i-Line Sensitive Photoacid Generators Using Thianthrenium Derivatives

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1. Introduction
i-Line (365 nm) sensitive photoacid generators (PAGs) [1-19] have been getting more important due to the wide applicability of photo-induced acid-catalyzed crosslinking systems [20], especially for the UV curing system of the materials having strong absorption in deep UV region. We have developed a series of imidosulfonate derivatives having thianthrene skeleton which work as i-line sensitive PAGs [8,9]. Onium type PAGs have been extensively used on i-line irradiation in combination with sensitizers [13-19]. Although, PAGs having 5-aryl-thianthrenium skeleton [7] were reported by Crivello et al., they have poor absorption at i-line.

In this paper, we report novel i-line sensitive PAGs based on thianthrenium skeleton. Photochemical property and solubility of the PAGs in organic solvents were discussed. The application of the PAGs to photo-induced insolubilization of poly(glycidyl methacrylate) was also investigated.

2. Experimental
A thianthrene derivative, 7-tert-butylothianthrene-2,3-dicarboxylic imide (1), was prepared as described [10] using 4-tert-butylbenzene-1,2-dithiol and 4,5-dichloro-pthalimide. Glycidyl methacrylate (GMA) was purchased from Tokyo Kasei and distilled before use. Poly(GMA) (PGMA) ($M_n = 2.9 \times 10^4$) was prepared by conventional radical polymerization of GMA using 2,2'-azobis(isobutyronitrile) as an initiator.

New thianthrenium PAGs, 3a, 3b, 3c, and 4, were prepared using 1 as a starting material as shown in Scheme 1.

1 (3.41 g, 9.98 mmol) was dissolved in acetic acid (40 mL). Nitric acid (1 N, 14 mL, 14 mmol) was added dropwise to the solution with stirring. The reaction mixture was refluxed for 20 min. The mixture was poured into ice-cold water to give white solid. The solid was filtered and washed with deionized water twice, and dried. Mixture of isomers, (7- or 8)-tert-butylothianthrene-2,3-dicarboxylic imide-S-oxide (2) was obtained as white solid; yield 3.17 g (88%). mp: 234 °C, $^1$H NMR (CDCl$_3$): δ 8.45–7.50 (5H, aromatic), 1.35 (9H, d, -C(CH$_3$)$_3$); IR (KBr) 3222, (N-H), 1732 cm$^{-1}$ (C=O). Anal. Calcd for C$_{18}$H$_{15}$NO$_3$S$_2$: C, 60.48; H, 4.23; N, 3.92. Found: C, 60.09; H, 3.96; N, 3.75. MS (EI), m/z 357 (M$^+$, 20), 294 (M$^+$-63, 100).

Scheme 1. Synthesis of PAGs.

3a, 3b, 3c, and 4 were prepared as described [10]. Phosphorous pentoxide (1.14 g, 4.02 mmol) was dissolved in methanesulfonic acid (14.5 mL, 164 mmol). The solution was added dropwise into a solution of 2 (4.99 g, 14.0 mmol) in anisole (0.77
mL, 14.3 mmol). The reaction was continued at 30 °C for 2 h and cooled to r.t. overnight with stirring. The reaction mixture was poured into 100 mL of ice-cold water. To this mixture with stirring were added 2.98 g (15.8 mmol) of potassium trifluoromethanesulfonate, then, a pale yellow solid precipitated. The solid was collected by filtration and purified by column chromatography (silica gel, eluent; first; CHCl₃, second; AcOEt) to give a pale yellow solid 3a; yield 1.13 g (19 %). mp: 158-162 °C; Td: 317 °C from TGA analysis. ¹H NMR (CDCl₃) δ 8.97-6.88 (m, 9H, aromatic), 3.69 (d, 3H, -CH₃), 1.35 (d, 9H, -C(CH₃)₃); IR (KBr) 3490 (N-H), 1734 cm⁻¹ (C=O); UV (acetonitrile): ε₃65 = 3460 (L/mol · cm). Anal. Calcd for C₂₆H₂₂F₃NO₆S₃: C, 52.25; H, 3.71; N, 2.34. Found: C, 51.61; H, 4.27; N, 2.15.

3b: pale yellow solid; yield 8 %. mp: 164-168 °C; Td: 268 °C from TGA analysis. ¹H NMR (CDCl₃) δ 8.85-6.88 (m, 9H, aromatic), 3.69 (d, 3H, -CH₃), 1.32 (d, 9H, -C(CH₃)₃); IR (KBr) 3453 (N-H), 1733 cm⁻¹ (C=O); UV (acetonitrile): ε₃65 = 3270 (L/mol · cm). Anal. Calcd for C₂₅H₂₂F₆NO₃PS₂: C, 50.59; H, 3.74; N, 2.36. Found: C, 50.18; H, 3.19; N, 2.15.

