Oxime Type Photoacid Generators Having Adamantyl Group

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Oxime esters have been known to be excellent photo-acid generators (PAGs). However, the behaviors of alicyclic oxime esters to act as PAG have yet to become clear. Some oxime esters with adamantyl groups were prepared, and their spectra and thermal stabilities were measured. The quantum yields of acid generation ($\phi_{\text{acid}}$) in acetonitrile were measured. These PAGs were then evaluated for lithography materials with a base polymer. They have a good transparency in DUV areas. These physical properties and the performance of PAG depended on the acid precursor group and the substitution group at the C atom of C=N-O part in the oxime esters.

Keywords: photo-acid generator, oxime ester, adamantane, chemically amplified photoresist, super strong acid

I. Introduction

$O$-acyl aromatic ketoximes undergo homolytic cleavage into iminyl radicals and acyloxyl radicals from the triplet excited states [1]. Oxime esters have been known to be excellent photo-radical [2], photo-base [3] and photo-acid generators (PAGs) [4] to be started by the N-O bond cleavage in high yield. We studied sensitization reaction and the application of $O$-acyloximes [5, 6] and $N$-acyloxyphthalimides [7-9], and found an oxime type PAG, (Z,E)-2-(4-methoxyphenyl)-2-[(4-methylphenyl-sulphonyl)oxyimino]-acetonitrile (PAIOTos, Fig. 1), has a high quantum yield of acid generation in the sensitization reaction.

![Figure 1. PAIOTos](image)

On the other hand, the non-ionic PAGs, oxime sulfonates, tried to apply for the ArF (193 nm) [10] and 157-nm [4] lithography. In the reference [4], for example, PAIOTos was evaluated as a PAG in a monocyclic polymer with blocking groups with an alicyclic structure. They concluded that the compounds to generate 4-methylbenzenesulfonic acid, which has a lower acidity than perfluoroalkylsulfonic acids do, gave poor resist patterns. In deep ultra violet (DUV, < 300 nm), PAGs does not need to have an aromatic group to become excited. Base polymers for DUV resists were also designed to have an alicyclic structure to have good transparency and etching resistance. In the molecular design of oxime ester as PAG, it should be expected to generate super strong acid and to have an alicyclic structure. Such alicyclic oxime esters have not been reported, and the reactions and potential in DUV regions have yet to be known.

We prepared novel oxime esters with adamantyl groups, and reported, here, their photo generation of acid in solution and in a typical base polymer.

2. Materials and Methods

2.1. Materials

Oxime type PAGs having adamantyl group, (Z,E)-1-adamantylethanone $O$-tosyl oxime (AMIOT), (Z,E)-1-$N$-(tosyloxy) adamantine-1-carbimidoyl cyanide (ACIOT) and (Z,E)-$N$-((trifluoro-methyl)sulfonyl)oxy) adamantine -1-carbimidoyl cyanide (ACIOF) were prepared. Figure 2 shows their molecular structures. PAIOTos as shown in Fig. 1 was purchased from Midori Kagaku.
2.1.1. Synthesis of AMIOT

1-Acetyladamantane (5.0 g, 2.80×10⁻² mol, (Tokyo Chemical Industry Co.)) and hydroxylamine hydrochloride (5.0 g, 7.19×10⁻² mol, (Tokyo Chemical Industry Co.)) were mixed with 50 ml pyridine. After the mixture was stirred vigorously for 18 h, they were mixed with 50 ml distilled water. Then solvent was removed under reduced pressure in a rotary evaporator. The residual solution was poured into chloroform and separated from the aqueous layer. Then, the solvent was removed to give a white precipitate and dried in a vacuum overnight. 1-Adamantylethanone oxime was obtained (3.83 g, yield 77%).

The oxime (0.3 g, 1.55×10⁻³ mol) was mixed with 50 ml tetrahydrofuran. After the mixture was cooled to 5 °C, p-toluenesulfonyl chloride was added (0.5 g, 2.64×10⁻³ mol, (Tokyo Chemical Industry Co.)). After stirring vigorously for 3 h, 100 ml of distilled water was poured into the solution. Then, tetrahydrofuran (THF) was removed under reduced pressure in a rotary evaporator. The residual solution was poured into chloroform and separated from the aqueous layer. Then, the solvent was removed to give a yellow-white precipitate and dried in a vacuum overnight. The yield was 17.4%. ¹H-NMR (CDCl₃, 400 MHz) : 7.92 (d, 1H), 7.78 (d, 1H), 7.40 (d, 1H), 7.25 (d, 1H), 2.48 (s, 1H), 2.36 (s, 1H), 1.97 (s, 1H), 1.89 (s, 1H), 1.78 (d, 2H), 1.72-1.62 (m, 1H).

