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A Retrospective on 2-Nitrobenzyl Sulfonate Photoacid Generators

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An overview on the utility of 2-nitrobenzyl sulfonate photoacid generators (PAG) in chemically amplified deep UV (248 nm) photoresists is presented. This article will detail how structural changes in photoacid generators affect properties such as quantum yield, thermal stability, etc., and will also illustrate how these properties influence the lithographic characteristics of photoresist formulations.

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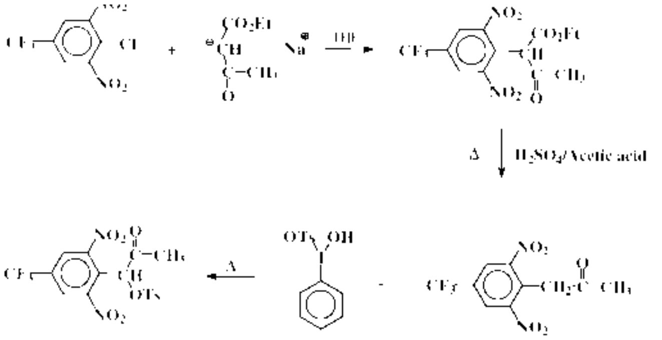
Introduction

The drive toward smaller feature sizes in the microelectronics industry has led to the development of chemically amplified (CA) photoresists. These resists exhibit high inherent sensitivity because the photoproduct from the initial photoevent catalyzes a cascade of reactions that completely transforms the irradiated portion of the resist. A typical example of one of the first approaches toward chemical amplification is the acidolytic deprotection of poly(*t*-butoxycarbonyloxystyrene) during a postexposure bake (PEB) step initiated by the photogenerated acid.[1] Consequently, the study of photoacid generators (PAGs) is an important area of research. The first PAGs employed in chemically amplified photoresists were ’onium salts, such as triphenylsulfonium hexafluoroarsenate. Subsequently, following our own work on 2-nitrobenzylsulfonate,[2] much work was done on non-ionic PAGs by other researchers who reported examples of covalent compounds capable of photogenerating aryl sulfonic acids,[3–6] methanesulfonic acid,[7] and hydrogen halides.[8,9] We will detail here an overview of our work over the years[2,10–14] on 2-nitrobenzyl sulfonate PAGs.

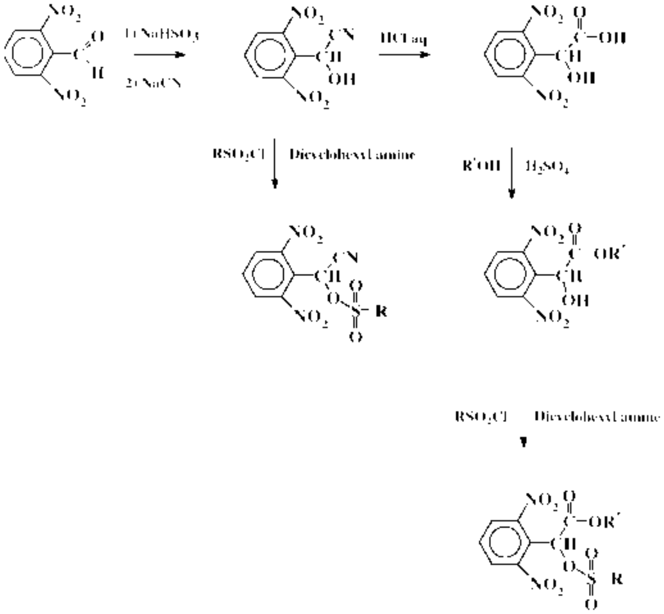
Synthesis

The 2-nitrobenzyl sulfonate esters are readily made either by esterification of 2-nitrobenzyl alcohol with sulfonyl halides or by reaction of 2-nitrobenzyl halides (preferably bromides) with a silver sulfonate salt.[2,10–14] The α-substituted esters were synthesized by one of the two routes shown in Schemes 1 and 2.

Most simple non-α substituted 2-nitrobenzyl alcohols can be readily obtained by high-temperature bromination of 2-nitrotoluenes followed by basic hydrolysis.[11] In some instances,[11c] gentle carbon–carbon coupling reactions such as the Ullman or Suzuki coupling may be used on 2-nitroarylhalides to obtain noncommercially available toluene precursors. Alternatively, commercially available 2-nitro-substituted benzoic acids or benzaldehydes also may be used as source material by reducing with BH_3(THF) or $NaBH_4$, respectively.[11c]



Scheme 1



Scheme 2

For the preparation of 2-nitrobenzyl chromophores with electron withdrawing groups, two synthetic approaches are useful. The first approach, which leads to α-acetyl substitution, takes advantage of the tendency of aryl compounds substituted with electron withdrawing substituents to undergo nucleophilic aromatic substitution (Scheme 1).

