The Synthesis, Characterization and Lithography of Photo-Acid Generators with Improved Thermal Stability.

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ABSTRACT:
Photo-acid generators (PAG's) are vital components in the formulation of deep-UV chemically amplified resists. A new series of α-substituted-2-nitrobenzyl arylsulfonate PAG's was synthesized. Because the thermal stability of these PAG's correlates with the upper limit of the post-exposure bake (PEB) temperature of resists formulated with these, a study of the thermal stability was done looking at the effect of varying the α-substituent. The best thermal stabilities were obtained by having a bulky electron withdrawing group situated at both the α- and α-positions of the 2-nitrobenzyl chromophore. This substitution pattern enhances thermal stability by suppressing the nucleophilic displacement reaction of the sulfonate moiety by the nitro group oxygen. When used in resist formulations, PAG's based on these new chromophores conveyed higher thermal stability than was observed for similar PAG's based on the 2-(trifluoromethyl)-6-nitrobenzyl chromophore. Through a study done on the lithographic sensitivities of a series of resists formulated with poly(4-(t-butyloxycarbonyloxy)styrene-sulfone) (PTBOCSS) and the new PAG's, it was found that the quantum yield of acid decreased as the electron withdrawing power of the PAG's α-substituent increased.

1. Introduction
Chemically amplified resists are of great importance in the field of microlithography [1]. These resists are designed to be very sensitive to radiation by amplifying the effect of absorbed photons by having them initiate a catalytic chemical reaction. Photo-acid generators (PAG's) are vital components in the formulation of deep-UV chemically amplified resists.
nents in several highly sensitive chemically amplified resist schemes [1] for use in the deep-UV (~250 nm). The liberated acid initiates the catalytic cleavage (acidolysis) of a protective group in the resist matrix. The initial resist system of this type [2] was formulated with poly(4-(t-butoxycarbonyloxy)styrene) and the triphenylsulfonium or diphenyliodonium salts described by Crivello [3]. The amplifying process is the deprotection of the t-butoxycarbonyl (t-BOC) group during post-exposure bake (PEB).

We have previously described a class of non metallic PAG's based on covalent 2-nitrobenzyl sulfonates [4-6]. Previously, we have described modifications to the basic 2-nitrobenzyl chromophore to optimize the thermal stability of the esters [7,8] through the introduction of electron withdrawing bulky substituents at the α-position of the 2-nitrobenzyl chromophore which disfavor nucleophilic displacement. This strategy provided access to thermally stable covalent photochemical sources of powerful organic acids such as 2,2,2-trifluoroethanesulfonic acid (trecis acid) [7]. Other workers have reported examples of covalent compounds capable of photo-generating aryl sulfonic acids [9-12], methanesulfonic acid [13], and hydrogen halides [14, 15]. We have now studied the effect of the introduction of bulky electron withdrawing substituents at the α-position of the 2-nitrobenzyl chromophore. Our initial goal was to examine the thermal stability of the easily accessible tosylate esters of these new α-substituted 2-nitrobenzyl chromophores. Since this gave a relative ordering of the ease of nucleophilic displacement on the α-substituted 2-nitrobenzyl chromophore, we were able to prepare PAG's with improved thermal stability based on strong acids. These materials were important targets since photogeneration of strong non-nucleophilic acid leads to chemically amplified resists with better lithographic sensitivity [7]. Initial lithographic studies were done on resists formulated with poly(4-(t-butoxycarbonyloxy)styrene-sulfone) (PTBOCSS) and α-substituted PAG's derivatized as the tosylates.

2. Method:

Materials Synthesis

The synthesis of the α-substituted PAG's will be described in a more detailed account of this work [16]. Poly(4-(t-butoxycarbonyloxy)styrene-sulfone), PTBOCSS (3:1, Mw = 150,000, D=1.9 was synthesized as previously described [17]. 2,6-Dinitrobenzyl tosylate[5] and 2-(trifluoromethyl)-6-nitrobenzyl tosylate[7] were prepared as before.

Material Characterization

Differential scanning calorimetry (DSC) data for the solid samples were obtained using a Perkin-Elmer DSC-7 differential scanning calorimeter. All samples were heated from 30 to 450° C at a heating rate of 10° C per minute. The thermal stabilities of the new α-substituted PAG's are summarized in Table 4. UV spectra were taken with a Hewlett Packard 8452A diode array spectrophotometer.
Lithographic Evaluation

Exposures were done using a Laserstep® prototype deep-UV exposure tool (NA= 0.35, 5X optics) operating at 248 nm. The photoresist solutions of α-substituted PAG's derivatized as the tosylates were prepared and processed as follows: PTBOCSS (4 g) and an α-substituted-2-nitrobenzyl ester (6.0 mole % relative to the polymer's pendent t-BOC groups) were dissolved in 1,2-dimethoxyethane (24 mL). For comparison a photoresist solution was prepared in the same way with 2,6-dinitrobenzyl tosylate or 2-(trifluoromethane)-6-nitrobenzyl tosylate as the PAG component. Photoresist films were spin coated and prebaked at 105°C for 60 s. After exposure, the substrates were post-exposure baked at 115°C for 30 s. Development was done in 0.17 N tetramethylammonium hydroxide (TMAH) for 30 s.