2.1.2. Synthesis of ACIOT

Bromomethyl 1-adamantyl ketone (4.0 g, 1.56×10⁻² mol, (Aldrich)) was mixed with 30 ml ethanol. The solution of hydroxylammonium chloride (6.5 g, 9.35×10⁻² mol, (Tokyo Chemical Industry Co.)) in 15 ml ethanol and NaOH 3.7 g in 30 ml distilled water was dropped into the mixture solution. The mixture was refluxed by stirring vigorously for 1 h. After cooling the solution to room temperature, distilled water was added until the mixture became cloudy. After the solution was cooled to 0 °C, the precipitate was collected, washed with distilled water, and then dried overnight under a vacuum. 1-Adamantyl-amphi-glyoxime was obtained (3.2 g, yield 94%).

The oxime product (0.46 g, 2.07×10⁻³ mol) was added to 10 ml ethanol and stirred. Then, 0.9 ml NaOH aq. was added and refluxed by stirring vigorously for 15 min. Then ethanol was removed from the solution by distillation. The residual solution was cooled to room temperature and diluted with distilled water, and then glacial acetic acid was added until the solution showed pH 7. After cooling the solution to 0 °C, the precipitate was collected and washed with distilled water and then dried overnight under a vacuum to produce a gray precipitate. 1-Adamantyl 2-hydroxy iminoacetonitrile was obtained (0.33 g, yield 78%).

The mixtures of 1-adamantyl 2-hydroxyiminoacetonitrile (0.16 g, 7.84×10⁻⁴ mol) and triethylamine (3 ml) in 50 ml THF were stirred. Then p-toluenesulfonyl chloride (0.50 g) was added and stirred overnight at 5 °C. A large amount of distilled water was poured into the solution. After that, THF and water were removed, the residual was dissolved in chloroform, and then it was washed by distilled water. Chloroform was removed to give a yellow-white precipitate and dried in a vacuum overnight. The yield was 82%. ¹H-NMR (CDCl₃, 400 MHz): 1.662-2.067 (m, 15H), 2.462 (s, 1H), 7.257-7.373, 7.665-7.867 (s, 4H).

2.1.3. Synthesis of ACIOF

ACIOF was prepared from 1-adamantyl 2-hydroxyiminoacetonitrile and trifluoromethanesulfonic acid (Wako) with same condition as the preparation of ACIOT. The yield was 26%. ¹H-NMR (CDCl₃, 400 MHz): 1.718-1.936 (m, 15H), 2.167 (s, 1H).

2.1.4. Base polymer for lithographic evaluation

A polymer (P1) solution (in propylene glycol
monoethyl acetate) was supplied from JSR Co. The chemical structure is shown in Fig. 3. The polymer solution was used as it was.

![Chemical structure of the base polymer (P1).](image)

**Figure 3.** Chemical structure of the base polymer (P1).

2. UV-Vis absorption spectra measurement in solution and films

Acetonitrile, which has a high transparency in the short wavelength region, was used as a solvent for the measurement of UV-Vis spectra in the solution.

2.3. Quantum yield of acid generation in the solution

The acetonitrile solution of PAG (3 ml, 6.7×10^{-6} mol dm^{-3}) in a quartz cell was irradiated at 222 nm by an excimer lamp (USHIO UER20-222). After irradiation, the solution was mixed with 1 ml of acetonitrile solution of sodium salt of tetrabromophenol blue (TBPBNa, 3.4×10^{-6} mol dm^{-3}) as an acid sensor, and the absorption spectrum of the mixture solution was measured. The changes of absorption band of TBPBNa at around 620 nm were compared to the calibration curve using 4-methylbenzenesulfonic acid or trifluoromethanesulfonic acid. The determination of the photoacid generation quantum yield (\(\phi_{\text{acid}}\)) was performed as described in the previous article [11].

2.4. Lithographic evaluation

P1 solution was diluted 10 times by cyclohexanone and mixed with PAG in the weight ratio of 100:5 (diluted P1 solution:PAG). The solutions were spin-coated on Si-wafer, and pre-baked (PB) at 60 °C for 5 min (1 μm thickness). The films were exposed at 222 nm, and the post exposure bake (PEB) was carried out at 130 °C for 5 min. They were developed in 2.38 wt% tetramethylammonium hydroxide (TMAH) solution.

3. Results and Discussion

We succeeded to prepare three alicyclic oxime esters designed for PAG. AMIOT and ACIOT were designed as precursors of 4-methylbenzenesulfonic acid, while ACIOF was the precursor of trifluoromethanesulfonic acid as known as a super strong acid. We also have tried to prepare the oxime ester with R\(_1\)= -CH\(_3\) and R\(_2\)= -CF\(_3\) to compare with ACIOF. It was not able to be prepared by the method described here.

3.1. Absorption spectra of PAGs in solution

The UV-Vis absorption spectra of the PAGs in acetonitrile are shown in Fig. 4. AMIOT, ACIOT and ACIOF did not have absorption in the wavelength region over 320 nm. Specially, ACIOF which did not have an aromatic group showed very small absorption, even in the region from 190-320 nm. ACIOT and AMIOT, which have the molecular part of the precursors of 4-methylbenzenesulfonic acid, showed roughly the same spectra, other than at the absorption band around 200-240 nm. This is considered the effect of substituted group at R\(_1\) position. At the position, ACIOT has a cyano group, an electron acceptor, compared to the AMIOT, which has a methyl group instead of a cyano group. These PAGs having adamantyl groups therefore seem to be suitable for DUV lithography due to their high transparency in the region.