The pathway to PAGs with α-cyano and α-alkoxycar-bonyl substituents is summarized in Scheme 2. We have found

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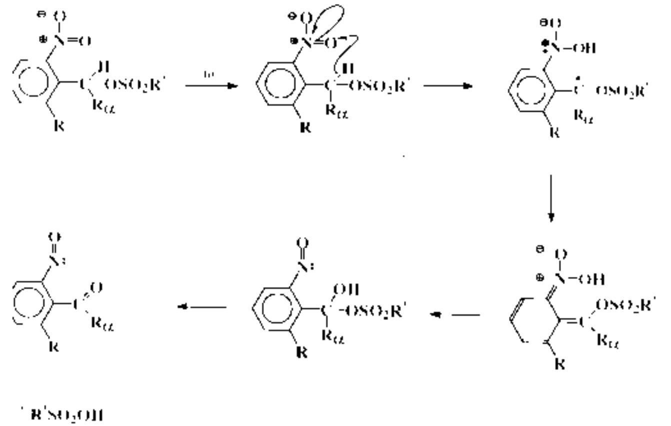
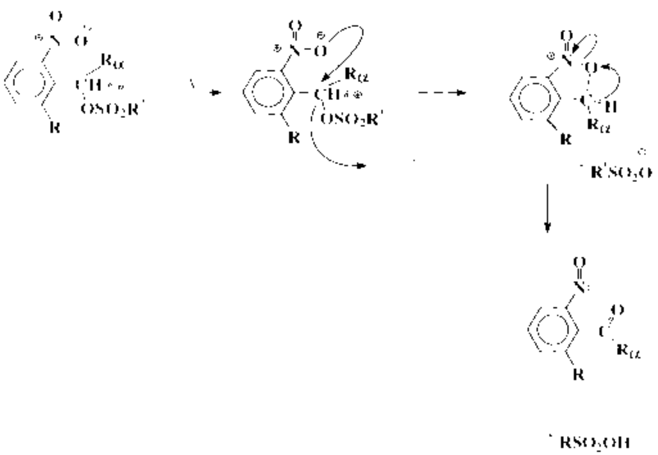


Scheme 3.



Scheme 4.

that 2-nitrobenzyl aldehydes easily undergo cyanohydrin formation in the presence of sodium cyanide. These materials may be stored indefinitely in the dark at room temperature without any conversion to acetal, as occurs in the case of benzaldehyde and mandelonitrile.[15] An equilibrium shift toward the cyanohydrin induced by the electron withdrawing nitro substituent may account for this increased stability.[16] These cyanohydrins may be reacted with a sulfonyl chloride to obtain directly an α-cyano-substituted PAG. Alternatively, they can be hydrolyzed to give derivatives of 2-nitromandelic acid. The 2-nitromandelic acid can be easily esterified under acid catalysis. By changing the nature of the alcohol used in this step, it is possible to modify easily the solubility of the PAGs obtained in the final step (Scheme 2). For instance, PAGs having an α-neopentylcarbonyl substituent have greater solubility than those with the α-ethoxycarbonyl substituent in less polar low-toxicity spin-casting solvents such as 3-ethyl ethoxypropionate (EEP). The final step is the reaction of these alkyl esters of mandelic acid with sulfonyl halides that yields the PAGs with α–alkoxycarbonyl substituents.

Formulation Advantages

Because of their covalent structure, 2-nitrobenzyl sulfonate PAGs have good solubility in a variety of commonly used “safe” spin-casting solvents such as EEP and do not tend to phase separate from spun-on resist polymer matrices even if these are very nonpolar. Unlike many other photogenerators of acid, 2-nitrobenzysulfonate PAGs have a photolysis mechanism (Scheme 3) that does not involve the photogeneration of intermediate radical or radical cations that may abstract protons from the medium. This together with the fact that nitro groups are well-known radical inhibitors means that deleterious cross-linking reactions induced by radicals are unlikely to occur in the exposed regions of resists formulated with 2-nitrobenzyl sulfonate PAGs.

