I-Line Sensitive Photoacid Generators Having Thianthrene Skeleton

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1. Introduction

I-line sensitive photoacid generators (PAGs) [1-6] have attracted much attention due to the wide applicability of photo-induced acid-catalyzed crosslinking systems [7], especially for the curing system of the materials having strong absorption in deep UV region. Derivatives of N-hydroxynaphthalene imide [1] and iodonium salts of 9,10-dimethoxyanthracene-2-sulfonic acid [2] are used as i-line sensitive PAGs. We have reported that sulfonate esters of fluorenone oxime [3], isopropylthioxanthone oxime [4], and N-hydroxyimide having thioxanthone skeleton [5] worked as i-line sensitive PAGs. Recently, Civello et. al., reported that a series of 5-aryltianthrenium salt worked as PAGs which have strong absorption at 313 nm [6].

In this paper, we report the preparation of novel i-line sensitive PAGs based on imidosulfonante derivatives with thianthrene moiety and their use for photoinduced insolubilization of polymeric materials.

2. Experimental

Acetonitrile and toluene-3,4-dithiol (Tokyo Kasei), and polystyrene (PS) (M_n = 2.8 x 10^5) (Aldrich) were used as received. Glycidyl methacrylate (GMA) was purchased from Tokyo Kasei and distilled before use. Poly(GMA) (PGMA) (M_n = 2.0 x 10^5) was prepared by conventional radical polymerization of GMA using 2,2'-azobis(isobutyronitrile) as an initiator.

Synthesis of PAGs, N-sulfonfyl-7-methylthianthrene-2,3-dicarboxylic imide derivatives, were prepared using toluene-3,4-dithiol as a starting material as shown in Scheme 1.

Scheme 1. Synthesis of PAGs.

Toluene-3,4-dithiol (1.50 g, 10.2 x 10^{-3} mol) and KOH (1.40 g, 25.0 x 10^{-3} mol) were dissolved in DMF (25 mL) and toluene (20 mL). The mixture was heated for 2 h to azetropically remove water generated in the reaction and excess toluene. The mixture was cooled to ambient temperature and N-phenyl-4,5-dichlorophthalamide (2.97 g, 10.2 x 10^{-3} mol), which was prepared according to the literature [8], was added and heated at 90 °C for 5 h with vigorous stirring. The reaction mixture was cooled, poured into methanol/water (1:1), and then yellow powder precipitated. The powder was filtered, washed with water and dried in vacuo to obtain N-phenyl-7-methylthianthrene-2,3-dicarboxylic imide; yield 3.22g (84%); mp: 222 °C. 1H NMR (CDCl_3): δ 7.96 (2H, s, aromatic), 7.45–7.26 (7H, m, aromatic), 7.07 (1H, d, aromatic),...
2.26 (3H, s, CH₃); IR (KBr) 1708 cm⁻¹ (ν –C=O); UV (acetonitrile) λ_max = 286 nm, log ε = 4.49 (L/mol · cm).

**N-phenyl-7-methylthianthrene-2,3-dicarboxylic imide (6.74 g, 17.9 x 10⁻³ mol)** was refluxed in a solution of potassium hydroxide (15.5 g, 17.5 x 10⁻³ mol) in 300 mL of water for 48 h. After cooling to ambient temperature, the reaction solution was filtered to remove insoluble material. The filtrate was acidified with diluted HCl to give a white precipitate. The product was collected by filtration, washed with water, and dried under vacuum to obtain 7-methylthianthrene-2,3-dicarboxylic acid; yield 4.00 g (70%); mp: 188 °C, ¹H NMR (DMSO-d₆): δ 7.84 (2H, s, aromatic), 7.47 (1H, d, aromatic), 7.38 (1H, d, aromatic), 7.20 (1H, d, aromatic), 2.29 (3H, s, CH₃); IR (KBr) 1688 (ν –C=O), 1459, 1357, 1264, 1116 cm⁻¹; UV (acetonitrile) λ_max = 270 nm, log ε = 4.44 (L/mol · cm).

