2.40 (3H, s), 3.88 (3H, s), 6.74–6.78 (2H, m), 7.22 (1H, s), 7.45–7.52 (5H, m), 8.04–8.09 (2H, m), 8.18 (2H, d,  $J=7.7$  Hz), 9.54 (1H, s); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  15.4, 55.5, 104.5, 107.1, 121.3, 122.0, 125.1 (2C), 125.2, 125.4, 125.6, 128.9 (2C), 129.8, 131.1, 132.0, 132.6, 133.1, 146.6, 147.6, 166.8, 167.4; (found: C, 73.00; H, 5.10; N, 3.82%. Calcd for C<sub>22</sub>H<sub>19</sub>NO<sub>3</sub>: C, 73.12; H, 5.30; N, 3.88%).

**1c**, mp 142.0–143.0 °C; IR (KBr, cm<sup>-1</sup>): 3221 (N–H), 1724 (OC=O), 1658 (NHC=O); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  2.40 (3H, s), 7.08 (1H, d,  $J=8.6$  Hz), 7.11 (1H, s), 7.23 (1H, s), 7.25 (1H, dd,  $J=6.9, 8.0$  Hz), 7.38 (1H, dd,  $J=6.3, 6.9$  Hz), 7.48–7.50 (3H, m), 7.67 (1H, d,  $J=8.0$  Hz), 7.75 (1H, d,  $J=8.6$  Hz), 7.76 (1H, d,  $J=6.3$  Hz), 8.18 (2H, d,  $J=7.4$  Hz), 9.72 (1H, s); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  16.0, 79.8, 109.2, 119.2, 123.2, 126.6, 126.7, 128.1, 128.3, 129.5 (2C), 129.9, 130.4, 131.6, 132.6 (2C), 133.2, 133.7, 155.9, 167.3, 168.0; (found: C, 76.06; H, 5.25; N, 4.23%. Calcd for C<sub>21</sub>H<sub>17</sub>NO<sub>3</sub>: C, 76.12; H, 5.17; N, 4.23%).

**1d**, mp 148.5–149.5 °C; IR (KBr, cm<sup>-1</sup>): 3275 (N–H), 1728 (OC=O), 1655 (NHC=O); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  2.43 (3H, s), 6.86 (1H, d,  $J=6.9$  Hz), 7.29 (1H, dd,  $J=7.4, 8.0$  Hz), 7.32 (1H, dd,  $J=6.9, 8.0$  Hz), 7.43–7.47 (2H, m), 7.62 (1H, dd,  $J=7.4, 8.6$  Hz), 7.60–7.66 (2H, m), 7.80 (1H, d,  $J=7.4$  Hz), 7.93 (1H, s), 8.03 (1H, d,  $J=7.4$  Hz), 8.09 (1H, d,  $J=8.6$  Hz), 8.11 (1H, d,  $J=8.0$  Hz), 8.35 (1H, d,  $J=8.6$  Hz), 8.74 (1H, d,  $J=7.4$  Hz), 10.1 (1H, s); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  15.4, 108.0, 118.3, 122.0, 123.0, 124.5, 124.6, 124.9, 125.6, 126.1, 126.4, 126.7, 127.3, 127.6, 128.7, 129.0, 130.9, 131.6, 133.3, 133.8, 134.2, 134.4, 153.1, 167.2, 167.5; (found: C, 78.38; H, 5.09; N, 3.67%. Calcd for C<sub>25</sub>H<sub>19</sub>NO<sub>3</sub>: C, 78.72; H, 5.02; N, 3.67%).

**1e**, mp 197.0–198.0 °C; IR (KBr, cm<sup>-1</sup>): 3218 (N–H), 1741 (OC=O), 1655 (NHC=O); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  2.43 (3H, s), 3.88 (3H, s), 6.74–6.76 (2H, m), 7.46–7.48 (2H, m), 7.61–7.69 (3H, m), 7.93 (1H, s), 7.92–8.10 (4H, m), 8.38 (1H, d,  $J=8.6$  Hz), 8.74 (1H, d,  $J=7.4$  Hz), 9.54 (1H, s); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  21.8, 55.4, 103.2, 117.7, 120.8, 121.0, 123.8, 124.4, 124.8, 125.1, 125.5, 125.8, 126.3, 126.6, 126.8, 127.1, 128.3, 128.4, 128.9, 129.8, 130.5, 132.8, 139.5, 152.4, 163.9, 169.7; (found: C, 75.62; H, 5.27; N, 3.55%. Calcd for C<sub>26</sub>H<sub>21</sub>NO<sub>4</sub>: C, 75.90; H, 5.14; N, 3.40%).