Thermal Stability

The thermal stability of the resist films during PEB is a very important property because thermal release of acid in unirradiated areas causes dark erosion and decreases contrast. Relative thermal stabilities of these materials were judged by measuring by DSC the temperature corresponding to the maximum rate of the exothermic decomposition (T_{min}) of the 2-nitrobenzyl sulfonate PAGs. As we have shown previously, the relative order of the T_{min}’s is useful for predicting the relative order of resist stability during thermal cycles of processing[10,11a,12] for resists formulated with 2-nitrobenzyl sulfonate PAGs. Be cautioned that this is not true for most other PAGs because the reactions occurring thermally in these PAGs may not parallel those occurring in a typical resist film or resist solution. This is because in the resist film usually some type of nucleophilic displacement is responsible for thermal generation of acid from the PAG; whereas, thermal decompostition of PAG’s in the solid form may occur by totally different mechanisms which may not necessarily release a sulfonic acid. However, for 2-nitrobenzyl sulfonate PAG’s both thermal decomposition in solid form and in the polymer matrix occurs through some type of nucleophilic displacement at the benzylic position of the PAG to release a sulfonic acid. Specifically, the thermal decomposition of these PAG’s in the solid form is governed by an intramolecular nucleophilic displacement by the nitro group (Scheme 4) at the benzylic position which releases the sulfonic acid. Therefore, this reaction is useful in predicting the relative ease of other nucleophilic displacements which may be occurring on the PAG in the resist matrix to release sulfonic acids. Indeed, we have correlated the relative tendency to undergo intramolecular nucleophilic displacement with improved resistance to thermal cycling during processing and also to better shelf life.[12a,b] This is not surprising since any intermolecular nucleophilic displacements such as hydrolysis or reaction with other nucleophilic moieties within the resist would be expected to follow the same relative ordering

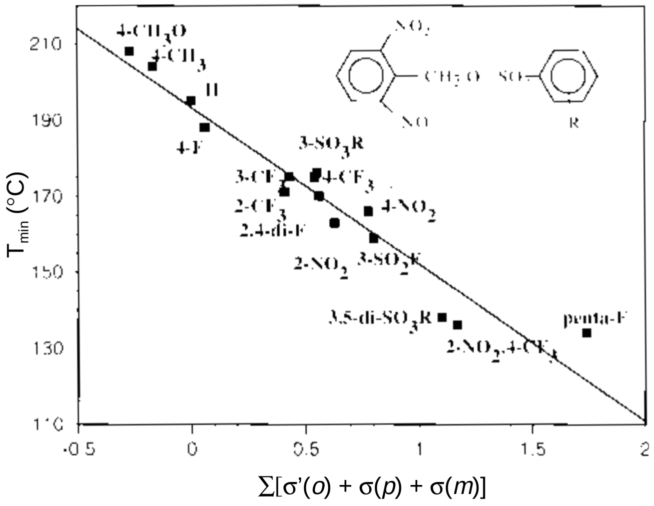


Figure 1. Plot of relative decomposition temperature T_{min} versus $\Sigma[\sigma'(o) + \sigma(p) + \sigma(m)]$ for the 2,6-dinitrobenzylbenzenesulfonate derivatives.

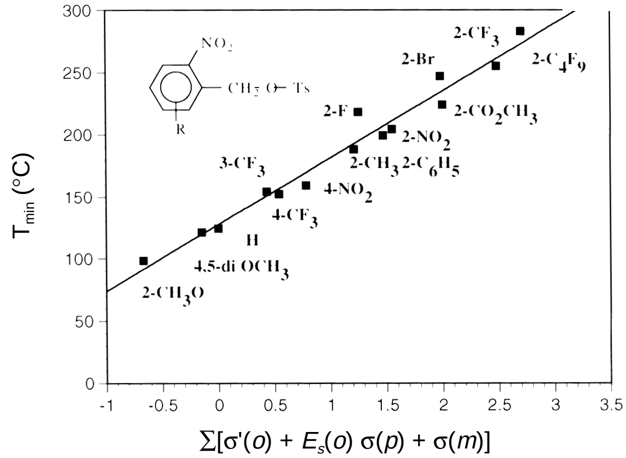


Figure 2. Plot of relative decomposition temperature T_{min} versus $\Sigma[\sigma'(o) + E_s(o)\ \sigma(p) + \sigma(m)]$ for the 2-nitrobenzyl tosylate derivatives.