7-Methylthianthrene-2,3-dicarboxylic acid (4.00 g, 12.5 x 10⁻³ mol) was stirred in 120 mL of acetic anhydride at 100 °C for 19 h under nitrogen. Acetic acid was removed by vacuum distillation. The yellow solid was dried to obtain 7-methylthianthrene-2,3-dicarboxylic anhydride; yield 3.76 g (99%); mp: 213 °C, ¹H NMR (DMSO-d₆): δ 8.24 (2H, s, aromatic), 7.51 (1H, d, aromatic), 7.46 (1H, s, aromatic), 7.25 (1H, d, aromatic), 2.30 (3H, s, CH₃); IR (KBr) 1853 (ν –C=O), 1780 (ν –C=O), 1626, 1466, 1379, 1314, 1254, 1086 (ν C=O–C), 946, 889 cm⁻¹; UV (acetonitrile) λ_max = 290 nm, log ε = 4.16 (L/mol · cm).

**N-hydroxy-7-methylthianthrene-2,3-dicarboxylic imide** was prepared from 7-methylthianthrene-2,3-dicarboxylic anhydride and hydroxylamine hydrochloride. To a solution of 7-methylthianthrene-2,3-dicarboxylic anhydride (1.00 g, 3.33 x 10⁻³ mol) in pyridine (60 mL) was slowly added hydroxylamine hydrochloride (0.270 g, 3.91 x 10⁻³ mol) in a portion wise. After the addition was completed, the reaction mixture was refluxed with vigorous stirring for 12 h. Then it was poured into 300 mL of ice-cold 1 M HCl and precipitated solid was collected by filtration. The solid was recrystallized from methanol to obtain the product; yield 0.765 g (72%); mp: 262 °C, ¹H NMR (DMSO-d₆): δ 10.89 (1H, s, OH), 7.93 (2H, s, aromatic), 7.47 (1H, d, aromatic), 7.43 (1H, s, aromatic), 7.22 (1H, d, aromatic), 2.30 (3H, s, CH₃); IR (KBr) 3432, 1785 (ν –C=O), 1698 (ν –C=O) cm⁻¹; UV (acetonitrile) λ_max = 285 nm, log ε = 4.22 (L/mol · cm).

**N-p-Toluenesulfonyloxy-7-methylthianthrene-2,3-dicarboxylic imide (THITTS)** was prepared from **N-hydroxy-7-methylthianthrene-2,3-dicarboxylic imide** and **p-toluenesulfonyl chloride**. p-Toluenesulfonyl chloride (121 mg, 6.34 x 10⁻⁴ mol) and **N-hydroxy-7-methylthianthrene-2,3-dicarboxylic imide** (200 mg, 6.34 x 10⁻⁴ mol) were dissolved in pyridine (20 mL) and cooled to –15 °C. Triethylamine (64.0 mg, 6.34 x 10⁻⁴ mol) was slowly added to the solution with vigorous stirring. After 15 min, the mixture was allowed to warm to ambient temperature and kept for 24 h. The reaction solution was poured into 50 mL of ice-cold 10 wt% HCl and extracted by CHCl₃. The solution was washed twice with brain, and dried over MgSO₄. The product was purified by recrystallization from CHCl₃/hexane (1:9); yield 100 mg (33%); mp: 266 °C, ¹H NMR (CDCl₃): δ 8.08 (2H, d, aromatic), 7.89 (1H, d, aromatic), 7.46 (1H, s, aromatic), 7.31 (4H, m, aromatic), 7.11 (1H, d, aromatic), 2.46 (3H, s, CH₃), 2.32 (3H, s, CH₃); IR (KBr) 1795 (ν –C=O), 1758 (ν –C=O), 1389, 1321, 11181, 966 cm⁻¹; UV (acetonitrile) λ_max = 290 nm, log ε = 4.25 (L/mol · cm).