**1f**, mp 158.0–159.0 °C; IR (KBr, cm<sup>-1</sup>): 3230 (N–H), 1732 (OC=O), 1653 (NHC=O); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  2.43 (3H, s), 7.08 (1H, d,  $J=8.6$  Hz), 7.11 (1H, s), 7.25 (1H, dd,  $J=6.9, 8.0$  Hz), 7.38 (1H, dd,  $J=6.3,$



Scheme 1 Structures of (*Z*)-**1a-f**.

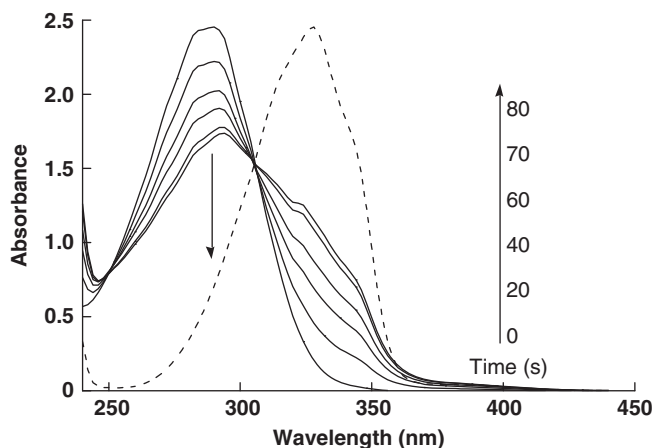
6.9 Hz), 7.62 (1H, dd,  $J=7.4, 8.0$  Hz), 7.66–7.70 (3H, m), 7.77–7.74 (2H, m), 7.93 (1H, s), 8.03 (1H, d,  $J=7.4$  Hz), 8.09 (1H, d,  $J=8.0$  Hz), 8.36 (1H, d,  $J=8.0$  Hz), 8.74 (1H, d,  $J=7.4$  Hz), 9.72 (1H, s);  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  15.5, 108.6, 118.6, 122.6, 123.0, 124.9, 125.7, 126.0, 126.1, 126.4, 127.5, 127.6, 127.8, 128.7, 129.0, 129.3, 130.9, 131.6, 131.7, 133.3, 133.8, 134.6, 155.3, 167.3, 167.6; (found: C, 78.54; H, 4.97; N, 3.67%. Calcd for  $\text{C}_{25}\text{H}_{19}\text{NO}_3$ : C, 78.72; H, 5.02; N, 3.67%).

PMMA (Wako, Osaka, Japan; polymerization degree=1000–1500) was used as a host polymer without further purification. Acetonitrile as a solvent was purified according to the standard method. All other chemicals used were obtained from commercial sources and were of the highest grade available. PMMA films containing 6.7 wt% **1a–d** and **1f** or 10 wt% **1a** were prepared through spin coating of a 2-methoxyethyl acetate solution onto silica glasses (for ultraviolet (UV) spectral measurements) and onto silicon wafers (for refractive index measurements), followed by vacuum drying at 40 °C. For preparing the film doped with 6.7 wt% **1e**, a mixture of 2-methoxyethyl acetate and dimethyl formamide (1:1 by volume) was used as a solvent.

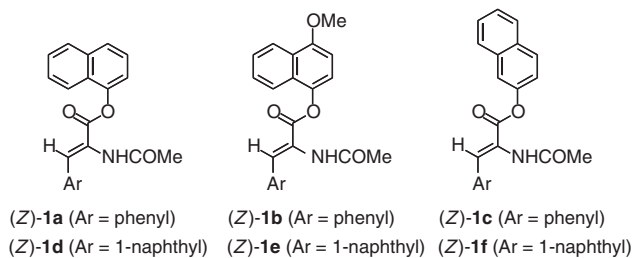
### Measurements

UV absorption spectra were recorded on a Hitachi UV-3300 spectrophotometer (Hitachi, Tokyo, Japan).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured with a JEOL JNM-A500 spectrometer (JEOL, Tokyo, Japan) using tetramethylsilane as an internal standard. Infrared spectra were recorded with a Shimadzu Prestige-21 infrared spectrophotometer (Shimadzu, Kyoto, Japan).