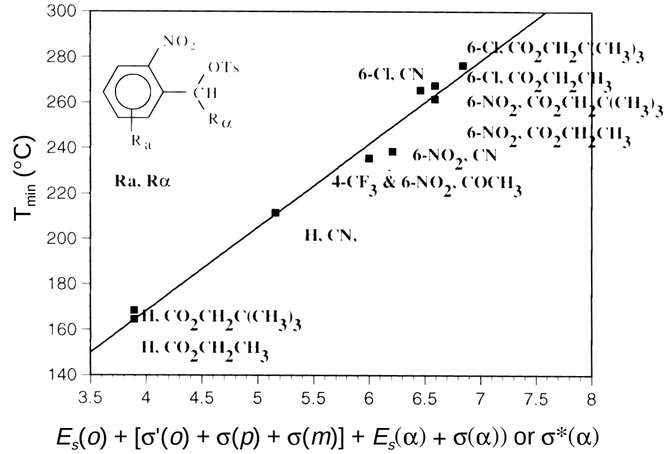


Figure 3. Plot of decomposition temperature T_{min} versus $E_s(o)$ + $[\sigma'(o) + \sigma(p) + \sigma(m)] + E_s(\alpha) + \sigma(\alpha)$ using $E_s(\alpha)$ based on u_{max} and $\sigma^*(\alpha)$ when α-substituents are in sterically difficult environments where coulombic repulsion occurs.

with changing substituents at the 2-nitrobenzylsulfonate PAGs as we have observed for the intramolecular decomposition of these materials. Confirming this result, others have recently demonstrated that factors disfavoring nucleophilic displacement of PAGs in phenolic resist matrices tend to increase their thermal stability.[17]

Figure 1 indicates that strong acid photoreleasing PAGs (which have aryl sulfonate moieties substituted with electron withdrawing groups) will tend to be thermally labile and afford resists with poor thermal stability. Fortunately, altering the PAGs by introducing sterically bulky electron withdrawing groups at the ortho position of the 2-nitrobenzyl chromophore makes it possible to improve thermal stability (Fig. 2). Similarly, the introduction of bulky electron withdrawing groups at the benzylic α-position[12] also greatly improves the stability of these PAGs (Fig. 3). Particularly advantageous are α-alkoxycarbonyl subsituents such as $CO_2CH_2CH_3$ whose steric-electronic properties favor conformations that maximize steric hindrance at the benzylic α-position. Increasing the electronic withdrawing ability and steric bulk of α or *o*-substituents tends to hinder thermolysis of PAGs occurring by intramolecular nucleophilic attack of the 2-nitro group on the benzylic position producing p-toluenesulfonic acid after rearrangement (Scheme 4). Figure 4 shows how an α-alkoxycarbonyl substituent is forced, by coulombic repulsion, to undergo a larger steric interaction with the benzyl position than for the acetyl substituent.

Moreover, as discussed before, structural changes that increase thermal stability of these PAGs tend to hinder other nucleophilic displacements such as hydrolysis that could also be detrimental to thermal stability or shelf life of resist formulations.

Dissolution Inhibition

PAGs can be effective dissolution inhibitors, especially in resin matrices that are heavily loaded with hydrophobic moieties. In these instances, materials such as 4-*t*-butoxycarbonyloxy-2,6-dinitrobenzyl tosylate[13] are useful because the photogenerated acid not only removes insolubilizing groups from the polymer but also from the PAG which makes both polymer and unphotoreacted PAGs soluble in aqueous base as illustrated in Scheme 5. Figure 5 shows how a poly-