![Absorption spectra of AMIOT, ACIOT, ACIOF and PAIOTos in solution (acetonitrile)](image)

**Figure 4.** Absorption spectra of AMIOT, ACIOT, ACIOF and PAIOTos in solution (acetonitrile)

3.2. Quantum yield of acid generation (\(\phi_{\text{acid}}\)) in solution and thermal stability

The \(\phi_{\text{acid}}\) values of AMIOT, ACIOT, ACIOF and PAIOTos in the solution were measured using TBPBNa as an acid indicator after photo generation of acid. The value of AMIOT was obtained to be 0.033. In addition, those of ACIOT and ACIOF were 0.24 and 1.4×10^{-5}, respectively. The \(\phi_{\text{acid}}\) of ACIOF was unexpectedly very low. As a result, the order of \(\phi_{\text{acid}}\) was ACIOT > PAIOTos > ACIOF > AMIOT.
> AMIOT >> ACIOF in acetonitrile.

The $\phi_{\text{acid}}$ values and thermal properties were summarized in Table 1. As shown in the table, the order of thermal stability was PAIOTos > ACIOT >> AMIOT > ACIOF in the temperature of the decomposition point. Consequently, the cyano group at the R1 position made the PAGs thermally stable.

Table 1. Thermal properties ($T_m$: temperature of melting point, $T_d$: temperature of decomposition point) and quantum yield of acid generation ($\phi_{\text{acid}}$) of oxime type PAGs

<table>
<thead>
<tr>
<th>PAG</th>
<th>$\phi_{\text{acid}}$</th>
<th>$T_m$ (°C)</th>
<th>$T_d$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACIOF</td>
<td>1.4×10^{-5}</td>
<td>48</td>
<td>120</td>
</tr>
<tr>
<td>AMIOT</td>
<td>0.033</td>
<td>-</td>
<td>136</td>
</tr>
<tr>
<td>ACIOT</td>
<td>0.24</td>
<td>155</td>
<td>249</td>
</tr>
<tr>
<td>PAIOTos</td>
<td>0.14</td>
<td>140</td>
<td>273</td>
</tr>
</tbody>
</table>

*1 at 222 nm in acetonitrile, *2 under N$_2$ atmosphere

3.3 Application to Photolithography

In the chemically amplified resist (CAR), PAGs play an important role in its sensitivity. The quantum yield of acid generation and strength of acidity are usually directly related to sensitivity. Photopolymer materials composed of P1 and AMIOT, ACIOT or ACIOF were prepared and evaluated on the characteristic curves.

Characteristic curves of P1 with AMIOT, ACIOT and ACIOF were obtained as shown in Fig. 5. In this primitive evaluation, AMIOT showed the highest sensitivity under 1 mJ cm$^{-2}$ among these PAGs. The sensitivity of ACIOF was the same level to that of the ACIOT, although its $\phi_{\text{acid}}$ was observed to be very low in acetonitrile. It is probably explained that ACIOF generates a super strong acid, trifluoromethanesulfonic acid, which directs P1 to cause de-protection easier than 4-methylbenzenesulfonic acid generated from ACIOT does. That is to say that the strength of acidity makes up for the low $\phi_{\text{acid}}$ and absorption of ACIOF.

ACIOT showed the highest $\phi_{\text{acid}}$ and $T_d$ in these PAGs. Whereas it is expected to be a PAG being balanced, the AMIOT photopolymer, after being prebaked at 130 °C, showed less sensitivity than that at 60 °C. The thermal decomposition of AMIOT probably occurred at 130 °C during the prebake and gave such a result. Moreover, it is difficult to explain why the photopolymer including AMIOT showed a higher sensitivity than the ACIOT did (Fig. 6.). We think there is a possibility that AMIOT has some chemical paths to generate acid products after photodecomposition.

Figure 6. Characteristic curve of P1 with AMIOT depended on the prebaking temperature

In the oxime esters, AMIOT, ACIOT and ACIOF, having adamantyl been a group prepared here, we found that ACIOT had a good thermal stability and acted as a PAG in a base polymer for CAR. AMIOT is supposed to generate 4-methylbenzenesulfonic acid the same as ACIOT does. It unexpectedly showed a high sensitivity with P1. Although we succeeded to prepare an ACIOF having the precursor of a super strong acid and a good transparency in DUV areas, it did not have a good thermal stability, and it had a low $\phi_{\text{acid}}$ value.

4. Conclusion

We have succeeded in synthesizing the three kinds of novel PAGs having adamantyl been grouped. They could be suitable for DUV lithography due to their high
transparency in the region. The cyano group at the R1 position made the PAGs thermally stable, and the acid precursor group in the molecules also affected their physical properties and performance of the photopolymer. One of them, AMIOT, showed a high sensitivity. There are probably some reaction paths to enhance acids generation from the products after the photochemical reaction.

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References