3c: pale yellow solid; yield 18 %. mp: 142-144 °C; Td: 312 °C from TGA analysis. ¹H NMR (CDCl₃) δ 8.93-6.85 (m, 9H, aromatic), 3.65 (d, 3H, -CH₃), 1.30 (d, 9H, -C(CH₃)₃); IR (KBr) 3446 (N-H), 1734 cm⁻¹ (C=O); UV (acetonitrile): ε₃65 = 3340 (L/mol · cm). Anal. Calcd for C₂₉H₂₂F₉NO₆S₃: C, 46.59; H, 2.89; N, 1.80. Found: C, 46.41; H, 2.89; N, 2.03.

4: pale yellow solid; yield 36 %. mp: 207-213 °C; Td: 295 °C from TGA analysis. ¹H NMR (CDCl₃) δ 9.00-6.84 (m, 9H, aromatic), 3.82-0.83 (m, 9H, -C₂H₅), 1.33 (d, 9H, -C(CH₃)₃); IR (KBr) 3446 (N-H), 1734 cm⁻¹ (C=O); UV (acetonitrile): ε₃65 = 5000 (L/mol · cm). Anal. Calcd for C₃₂H₂₈F₃NO₆S₃: C, 54.45; H, 4.41; N, 2.19. Found: C, 54.05; H, 4.22; N, 2.03.

Sample films (~ 1.0 μm) were prepared by spin-casting from cyclohexanone solution containing PGMA and PAGs onto silicon wafer.

Irradiation was performed at 365 nm using a medium-pressure mercury lamp (Ushtio UM-102, 100 W) with a TOSHIBA UV-D36B filter in air. The intensity of the light was measured with an Orc Light Measure UV-M02.

Baking of the films was carried out with a conventional hot plate. Irradiated polymer films were developed in THF and insoluble fraction was determined by comparing the film thickness before and after developments.

Thermal decomposition behavior was investigated with Shimadzu TGA 50 thermogravimetric analyzer (TGA) under nitrogen flow. UV-vis spectra were taken on a Shimadzu UV-2400 PC.

Solubility of the PAGs was measured as follows. All operations were conducted in an air-conditioned room kept at 20 °C. The PAG (1.00 mg) was mixed with 100 μL of a solvent in a centrifuge tube. After 10 min, the mixture was centrifuged. The supernatant (10 μL, measured by microsyringe) was diluted with a solvent and the concentration of the PAG was determined by measuring the UV absorption intensity at 365 nm.

3. Results and discussion

3.1 Synthesis and characteristics of PAGs

According to the literature [10], synthesis of PAGs having thianthrene chromophore was carried out as shown in Scheme 1. Oxidation of 1 smoothly proceeded to give corresponding S-oxide 2 in high yield. Absence of S-oxide was confirmed by MS spectroscopy and elemental analyses. ¹H NMR analysis suggested that compound 2 was the 1:1 mixture of isomers. Separation of the isomers using column chromatography was unsuccessful. Further reactions were carried out using the mixed isomers. Condensation of 2 and methoxybenzene or n-butoxybenzene successfully proceeded to give corresponding PAGs after exchange of anions from CH₃SO₃⁻ to CF₃SO₃⁻, PF₆⁻, and C₄F₉SO₃⁻. Relatively poor yields were due to the difficulty of purification. Thermal and optical properties of PAGs are shown in Table 1. Thermal decomposition temperatures of 3a, 3b, 3c, and 4 were around 300 °C. The good thermal stability is due to onium salt structures. Molar absorption coefficients of 3a, 3b, 3c, and 4 were ranged from

<table>
<thead>
<tr>
<th>PAG</th>
<th>Tₘ(°C)</th>
<th>Tₐ(°C)</th>
<th>ε(365 nm)(L/mol · cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>158</td>
<td>317</td>
<td>3460</td>
</tr>
<tr>
<td>3b</td>
<td>142</td>
<td>268</td>
<td>2750</td>
</tr>
<tr>
<td>3c</td>
<td>164</td>
<td>312</td>
<td>3340</td>
</tr>
<tr>
<td>4</td>
<td>207</td>
<td>295</td>
<td>5000</td>
</tr>
</tbody>
</table>

a) Melting Point. b) Onset temperature of thermal decomposition determined by TGA measurements under nitrogen. Heating rate; 10 °C/min. c) In acetonitrile.
2750 to 5000 (L/mol · cm), which were higher than those of non-ionic PAGs, tert-THITf (1950) [10] and N-trifluoro-methanesulfonyloxy-1,8-naphthaleneimide (NITf) (380) [1, 10].

Solubility of PAGs at 20 °C was investigated. PAGs 3a, 3b, 3c, and 4 had good solubility (10 mg/mL) in common organic solvents such as benzene, chloroform, ethyl acetate, ethanol, and methanol, except hexane and diethylether (> 1 mg/mL). Incorporation of tert-butyl group in the PAGs was effective to enhance the solubility.