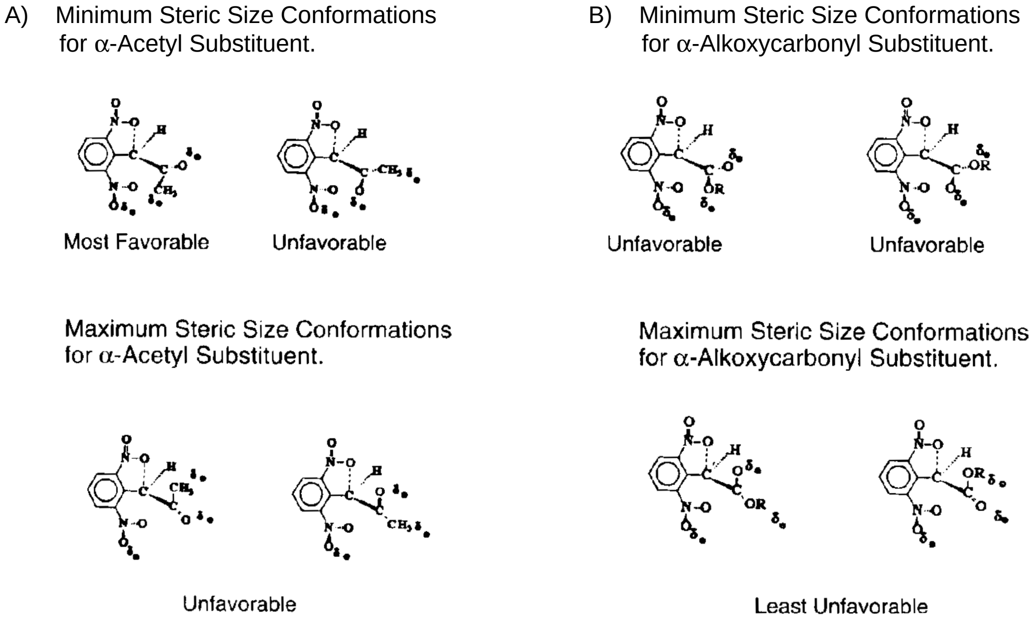
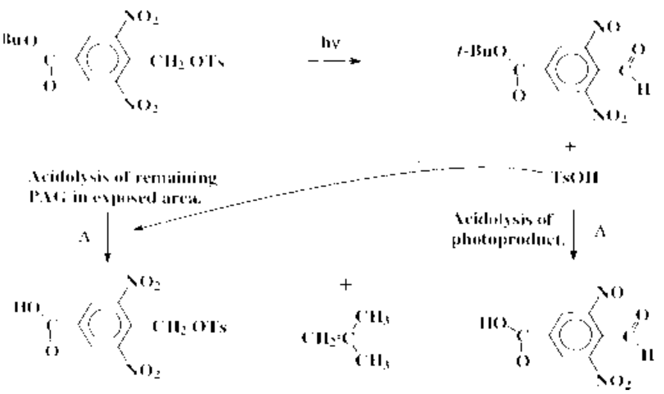


Figure 4. Comparison of steric/coulombic interactions in (a) α-acetyl and (b) α-alkoxycarbonyl substituents.



Scheme 5.

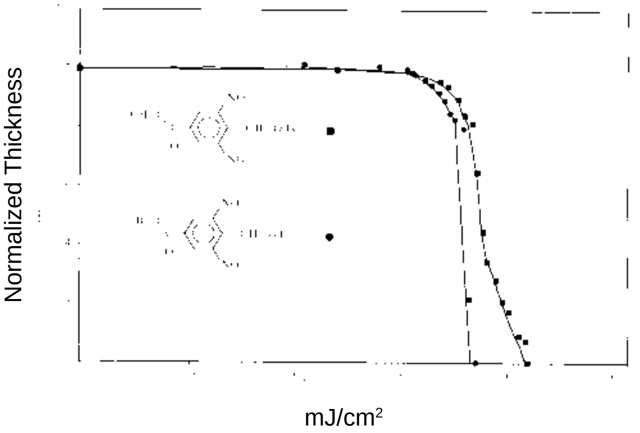


Figure 5. Comparison of the exposure–response curve for resists formulated with poly(4-mesyloxystyrene-4-*t*-butoxycarbonyloxystyrenesulfone) (0.84/1.00/0.47) and 6 mol% of either (●) 4-*t*-butoxycarbonyl-2,6-dinitrobenzyl tosylate or (■) 4-methoxy-2,6-dinitrobenzyl tosylate.

mer heavily loaded with hydrophobic mesylate groups has its exposure–response curve dramatically improved by formulating the resist with 4-*t*-butoxycarbonyl-2,6- dinitrobenzyl tosylate rather than with the nonacidolytically cleaveable methyl ester analog.

Structural Factors Affecting Lithographic Sensitivity

We have shown[11a] that a reciprocal relationship exists between the clearing dose D_p (i.e., lithographic sensitivity) for large lithographic features and the product of the linear absorption coefficient (%ABS/µm), with the quantum yield Φ and the catalytic chain length for the removal of *t*-butoxycarbonyl groups (chain length) (see Eq. 1 and Fig. 6).

$$D_p \propto 1/(\%\mathrm{ABS}/\mu\mathrm{m} * \Phi * \text{chain length}) \qquad (1)$$

Quantum Yield. Increasing sensitivity by increasing absorbance is of limited value because UV radiation must still be allowed to reach the bottom of the resist deposit. Similarly, as we will discuss shortly, large improvements in catalytic chain length can adversely affect the environmental stability of the resist. However, increasing the quantum yield for photogeneration of acid from 2-nitrobenzyl PAGs is not detrimental to resist properties.