Preparation of **N-pentafluorobenzensulfonyloxy-7-methylthianthrene-2,3-dicarboxylic imide (THIPS)** was carried out as follows: **N-hydroxy-7-methylthianthrene-2,3-dicarboxylic imide** (100 mg, 3.17 x 10⁻⁴ mol) and potassium tert-butoxide (36.0 mg, 3.17 x 10⁻⁴ mol) were dissolved in dry THF (1.50 mL). After stirring for 30 min, the mixture was evaporated to dryness. The resulting potassium salt was dissolved to dry DME (1.50 mL) and cooled to –78 °C. Pentafluorobenzensulfonyl chloride (90.0 mg, 3.37 x 10⁻³ mol) was added dropwise. After 2 h, the mixture was allowed to warm to ambient temperature. After 24 h, the reaction mixture was evaporated to dryness. The solid was purified by recrystallization from toluene/hexane (1:10) to obtain the product; yield 93.0 mg (53%); mp: 175 °C, Tg: 196 °C from TGA analysis. ¹H NMR (CDCl₃): δ 7.87 (2H, d, aromatic), 7.34 (1H, d, aromatic), 7.27 (1H, s, aromatic), 7.13 (1H, d, aromatic), 2.32 (3H, s, CH₃); IR (KBr) 1799 (ν –C=O), 1758, 1521, 1505 (ν C=O), 1318, 1203, 1107, 996 cm⁻¹; UV (acetonitrile) λ_max = 291 nm, log ε = 4.34 (L/mol · cm)

Preparation of **N-trifluoromethanesulfonyloxy-7-methylthianthrene-2,3-dicarboxylic imide (THITf)** was carried out as the same procedure of the synthesis of THIPS using **N-hydroxy-7-methylthianthrene-2,3-dicarboxylic imide** and trifluoromethanesulfonyl chloride; yield
50%, mp: 153 °C, Td: 154 °C from TGA analysis.

1H NMR (CDCl3): δ 7.90 (2H, d, aromatic), 7.30 (1H, d, aromatic), 7.24 (1H, s, aromatic), 7.09 (1H, d, aromatic), 2.28 (3H, s, CH3). IR (KBr) 1804 (v -C=O), 1758, 1454, 1377, 1321, 1246, 1118, 963 cm⁻¹. UV (acetonitrile) λ max = 290 nm, log ε = 4.01 (L/mol · cm).

Sample films (~ 6.0 μm) were prepared by spin-casting from polymer solutions containing polymer and PAGs onto quartz plate, CaF₂ plate, or silicon wafer. Cyclohexanone and diglyme were used as solvents.

Irradiation was performed at 254 nm using a low-pressure mercury lamp (Ushio ULO-6DQ, 6 W) without a filter and at 366 nm using a medium-pressure mercury lamp (Ushio UM-102, 100 W) with a TOSHIBA UV-D36B filter in air. The intensity of the light was measured with an Orca 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. In-situ FT-IR measurements were carried out by using a Litho Tech Japan PAGA-100.

Photolysis of PAGs was carried out in acetonitrile or in PS film. Decomposition degree of PAGs in PS films was determined by the peak intensity at about 1760 cm⁻¹ ascribed to C=O stretching of the film (film thickness: 2.0–2.5 μm). Characteristics of PAGs are shown in Table 1.

Table 1. Characteristics of PAGs.

<table>
<thead>
<tr>
<th>sample</th>
<th>Tm (°C)a</th>
<th>Td (°C)b</th>
<th>ε(366 nm)c (L/mol · cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THITS</td>
<td>231</td>
<td>266</td>
<td>1240</td>
</tr>
<tr>
<td>THIPS</td>
<td>175</td>
<td>196</td>
<td>1640</td>
</tr>
<tr>
<td>THITf</td>
<td>153</td>
<td>154</td>
<td>1120</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.