Solutions and PMMA films containing **1a–f** were irradiated with Pyrex-filtered light ( $\lambda > 280$  nm) and unfiltered light from a 450 W high-pressure mercury lamp, respectively. The Pyrex-filtered light was selected with a Toshiba IRA-25S glass filter (Toshiba, Tokyo, Japan).



**Figure 1** UV absorption spectral changes caused by the irradiation of a nitrogen-purged acetonitrile solution of (*Z*)-**1a** ( $1.0 \times 10^{-4}$  mol dm $^{-3}$ ) with Pyrex-filtered light at room temperature. Dashed line indicates UV spectrum of (*Z*)-**2a**.



**Scheme 2** Reaction mechanism proposed for the formation of (*Z*)-**2** and **3**.

The refractive indices of the films were measured before and after irradiation with a Gaertner L115B ellipsometer (Gaertner, Skokie, IL, USA). The light source for the index measurements was a 632.8-nm He-Ne laser.

### RESULTS AND DISCUSSION

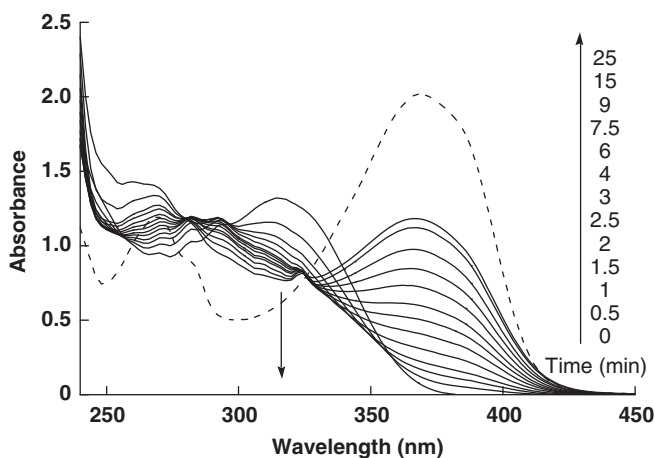
Figure 1 shows UV absorption spectral changes caused by the irradiation of a nitrogen-saturated acetonitrile solution of (*Z*)-**1a** ( $1.0 \times 10^{-4}$  mol dm $^{-3}$ ) with Pyrex-filtered light from a 450 W high-pressure lamp at room temperature. As the photoreaction proceeded, an intense UV absorption of the starting **1a** at 291 nm decreased with the appearance of the 328 nm absorption, with an isosbestic point at 300 nm. Because the absorption band appeared at longer wavelength, very similar to that of (*Z*)-4-benzylidene-2-methyl-5(4*H*)-oxazolone ((*Z*)-**2a**, dashed line in Figure 1), it may be concluded that (*Z*)-**1a** undergoes heterolytic cleavage of the ester C(=O)–O bond to afford (*Z*)-**2a** and 1-naphthol (**3a**). The other starting naphthyl esters (*Z*)-**1b–f** exhibited UV absorption spectra characteristic of the corresponding oxazolone derivatives, namely, (*Z*)-**2a** and (*Z*)-2-methyl-4-(1-naphthylmethylene)-5(4*H*)-oxazolone ((*Z*)-**2b**), upon irradiation of these esters with the filtered light in acetonitrile (Scheme 2). UV absorption spectral data of (*Z*)-**1**, (*Z*)-**2** and naphthol derivatives **3** (see Scheme 2) are collected in Table 1. In our previous paper, it was demonstrated that irradiation of (*Z*)-*N*-acetyl- $\alpha$ -dehydroarylanine naphthyl esters in acetonitrile with Pyrex-filtered light gave arylmethylene-substituted (*Z*) oxazolone and naphthol derivatives as major products, along with minor amounts of the Fries-rearranged products and the (*E*)-oxazolone isomers.<sup>27</sup> Furthermore, almost the same product distribution was observed when the (*E*)-isomer of the starting arylalanine naphthyl ester was irradiated under the same conditions,

**Table 1** Ultraviolet absorption spectral data of (*Z*)-**1a–f**, (*Z*)-**2a,b** and **3a–c**, obtained in acetonitrile at room temperature