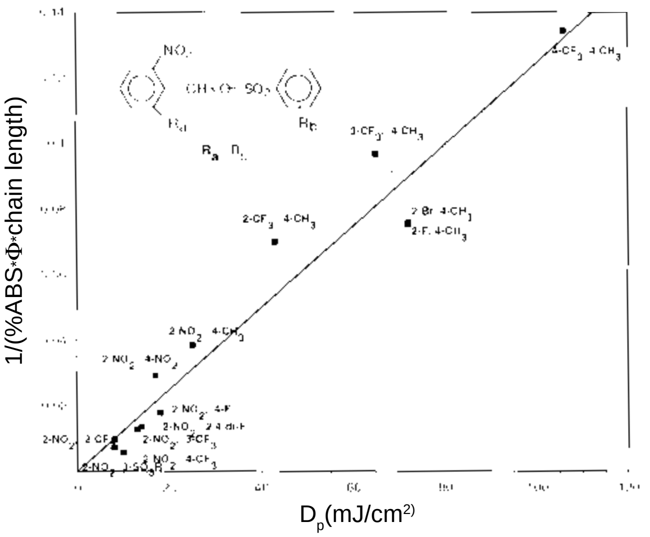
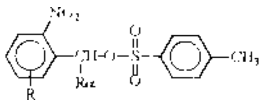


Figure 6. Plot of lithographic sensitivity (as measured by the clearing dose D_p) versus 1/(%ABS*Φ*chain length).

TABLE I. Quantum Yields



R	Rα	Quantum Yield
H	H	0.05
2-NO$_2$	H	0.16
4-NO$_2$	H	0.02
2-CF$_3$	H	0.11
3-CF$_3$	H	0.07
4-CF$_3$	H	0.05
2-NO$_2$	CN	0.04
2-NO$_2$	CO$_2$Et	0.08
2-NO$_2$	COCH$_3$	0.11

The data in the table[11-14] demonstrate that the quantum yield increases with an additional electron withdrawing substituent at the 2 or 3 positon of the arylring. Also, the further an inductively withdrawing substituent such CF_3 is located from the benzylic attachment point the less it increases the quantim yield (Table I); thus the inductive power of the substituent o-CF_3 > m-CF_3 > p-CF_3 parallels the increase in quantum yield. This probably occurs because decreasing the electron density of the aryl makes electron donation from the 2-nitro group to the benzylic position more difficult (Scheme 3). The increase of quantim yield with electron withdrawing power of the substituent only holds true if the additional subtituent on the 2-nitrobenzyl chromophore does not itself have a competitive UV absorbance as is the case for 4-NO_2 substitution. Introduction of a second ortho-nitro group at the 2-nitrobenzyl chromophore, incresases the statistical likelihood of the photochemical rearrangement.

Substituents at the α-position decrease the quantum yield, as their electron withdrawing ability increases (as measured by σ*, the inductive electron withdrawing ability) (Fig. 7). The probable reason is that the *o*-nitrobenzyl photochemical rearrangement goes through an intermediate in which exists nominal electron donation from the benzyl position to the 2-nitro substituent (Scheme 3), in contrast to thermal rearrangement where exactly the opposite occurs.

The above results imply that increasing electron withdrawing ability of an α-substituent will tend to increase thermal stability while decreasing quantum yield. Fortunately,

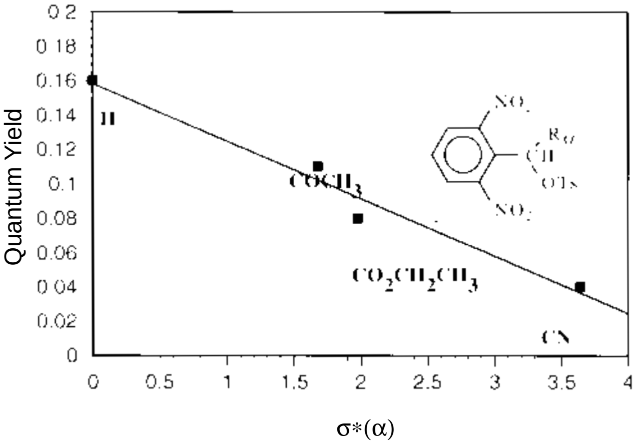
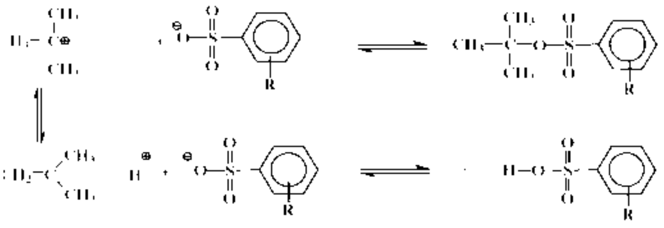


Figure 7. Plot of the quantum yield for photogeneration of acid versus the inductive electron withdrawing ability of α-substituents located at the *o*-nitrobenzyl chromophore of α-substituted -2,6-dinitrobenzyl tosylate PAGs.



