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Effect of *tert*-butyl substituents in triphenylsulfonium cation on spectral properties and photochemical activity of photoacid generators

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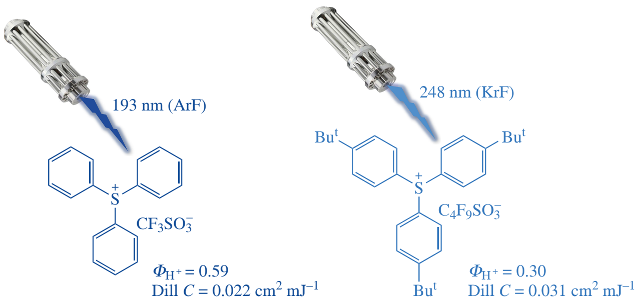
Four photoacid generators such as triphenylsulfonium triflate and nonaflate, 4-*tert*-butylphenyl(diphenyl)sulfonium nonaflate and tris(4-*tert*-butylphenyl)sulfonium nonaflate were synthesized, and their spectral characteristics were investigated in the polymer matrix. The dependence of the photosensitivity of resist films on the efficiency of absorption of actinic radiation and the quantum yields of acid generation was found. Triphenylsulfonium triflate salt and tris(4-*tert*-butylphenyl)sulfonium nonaflate were shown to be promising photoacid generators with a resist sensitive to irradiation by ArF and KrF excimer lasers, respectively.



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One of the key factors in the development of the microelectronic industry over the past few decades is the improvement of the lithographic process technology.[1–4] The fabrication of elements of the microcircuit of the required configuration is performed using a light-sensitive resist. Positive resists have become more widespread due to superior properties in terms of resolution as compared to negative ones. State-of-the-art chemically amplified positive resists with high sensitivity to irradiation by KrF (248 nm) and ArF (193 nm) excimer lasers allow one to obtain the elements with nanometer sizes.[5,6] Generally, chemically amplified positive resists represent a solution of a polymer with acid-labile protecting groups and a light-sensitive photoacid generator (PAG). Triphenylsulfonium salts with anions of strong acids such as trifluoromethanesulfonate (triflate) and perfluorobutanesulfonate (nonflate) are often used as PAGs.[7,8] As triphenylsulfonium triflate or tris(4-*tert*-butylphenyl)sulfonium nonaflate would decompose under exposure to light at the stage of post-exposure bake, it generates a strong acid (see Online Supplementary Materials, Scheme S1), which catalyzes the cleavage of the protecting groups in the polymer chain. Removing the protecting group changes the polarity of the polymer ensuring good solubility of the exposed areas of the resist film in an aqueous-alkaline developer such as tetramethylammonium hydroxide.[9,10] The efficiency of generation of photoacid is estimated by the quantum yield (Φ_{H^+}) determined as

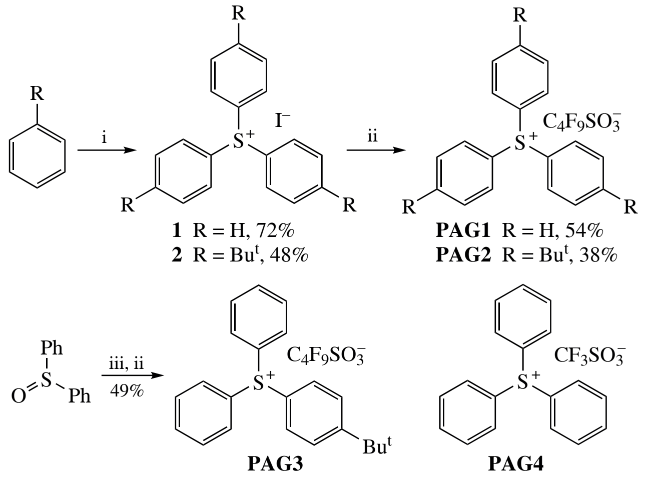
$$\Phi_{H^+} = \frac{n_{H^+}}{n_{ph}}, \qquad (1)$$

where n_{H^+} is the number of acid molecules formed, and n_{ph} is the number of absorbed photons. Next important lithographic characteristic of a resist is the Dill *C* parameter, which represents a rate constant of acid formation from the PAG in a resist film upon exposure to light according to first-order kinetics:[11–13]

$$\frac{\partial G}{\partial t} = -CGI. \qquad (2)$$

Here, *G* is a concentration of a sulfonium PAG at a given time *t*, *I* is the light intensity, and *C* is the rate constant of the decomposition of a sulfonium PAG to acid. The ideal PAG should efficiently absorb the actinic irradiation provided by lasers and generate a strong acid with a high quantum yield. However, the data on the acid generation efficiency of these compounds are insufficient. There are also no systematic studies on the influence of structural features of PAGs on spectral sensitivity to actinic radiation and Φ_{H^+} of acid generation. This work was aimed at investigating the influence of the structure of PAGs with structures **PAG1–PAG4** on their spectral characteristics and photochemical activity in the resist film (Scheme 1). Polymer I with a comonomers ratio of $n/m/p = 10:60:30$ mol% was used in the model resist composition as a polymer matrix (see Scheme S1).