Compound	$\lambda_{\text{max}}$ (nm) <sup>a</sup>	$\epsilon_{\text{max}}$ ( $10^3$ dm $^3$ mol $^{-1}$ cm $^{-1}$ ) <sup>b</sup>
( <i>Z</i> )- <b>1a</b>	291	24.7
( <i>Z</i> )- <b>1b</b>	292	23.8
( <i>Z</i> )- <b>1c</b>	283	20.8
( <i>Z</i> )- <b>1d</b>	315	13.2
( <i>Z</i> )- <b>1e</b>	314	17.8
( <i>Z</i> )- <b>1f</b>	317	13.7
( <i>Z</i> )- <b>2a</b>	328	24.8
( <i>Z</i> )- <b>2b</b>	370	20.0
<b>3a</b>	295	4.6
<b>3b</b>	320	6.2
<b>3c</b>	332	2.2

<sup>a</sup>Absorption maximum wavelength.

<sup>b</sup>Molar extinction coefficient at  $\lambda_{\text{max}}$ .

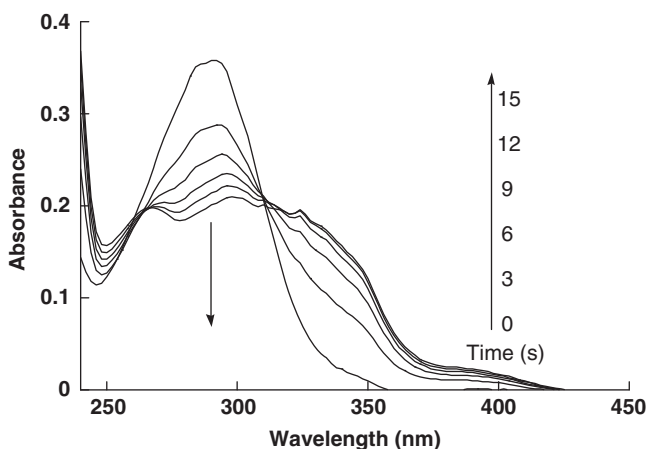


**Figure 2** UV absorption spectral changes caused by the irradiation of a nitrogen-purged acetonitrile solution of (Z)-1d ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) with Pyrex-filtered light at room temperature. Dashed line indicates UV spectrum of (Z)-2d.

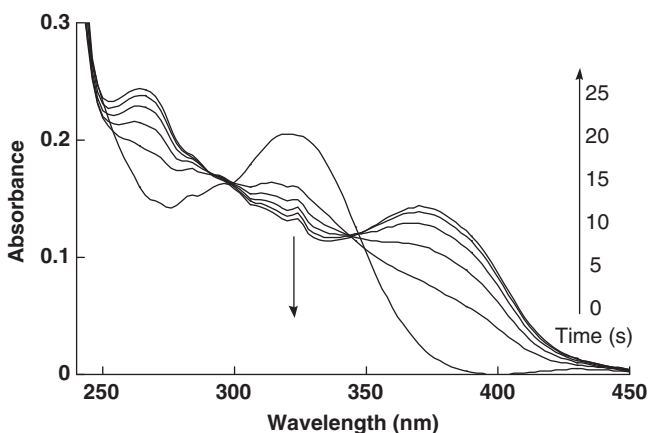
confirming that the (Z)-oxazolone isomer is thermodynamically more stable. Substituent and solvent effects on the product distribution substantiated the participation of an acylium ion intermediate (being a precursor of the oxazolone derivative) generated by the heterolysis of the ester  $\text{C}(=\text{O})\text{-O}$  bond in the singlet excited state. These previous findings are, therefore, consistent with the above conclusion.

On the other hand, the heterolytic  $\text{C}(=\text{O})\text{-O}$  bond cleavage reaction of (Z)-1a did not go to completion even though an acetonitrile solution of this 1-naphthyl ester derivative was irradiated for a long period of time. The (Z)-isomer of 2a as a major product readily undergoes photoisomerization into the (E)-isomer to decrease the first absorption of (Z)-2a and, in addition, both of these oxazolone isomers act to cutoff the filtered light. The latter cutoff effect by the photoproducts is considered to be the major cause of the lower than expected conversion of the starting (Z)-1a. As shown in Figure 2, replacement of the phenyl substituent in (Z)-1a by the 1-naphthyl ((Z)-1d) resulted in similar UV absorption spectral changes under the same irradiation conditions, although this replacement lowered the photoreactivity of 1 and then shifted the isobestic point from 296 to 280 nm during the reaction, owing mainly to the (Z)  $\rightarrow$  (E) photoisomerization of 1 and 2. The aryl substituent exerts its electronic effect on the relative rates for the heterolytic  $\text{C}(=\text{O})\text{-O}$  bond cleavage in the excited-state 1 and for these isomerizations in a complex manner. In any derivatives, the ester bond heterolysis and the subsequent ring-closure reactions of acylium ion intermediates are very likely to afford the corresponding (Z)-oxazolone ((Z)-2a, (Z)-2b) and naphthol (3a-c) derivatives as major products without undergoing remarkable side reactions (Scheme 2).