Photolysis of PAGs were carried out in acetonitrile and in poly(methacrylonitrile) (PMAN) film at 365 nm. Figure 1 shows the UV spectral changes of 3a on irradiation at 365 nm in acetonitrile under N2. The absorption band at 360 nm decreased on irradiation. The spectral changes in photolysis were similar to that of 3b, 3c, and 4, which strongly suggests that photolysis occurred in the same reaction mechanism.

Photolysis degree of 3a, 3b, 3c, and 4 was measured by the decrease of the peak at 360 nm. All PAGs showed first-order photolysis profiles, which suggested that the photolysis occurred by a single reaction on irradiation below 100 mJ/cm². Photolysis rate of the PAGs was estimated by the slope of the first order plots for the photolysis of the PAGs. In this work, NITf was chosen as a standard. It is a simple and versatile method to normalize the photolysis conditions [21]. The quantum yields of decomposition (Φd) of PAGs were calculated by the relative decomposition rate using the following equation:

\[ \Phi_d = \Phi_{d_{\text{NITf}}} \times \frac{Rd(1 - 10^{-e_{\text{NITf}}c_{\text{NITf}}})}{Rd_{\text{NITf}}(1 - 10^{-e_{\text{NITf}}c}} \]  

where \( \Phi_{d_{\text{NITf}}} \) is a quantum yield for the photolysis of NITf (0.17) [1, 21], \( l \) is optical length, \( Rd \) and \( Rd_{\text{NITf}} \) are decomposition rate, \( e \) and \( e_{\text{NITf}} \) are molar absorption coefficient, \( c \) and \( c_{\text{NITf}} \) are molar concentration of the sample and NITf in acetonitrile, respectively. The \( e \) and \( c_{\text{NITf}} \) values were approximately 1 x 10⁴ M on each measurement. Using the \( Rd \) value of NITf in acetonitrile on irradiation at 365 nm, \( \Phi_d \) values of the PAGs were evaluated. Photolysis of PAGs in PMAN films was also carried out. Photolysis degree of PAGs was estimated by UV spectral changes. PAG contents was 10 wt% for PMAN by weight and thickness of the films was 2.0 μm on measurements. The spectral changes of PMAN films containing PAGs were almost similar with those in acetonitrile. The results are summarized in Table 2. The \( \Phi_d \) values of the PAGs in acetonitrile under N₂ and in PMAN in air were almost identical for each of PAGs. The \( \Phi_d \) values of the PAGs in acetonitrile in air were smaller than those under N₂. The results suggest that photolysis reaction generates radical species. The high \( \Phi_d \) values in PMAN films may be due to effective inhibition of the diffusion of oxygen. The \( \Phi_d \) values of the PAGs in acetonitrile under N₂ increased in the order 4 < 3a < 3c < 3b. The \( \Phi_d \) values affected by the structure of the PAGs, especially the structure of R groups and counter anions shown in Scheme 1. The PAG 3b has the highest \( \Phi_d \) value among the PAGs and the lowest thermal stability as discussed in the previous report [10].

### Table 2. Quantum yields (\( \Phi_d \)) of PAGs.

<table>
<thead>
<tr>
<th>PAG</th>
<th>( \Phi_d ) in acetonitrile under N₂</th>
<th>( \Phi_d ) in air</th>
<th>( \Phi_d ) in PMAN in air</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>0.24</td>
<td>0.080</td>
<td>0.27</td>
</tr>
<tr>
<td>3b</td>
<td>0.43</td>
<td>0.090</td>
<td>0.32</td>
</tr>
<tr>
<td>3c</td>
<td>0.28</td>
<td>0.064</td>
<td>0.28</td>
</tr>
<tr>
<td>4</td>
<td>0.17</td>
<td>0.052</td>
<td>0.16</td>
</tr>
</tbody>
</table>

3.2 Photocrosslinking of PGMA

The PAGs 3a, 3b, 3c, and 4 are applicable to photopolymer systems. Figure 2 shows the photocrosslinking properties of PGMA containing the PAGs on irradiation at 365 nm. A
photocrosslinking profile of NITf is also shown for comparison. Photocrosslinking efficiency of PGMA films increased in the order NITf ~ 3c < 3a ~ 4 < 3b. Generally, photocrosslinking efficiency is affected by both the strength of acid generated and the quantum yields of acid generation of PAGs. In this case, the PAGs 3a, 3b, and 4 were useful for photocrosslinking of PGMA.

Fig. 2. Insolubilization of PGMA film containing 1.0 mol% of PAGs on irradiation. PAG: (Ο) 3a, (△) 3b, (□) 3c, (▽) 4, (X) NITf. Development: THF for 10 min.

References