Scheme 6.

the α-alkoxycarbonyl substituent offers a nice compromise between quantum yield and thermal stability, mostly due to its steric bulk that enhances thermal stability without added penalty in quantum yield. In contrast to the 2-nitrobenzyl chromophore, changing substituents on the sulfonate moiety has little effect on quantum yield unless it causes a competitive absorbance at 248 nm, e.g., as with the 4-methoxy and 4-nitrobenzenesulfonates.[11a,14]

Catalytic Chain Length. Differing substituents on the arylsulfonate moiety of 2-nitrobenzyl sulfonate PAGs may affect the chain length for *t*-BOC acidolysis through reactions that: (a) directly change the concentration of 'free' H$^+$; or (b) affect its concentration indirectly by changing the concentration of the intermediate *t*-butyl cation (Scheme 6). Because chain length is a measure of *t*-BOC removal efficiency, it is reasonable to expect chain length for acidolysis of *t*-BOC should increase with an increase in Hammett sigma values as embodied in Eq. 2:

$$\text{Log (chain length)} \propto \rho\sigma \qquad (2)$$

Indeed, in a resist formulated with poly(4-*t*-butoxycarbonyloxystyrene-sulfone) (PTBSS) this relationship is true, but only when airborne basic contaminants are excluded (Fig. 8) by use of a protective overcoat.[14]

Such basic airborne contaminants are known to neutralize acid in the exposed resist matrix causing formation of a developer-insoluble surface layer leading to lines exhibiting a T-shaped cross-section (T-topping), and to loss of resolution of small features.[18,19] This phenomenon is also known as the postexposure delay (PED) effect. Methods have been described in the literature to reduce the PED effect by use of protective overcoats,[18] filtering the basic impurities from the air,[19] and by reducing the polymer free volume by annealing.[20]

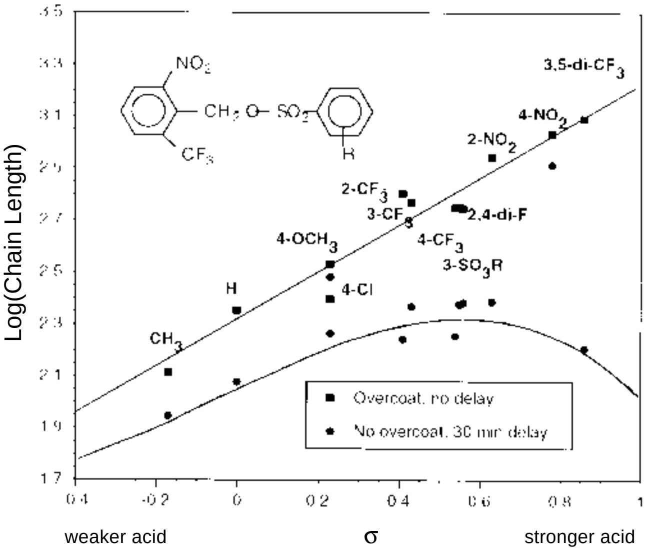


Figure 8. Plots of log(chain length) versus the Hammett sigma values for substitution at the benzenesulfonyl moiety of 2-trifluoromethyl-6-nitrobenzyl benzenesulfonate in a PTBSS resist matrix. Resists processed either with an overcoat and no PED or without an overcoat and with a 30-min PED.

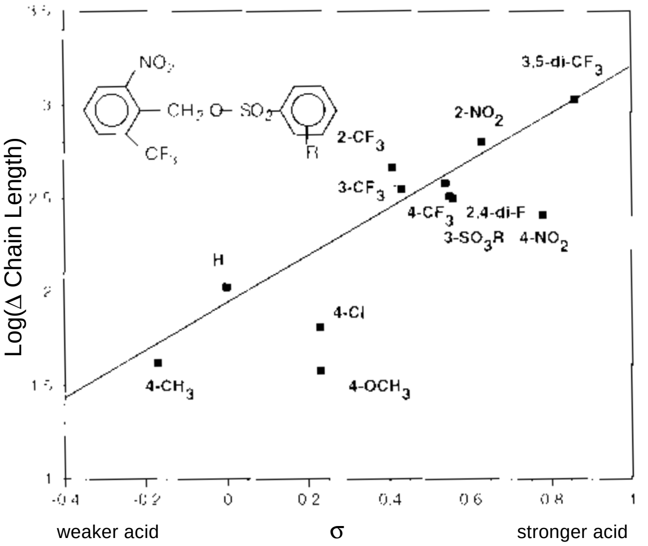


Figure 9. Plot of log(Δchain length) versus the Hammett sigma values for substitution at the benzenesulfonyl moiety of 2-trifluoromethyl-6-nitrobenzyl benzenesulfonate in a PTBSS resist matrix.