3. Results and Discussion

Materials Synthesis.

The α-substituted esters were synthesized by one of the two routes shown in Schemes 1 and 2.

![Scheme 1](image1)

![Scheme 2](image2)
Thermal analysis.

Scheme 3 depicts the proposed mechanism [4-6,7] for the thermal decomposition.

\[ \text{Scheme 3} \]

From this mechanism it was expected that large and/or inductively withdrawing \( \alpha \)-substituents would be the most advantageous in increasing thermal stability by disfavoring nucleophilic displacement.

The minima for the DSC exotherms of decomposition (\( T_{\text{min}} \)) of the new \( \alpha \)-substituted PAG's are given in Table 1. A comparison of the decomposition temperatures shows that the highest thermal stabilities are obtained when both a second \( \sigma \)-substituent and an \( \alpha \)-substituent are present. In this way, decomposition temperatures as high as 276\(^\circ\)C were achieved. This compares favorably with decomposition temperatures previously reported [7] for 2-(trifluoromethyl)-6-nitrobenzyl tosylate (255\(^\circ\)C). The greatest amount of stabilization (87\(^\circ\)C) arises when only \( \alpha \)-substitution by cyano is present. Conversely, the least amount of stabilization (11\(^\circ\)C) occurs when both \( \alpha \)-substitution by acetyl and \( \sigma \)-substitution by nitro are present.

An empirical relationship was developed to predict the temperature of decomposition (Figure 1). In this relationship to measure steric interactions of both \( \sigma \)-substituents, and \( \alpha \)-substituents, Taft steric parameters (\( E_\sigma(\sigma) \) and \( E_\alpha(\alpha) \), respectively) were calculated from Charton steric values (\( \nu \)) [18]. In most cases, the minimal value of \( \nu (\nu_{\text{min}}) \) was chosen to calculate \( E_\sigma \) for substituents with large conformation dependence (LCD). This was done to remain in conformance with the principle of minimal steric interaction [19]. However, for \( \alpha \)-alkoxy carbonyl substituents which could undergo coulombic repulsion in the conformation leading to \( \nu_{\text{min}} \), the \( \nu_{\text{max}} \) values were used instead to calculated \( E_\sigma(\alpha) \). As before [7,8], \( \sigma' \) constants [20] were used to determine the inductive effects of \( \sigma \)-substituents, whose resonance interaction is sterically suppressed. Electronic effects at the \( \alpha \)-position were assessed using \( \sigma^*(\alpha) \) values. This constant measures inductive electronic effects for direct attachment of a substituent on an aliphatic site [20]. A final refinement to this empirical model was to introduce the possibility for the \( \alpha \)-substituent to undergo resonance interactions.

Thus, an estimate was made of combined resonance, inductive effects for \( \alpha \)-substituents by defining the following: \( \sigma(\alpha) = \left( \sigma_R/\sigma_I \right) \sigma^*(\alpha) + \sigma^*(\alpha), \) where \( \sigma_R \) and \( \sigma_I \) are respectively resonance and inductive component of the \( \sigma \) constant for substitution onto an aryl moiety [21]. From space-filling
Table 1
Thermal decomposition temperature ($T_{\text{min}}$) of $\alpha$-substituted 2-nitrobenzyl tosylate (Ts) or 1,3-benzenedisulfonate(Bis) PAG derivatives.

<table>
<thead>
<tr>
<th>$R_a$</th>
<th>$R_{\alpha}$</th>
<th>$R_b$</th>
<th>$T_{\text{C}}$</th>
<th>$T_{\text{min}}$</th>
<th>$T_{\text{C}}$</th>
<th>$\Delta T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-CF$_3$ &amp; 6-NO$_2$,</td>
<td>COCH$_3$,</td>
<td>Ts</td>
<td>235</td>
<td>224</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>H,</td>
<td>CN,</td>
<td>Ts</td>
<td>211</td>
<td>124</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>6-NO$_2$,</td>
<td>CN,</td>
<td>Ts</td>
<td>238</td>
<td>204</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>6-Cl,</td>
<td>CN,</td>
<td>Ts</td>
<td>265</td>
<td>218</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>H,</td>
<td>CO$_2$CH$_2$CH$_3$,</td>
<td>Ts</td>
<td>164</td>
<td>124</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>H,</td>
<td>CO$_2$CH$_2$C(CH$_3$)$_2$,</td>
<td>Ts</td>
<td>168</td>
<td>124</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>6-NO$_2$,</td>
<td>CO$_2$CH$_2$CH$_3$,</td>
<td>Ts</td>
<td>261</td>
<td>204</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>6-NO$_2$,</td>
<td>CO$_2$CH$_2$C(CH$_3$)$_2$,</td>
<td>Ts</td>
<td>267</td>
<td>204</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>6-Cl,</td>
<td>CO$_2$CH$_2$CH$_3$,</td>
<td>Ts</td>
<td>276</td>
<td>218</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>6-Cl,</td>
<td>CO$_2$CH$_2$C(CH$_3$)$_2$,</td>
<td>Ts</td>
<td>276</td>
<td>218</td>
<td>58</td>
<td></td>
</tr>
</tbody>
</table>