We next directed our attention to the UV absorption spectral and refractive index changes caused by the irradiation of PMMA film containing the arylalanine naphthyl ester derivative 1. PMMA films doped with 1a-f were made on both silica glasses and silicon wafers by spin coating of 2-methoxyethyl acetate solutions. The thickness of the transparent films was about 1  $\mu\text{m}$ . Figures 3 and 4 present UV absorption spectral changes caused by the irradiation of the films containing 6.7 wt% (Z)-1a and 6.7 wt% (Z)-1d, respectively, with the unfiltered light. This light was used to complete the reaction of (Z)-1 as quickly as possible, from a practical point of view. As expected, the photoheterolysis in the film (Figures 3 and 4) proceeded much more rapidly compared with that in acetonitrile (Figures 1 and 2), although



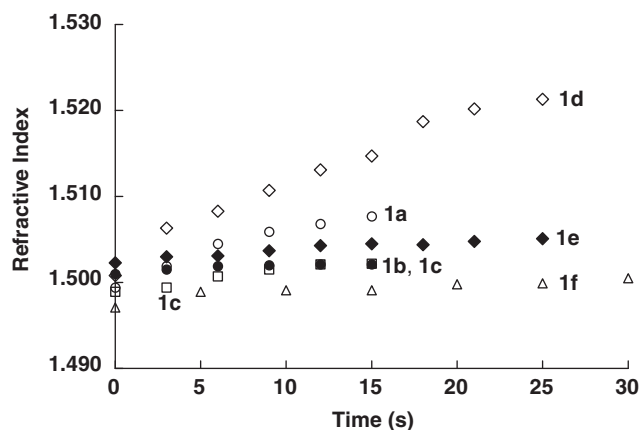
**Figure 3** UV absorption spectral changes caused by the irradiation of PMMA film, doped with (Z)-1a (6.7 wt%) and prepared on silica glass, with unfiltered light at room temperature.



**Figure 4** UV absorption spectral changes caused by the irradiation of PMMA film, doped with (Z)-1d (6.7 wt%) and prepared on silica glass, with unfiltered light at room temperature.

the much weaker absorption of (Z)-1 in the film state contributes greatly to an increase in the apparent reaction rate. In addition, the unfiltered light induced almost the same absorption spectral changes as the filtered light. Thus, irradiation at wavelengths shorter than 280 nm (mainly 254 nm) is considered to have only a minor effect on the photochemical process observed.

As predicted in the introduction, the refractive index of PMMA film doped with (Z)-1 was enhanced at 632.8 nm when the film was irradiated for a given period of time. Light of this wavelength is generally and widely used for the measurement of refractive indices of many optical materials, and in addition the magnitude of  $\Delta n$  is not very dependent on the measuring wavelength.<sup>4-26</sup> The plots of refractive index versus irradiation time, depicted in Figure 5, demonstrate that the refractive index increases with irradiation time, and the largest refractive index change of  $\Delta n = +0.020$  is achieved only by the 25 s irradiation of PMMA film doped with 6.7 wt% (Z)-1d. Furthermore, an inspection of the refractive index changes summarized in Table 2 established that (1) the increased concentration of (Z)-1 in PMMA film gave larger  $\Delta n$ , (2) the generation of the oxazolone derivative 2a induced greater  $\Delta n$  than that of 2b and (3) the  $\Delta n$  value was increased in the order of 1c, < 1b, < 1a in  $\alpha$ -dehydrophenylalanine naphthyl esters and in the order of 1f, < 1e, < 1d in



**Figure 5** Refractive index of PMMA films, doped with (Z)-1a-f (6.7 wt%) and prepared on Si wafers, as a function of the irradiation time.