We have found that the structure of the PAG formulated into the resist also plays a very important role in the PED effect.[11,14] This information proved helpful in the rational design of PAGs that are less susceptible to the PED effect. For instance, Fig. 8 may be interpreted as showing how, in the presence of basic airborne contaminants, the reactivity of basic airborne contaminants toward photoacids (Fig. 8) increases with increasing substituent polarity leading to shorter and shorter catalytic chain length.[14] The PAGs with polar substituents gave lower log(Δchain length) values than expected from the regression line found for the other PAGs in the plot of log(Δchain length) versus σ (Fig. 9). This means that the

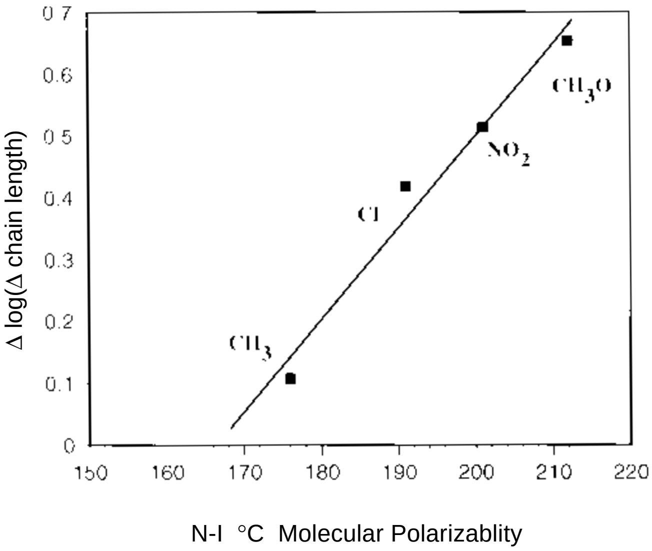


Figure 10. Plot of Δlog(Δchain length) versus molecular polarizability as measure by the N–I transition temperature in similarly substituted liquid crystals.[14]

sensitivity and resolution of resist formulation will start to suffer more and more with increasing photoacid strength because of the PED effect.

This occurs because of the formation of an acid depleted top surface areas which leads, due to the highly non-linear dissolution characteristics of these resist matrixes, to an aqueous base-insoluble surface skin. In imaging, upon development, this manifests itself as completely or partially closed lines called 'T-toppings' which effectively limits both the resolution and sensitity of the resist.

A few of the PAGs that have polar or polarizable substituents impart greater resistance to airborne contaminants than expected[14] (4-Cl, 4-CH_3O, 4-NO_2). Other substituents which are not polar or polarizable do not show this effect (4-F, 4-CH_3, 4-CF_3) at the 4-position, furthermore, when the position of the polar group is changed (i.e., 2-NO_2) the effect is not seen. This is indicative that the effect is due to molecular polarizability which is strongly dependent on the orientation, polarity and polarizability of substituents. To confirm this, the difference between the observed and expected value of Log(Δ Chain Length) from the regression line established by the 'non-anomalous' substituents was calculated and used to see if there was any correlation between this difference [ΔLog(Δ Chain Length)] and the expected molecular ploarizability of the substituents. Indeed, Figure 10 shows that increaseing ΔLog(Δ Chain Length) values correlate well with the expected increasing molecular polarizabilities imparted by the substituent, (4-CH_3O > 4-NO_2 > 4-Cl > 4-CH_3) to the PAG. The correlation between polarizability and the unusual PED behavior points toward a mechanism whereby polarizability induces interactions that reduce the tendency for the photoacid to encounter base either by "tying-up" the base, or the photoacid or both to prevent them from diffusing toward each other.

Summary

We have given an overview of the molecular design considerations for tailoring 2-nitrobenzyl sulfonate PAG structures to optimize the various properties desired for a deep UV, chemically amplified resist. We have found that 2-nitrobenzyl sulfonate is a very flexible PAG platform that lends itself to easy incorporation into state-of-the-art chemically amplified resists.

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