a) Calculated from previous previously described empirical relationship based on values of $\sigma$ and $\nu$ taken from the literature$^{18}$.  
b) Taken from the literature$^7$.

Scheme 4
Figure 1.
Decomposition Temperature versus $E(o) + [\sigma'(o) + \sigma(m) + \sigma(p)] + E(\alpha) + \sigma(\alpha)$ using $E(\alpha)$ based on $u_{max}$ and $\sigma'(\alpha)$ when substituents are in sterically difficult environments.

Figure 2
Plot of the quantum yield for photogeneration of acid versus the inductive electron withdrawing ability of $\alpha$–substituents located at the o-nitrobenzyl chromophore of 2,6-dinitrobenzyl tosylate PAG's.
molecular models it can be seen that because of steric interactions only the α-cyano-2-nitrobenzyl, α-alkoxycarbonyl-2-nitrobenzyl, and the α-acetyl-2,6-dinitrobenzyl materials show major resonance interactions of the α-substituent with the benzyl carbon σ orbital in the transition state for nucleophilic displacement (Scheme 3).

**Lithography of α-Substituted-2-nitrobenzyl Tosylates.**

Table 2 compares the UV absorbance characteristics, quantum yields and lithographic behavior of three new α-substituted tosylate PAG's with those obtained with PAG's having no α-substitution. All the new PAG's have usable UV absorbance at 248 nm, the exposure wavelength of our exposure tool (Table 2). As expected, the α-substituted materials with dinitro-substitution have roughly twice as much absorbance as the 2-(trifluoromethyl)-6-nitrobenzyl tosylate.

Lithographic evaluations were done with resists formulated with PTBOCSS. It was found that the least sensitive resist was the one that was based on α-cyano-2,6-dinitrobenzyl tosylate. This resist nonetheless gave a lithographic sensitivity similar to that achieved employing 2-(trifluoromethyl)-6-nitrobenzyl tosylate. Moreover, when the resists were formulated with PAG's bearing either α-acetyl or α-ethoxycarbonyl substituents their sensitivities were approximately twice that of using 2-(trifluoromethyl)-6-nitrobenzyl tosylate PAG. Indeed, these materials approached the sensitivity (~0.6 times) of the resist formulated with 2,6-dinitrobenzyl tosylate.

Since all the tosylate PAG's photochemically generate the same acid, (e.i., tosic acid), the assumption was made that the catalytic chain length for acidolytic t-BOC removal is the same. Since there is a proportionality [7] between the lithographic sensitivity and the product of the quantum yield (Φ), the absorbance (ABS/μm) and the catalytic chain length for t-BOC removal, it is possible to estimate Φ. Thus, knowing the relative absorbance of the α-substituted materials (table 5) and the quantum yields of 2,6-dinitrobenzyl tosylate (0.16) [5] and 2-(trifluoromethyl)-6-nitrobenzyl tosylates (0.11) [7] an average value of Φ can be calculated (Table 2). The quantum yields were examined for possible correlations with electronic or steric factors induced by the α-substituent. A good correlation was found between σ*(α), the inductive electron withdrawing ability [20], and the quantum yield for photo-generation of acid (Figure 2). This substituent effect is in line with the proposed mechanism for the photochemical rearrangement (Scheme 4).

**Lithography of α-Alkoxycarbonyl Substituted PAG's of Strong Acids.**

Taking into account the trends we have described for changes of quantum yields and thermal stabilities, the α-alkoxycarbonyl PAG system was chosen for further study since it provided a good compromise between these two properties. We have previously found that PAG's of strong acid tend to give improved lithographic sensitivity to resists formulated with t-BOC styrene based polymers [7]. Using the new α-substituted chromophores, PAG's based on strong sulfonic acids can be prepared with enhanced thermal stabilities. Moreover, since lithographic sensitivity in this type of
Table 2
Lithographic Sensitivity of Resists Formulated with PTBOCSS and α–Substituted Tosylate (Ts) PAG's.