3. Results and Discussion

3.1 Synthesis and characteristics of THITS, THIPS, and THITf.

Novel i-line sensitive PAGs having thianthrene skeleton were prepared. Synthesis of THITS, THIPS, and THITf were carried out according to Scheme 1. Molar absorption coefficients of THITS, THIPS, and THITf at 366 nm in acetonitrile were 1240, 1640, and 1120 (L/mol · cm), respectively. The values were higher than molar absorption coefficients of imide derivatives having naphthalene or thioxanthone skeleton, such as N-trifluoromethanesulfonlyoxy-1,8-naphthalencemide (NITf) (ε = 380 (L/mol · cm) at 365 nm) and 2-nonafluorobuthanesulfonlyoxy-11-thia-2-aza-cyclopenta[a]anthracene-1,3,6-trione (TXINf) (ε = 856 (L/mol · cm) at 365 nm) [7]. Photolysis of THITS, THIPS, and THITf were carried out in acetonitrile solution or in PS films on irradiation at 366 nm. Figure 1 shows the UV spectral changes of THITf on irradiation at 366 nm in acetonitrile. The photolysis profile was similar to that for NITf and TXINf [7], which strongly suggests that photolysis occurred in the same reaction mechanism as NITf. The relative decomposition rates of THITS, THIPS, and THITf on irradiation were in the order THITS < THIPS < THITf by brief estimation based on UV spectral changes.

Fig. 1. UV spectral changes of THITf (2.03 × 10⁻⁵ M) on irradiation at 366 nm in acetonitrile.

Fig. 2. FT-IR spectral changes of THITf in a PS film (10 wt%) on irradiation at 366 nm. Film thickness: 2.0 μm. Exposure dose: 4.72 mJ/cm².
The decomposition degree of THITS, THIPS, and THITf in PS film on irradiation was also followed by IR measurement using the peak at about 1760 cm⁻¹ ascribed to C=O stretching of an imide unit (Fig. 2). Figure 3 shows the photolysis of THITS, THIPS, and THITf in PS films on irradiation at 366 nm from in-situ FT-IR measurements. The relative decomposition rates of THITS, THIPS, and THITf in PS films were 1.0, 89, and 340, respectively, using the result in Fig 3. It seems that quantum yields of photo-decomposition (Φ₆) of THITS, THIPS, and THITf in PS films are very different with each other. It is known that photolysis of NITf occurred through the heterolytic cleavage of a N-O bond to produce sulfonate anion and imide cation. On the other hand, hemolytic cleavage of N-toluenesulfonfolyxy-1,8-naphthalencimide (NITS) was proposed on irradiation [1]. The lower Φ₆ value of NITS than that of NITf was considered to be the difference of the photolysis mechanism. It is interesting that the structure of sulfonate ester of PAGs having thianthrene skeleton affects the reaction mechanism and the Φ₆ values. Precise investigation is in progress.

THITS, THIPS, and THITf showed good thermal stability (T₆₅: 154–266 °C). Their T₆₅ value decreased in the order THITS > THIPS > THITf, which was opposite for the order of photolysis rate. The phenomenon was also observed for PAGs having iminosulfonate skeleton [4].

3.2 Photocrosslinking of PGMA
THITS, THIPS, and THITf are applicable to photopolymer system. Figure 4 shows the photocrosslinking properties of PGMA containing THITS, THIPS, and THITf on irradiation at 366 nm. Photocrosslinking efficiency of PGMA films were in the order THITS < THIPS < THITf. The photocrosslinking efficiency was affected by both the strength of acid generated and the Φ₆ value of PAG. In this case, THIPS and THITf were useful for photocrosslinking of PGMA.

![Graph showing insolubilization of PGMA film containing 1.0 wt% of PAGs on irradiation.](image)

Fig. 4. Insolubilization of PGMA film containing 1.0 wt% of PAGs on irradiation.
PAG: THITS (○), THIPS (△), THITf (□).
Development: THF for 10 min.

References