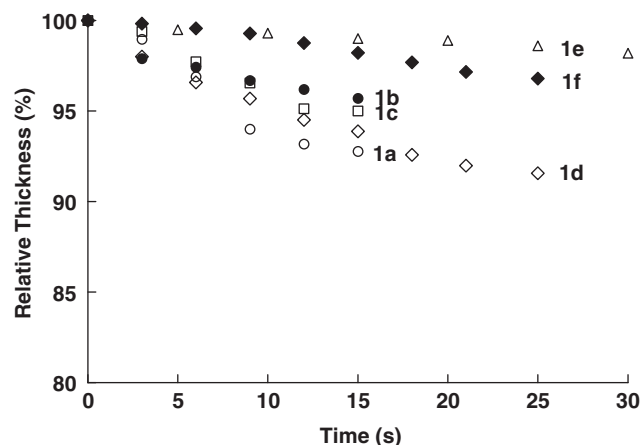
**Table 2** Changes in the refractive index and thickness of PMMA films doped with (Z)-1a-f, caused by the irradiation of these films at room temperature

Compound	Concentration (wt%)	$\Delta n^a$	Relative thickness (%) <sup>b</sup>
(Z)-1a	6.7	+0.009	93
	10	+0.013	94
(Z)-1b	6.7	+0.003	95
(Z)-1c	6.7	+0.001	96
(Z)-1d	6.7	+0.020	92
(Z)-1e	6.7	+0.005	97
(Z)-1f	6.7	+0.003	97

<sup>a</sup>Refractive index change.

<sup>b</sup>Thickness relative to that of unirradiated poly(methyl methacrylate) (PMMA) film (100).

$\alpha$ -dehydro(1-naphthyl)alanine naphthyl esters. From analysis of the molecular size effects of diarylnitron additive on the refractive index change in PMMA film, it was found that the magnitude of  $\Delta n$  has a clear tendency to increase as the maximum wavelength of the first absorption band in a given additive is shifted to longer wavelengths.<sup>17</sup> As PMMA film doped with (Z)-1 showed no absorption in the 450–700 nm region, it is anticipated on the basis of this finding that the 1d-f-derived oxazolone derivative 2b exhibits its absorption at longer wavelengths than does the 1a-c-derived oxazolone 2a and, hence, (Z)-1d-f give larger  $\Delta n$  values than (Z)-1a-c. The results obtained are compatible with our prediction, shedding much light on the application to new optical materials. Ellipsometer analysis of the polymer film carried out before and after irradiation showed that the film thickness decreased by about 3–8% as the photoreaction proceeded (Table 2 and Figure 6). As can be seen from the Lorentz-Lorenz equation (1), a decrease in thickness of PMMA film is thought to increase the magnitude of  $N$  to result in an enhancement of the refractive index  $n$  for this polymer film. To investigate this, PMMA film doped with 10 wt% photochemically stable 2-hydroxybenzophenone was irradiated for 5 min with the unfiltered light. As the UV absorption spectrum of this additive underwent a negligible change, the  $n$  was reduced by 0.003 with a 5% decrease in the film thickness. This unexpected finding suggests that the relationship between film refractive index and film thickness is much more complicated than expected from equation (1). Accordingly, the magnitude of  $\Delta n$  given in Table 2 should be considered to be underestimated. It is likely that



**Figure 6** Relative thickness of PMMA films, doped with (Z)-1a-f (6.7 wt%) and prepared on Si wafers, as a function of the irradiation time.

light energy absorbed by the dopant is partly converted into kinetic energy to cause the rearrangement of this dopant in PMMA film. Such a rearrangement in the film may be responsible for the observed decrease in the film thickness.

On the other hand, it is worthwhile to consider the reason why the refractive index change in the film doped with (Z)-1 bearing the arylmethylene chromophore is dependent on the structure of the naphthyl substituent introduced into the ester moiety. A comparison of the UV absorption spectral data of 1-naphthol, 4-methoxy-1-naphthol and 2-naphthol in acetonitrile, given in Table 1, demonstrates that the appearance of the naphthol derivative with its shorter wavelength absorption has a tendency to accompany a greater increase in the refractive index  $n$ . Because these absorption bands overlap strongly with those of the oxazolone derivatives 2a and 2b, we propose that the extent to which the linear polarizability of PMMA film doped with (Z)-1 is increased upon photoheterolysis is diminished as the overlapping between the oxazolone and naphthol absorption bands is strengthened.

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