<table>
<thead>
<tr>
<th>R₁ &amp; R₂</th>
<th>Rα</th>
<th>Lithographic Sensitivity a mJ/cm²</th>
<th>λmax nm</th>
<th>εmax litre mole⁻¹ cm⁻¹ m⁻¹</th>
<th>ε248 litre mole⁻¹ cm⁻¹ m⁻¹</th>
<th>Φ248</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-CF₃ &amp; 6-NO₂</td>
<td>COCH₃</td>
<td>50</td>
<td>222</td>
<td>25,700</td>
<td>9,300</td>
<td>0.11 b</td>
</tr>
<tr>
<td>6-NO₂</td>
<td>CN</td>
<td>130</td>
<td>229</td>
<td>25,700</td>
<td>9,900</td>
<td>0.04 b</td>
</tr>
<tr>
<td>6-NO₂</td>
<td>CO₂CH₂CH₃</td>
<td>56</td>
<td>228</td>
<td>27,900</td>
<td>12,000</td>
<td>0.08 b</td>
</tr>
<tr>
<td>6-NO₂</td>
<td>CO₂CH₂(CH₃)₂</td>
<td>66</td>
<td>227</td>
<td>28,500</td>
<td>12,000</td>
<td>0.07 b</td>
</tr>
<tr>
<td>6-NO₂</td>
<td>H</td>
<td>30</td>
<td>227</td>
<td>25,700</td>
<td>9,300</td>
<td>0.16 c</td>
</tr>
<tr>
<td>6-CF₃</td>
<td>H</td>
<td>110</td>
<td>221</td>
<td>28,520</td>
<td>5,100</td>
<td>0.11 c</td>
</tr>
</tbody>
</table>

a) For the lithographic processing conditions see the experimental lithography section.
b) Calculated based on the known quantum yields of 2,6-dinitrobenzyl tosylate and 2-(trifluoromethyl)-6-nitrobenzyl tosylate.
c) Taken from the literature 3,7

Figure 3
Cross-section SEM photographs of dark field (right) and bright field (left) 0.50 µm (top), and 0.35 µm (bottom) lines and spaces. The images were obtained with a resist formulated with 2.5 mole % of an α–substituted PAG of a strong acid in poly(t-butoxycarbonyloxystyrene acetoxy styrene sulphone). The resolution dose was 92 mJ/cm² using a PEB of 125°C for 60 s and development with 0.26 N TMAH for 60 s.
chemically amplified resist generally increased with increased PEB time and temperature, this meant that resists formulated with these new PAG's could be subjected to a higher temperature (up to 135°C for several minutes) post-exposure bake (PEB) to give enhanced sensitivity without losing resolution of small features (~0.35 µm). Conversely, since these resist are more thermally stable a lower molar loading of these PAG's is needed to give the same sensitivity and resolution as a resist formulated with an equivalent molar amount of a lower stability PAG heated under less harsh PEB conditions (115°C). Figure 3 shows an example of an image obtained at a low loading of an α-substituted PAG using a high temperature PEB. Under these conditions resists formulated with the PAG's of the same acid prepared with o-CF₃ or o-NO₂ substituted o-nitrobenzyl chromophores gave complete loss of features.

4. Conclusion

The introduction of an α-substituent onto the benzyl position of a 2-nitrobenzyl PAG appears to affect thermal stability by suppressing nucleophilic displacement mainly through a combination of steric and inductive effects. Resonance induced deactivation of the nucleophilic displacement by electron withdrawing α-substituents is also possible. However, except for the small α-cyano group, in a sterically undemanding environment, this effect is comparatively small. Thus, two approaches towards enhancing thermal stability. One approach is to use small α-substituents that can strongly withdraw electrons by resonance in a PAG chromophore with few steric interactions (i.e., no second o-substituent). Alternatively, large, inductively withdrawing α-substituent substituents can be chosen for PAG chromophores with large steric interactions (i.e., large second o-substituent). Although both approaches can enhance the thermal stability of a PAG, it was found that the second approach or a mixture of the two is more likely to yield PAG's with high thermal stability. This effect is simply because of the additivity of α and o-stabilization substituent effects in suppressing nucleophilic displacement. The quantum yield of these new PAG's decreased with increasing electron withdrawing ability of the α-substituent in the 2,6-dinitrobenzyl chromophores. The best compromise between thermal stability and sensitivity is achieved by using PAG's containing the α-alkoxy-carbonyl-2,6-dinitrobenzyl chromophore. This new chromophore is useful in the preparation of PAG's based on a strong acid which can be used to obtain enhanced lithographic sensitivity and resolution without sacrificing the thermal stability of the resist.

References