Salts **PAG1**[14,15] and **PAG2**[16] are well-known compounds that are generally obtained through a complex multi-step synthesis using reagents, which are often unstable under standard conditions (Scheme S2). In our work, symmetrical molecules **PAG1** and **PAG2** were obtained by a simplified two-step procedure (see Scheme 1). The main advantage of the proposed method is the use of arene and thionyl chloride to form the triarylsulfonium cation instead of diphenylsulfoxide and arylmagnesium bromide. The nonaflate anion is introduced by a



Scheme 1 *Reagents and conditions*: i, $SOCl_2/AlCl_3$, KI; ii, $C_4F_9SO_3Na$, H_2O, CH_2Cl_2; iii, $4\text{-}Bu^tC_6H_4MgBr$, Me_3SiCl, THF, CH_2Cl_2.

simple ion-exchange reaction using sodium perfluorobutanesulfonate instead of the expensive anhydride or unstable trimethylsilyl ester of the corresponding acid. In fact, the Friedel–Crafts reaction of benzene or *tert*-butylbenzene and thionyl chloride in the presence of anhydrous aluminum chloride resulted in the formation of triarylsulfonium chloride, which was converted into more preferred iodides by treating with a solution of potassium iodide (see Scheme 1, step i). The reaction of compounds **1** and **2** with sodium perfluorobutanesulfonate in water yielded the target **PAG1** and **PAG2**. Non-symmetric **PAG3** was prepared in a conventional way from diphenyl sulfoxide and Grignard reagent $4\text{-}Bu^tC_6H_4MgBr$ (see Scheme 1, step iii) followed by anoin exchange. The success and completeness of ion exchange was confirmed by atomic emission spectra, where no emission bands of iodine were observed (Figure S13). All key compounds were characterized by HPLC chromatography and NMR spectroscopy. The purity of the target PAGs was 98–99%.

The polymer matrix (terpolymer I) has weak absorption in the spectral range of 190–240 nm and is completely transparent to exposure to UV light ($\lambda_{\text{exp}} = 257 \pm 5$ nm) (Figure 1).

By subtracting the absorption bands of polymer I from the absorption bands of the resist film, the optical spectra of the photoacid generators **PAG1–PAG4** were obtained (Figure 2).

The spectra of **PAG1** and **PAG4** are identical since the chromophore in both salts is the triphenylsulfonium cation. Solution of **PAG4** in methanol exhibits an absorption band with maxima of 235 nm ($\varepsilon = 18600$ dm^3 mol^{-1} cm^{-1}), 267 nm ($\varepsilon = 3925$ dm^3 mol^{-1} cm^{-1}) and 275 nm ($\varepsilon = 2772$ dm^3 mol^{-1} cm^{-1}) (see Online Supplementary Materials, Table S1).[17] We also observe these bands in the optical spectra of **PAG2** and **PAG3**. There is no data in the literature on the absorption of PAGs in the spectral region below 220 nm. Here, we found that in this range there is a band with a maximum of 190–195 nm and a larger intensity than that for the band with $\lambda_{\max} = 235$ nm. The functionalization of triphenylsulfonium cation by the introduction of *tert*-butyl substituents affects the optical properties. When going from **PAG1** to **PAG2**, broadening and a bathochromic shift of the bands, as well as an increase in the absorption intensity in the region of 235–240 nm are observed. From a practical point of view, the molar absorption coefficients (ε) of photogenerators at 193 and 248 nm are important. The value of ε at 248 nm for **PAG4** in the polymer matrix (14 000 dm^3 mol^{-1} cm^{-1}) agrees well with ε known from the literature for its solution in methanol (13 302 dm^3 mol^{-1} cm^{-1}).[17] Based on this fact, it can be assumed that **PAG4** and probably other PAGs are in a monomolecular state in the resist film. The ε values at 193 nm are close for all PAGs and 3–5 times higher than the spectral sensitivity at 248 nm.

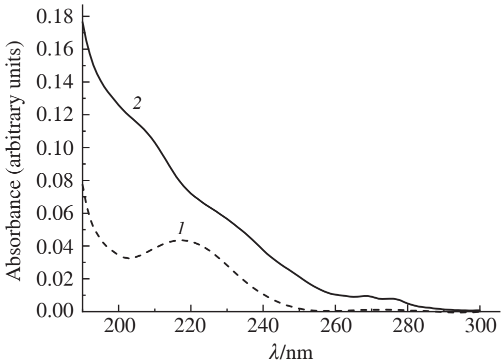


Figure 1 Absorption spectra of the terpolymer I film (line *1*), and the resist based on I with **PAG1** (line *2*), normalized to a film of 300 nm thickness.

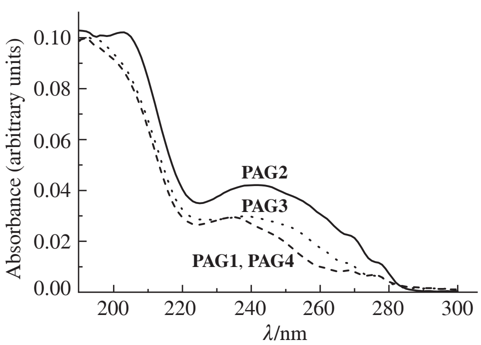


Figure 2 Absorption spectra of **PAG1–PAG4** in polymer matrix I. The layer thickness is 300 nm and the concentration of PAGs is 5.2×10^{-2} mol dm^{-3}.

The Dill parameter C for the prepared resist samples and Φ_{H^+} for the synthesized PAGs in the polymer matrix film (I) were determined by the titration method.[18] In lithography, the exposure threshold dose E_0 is used to estimate the sensitivity of the resist to radiation. This is the minimum dose of light sufficient for the complete removal of the resist film for 60 s when developing. The titration is based on the preparation of a series of resist samples with different base concentrations and the determination of the threshold dose E_0 for them under the same process conditions. The base in the resist composition neutralizes the acid formed during photolysis until it is used up. The E_0 value becomes larger and this increase in E_0 can be used as an indicator of the formation of acid, which amount is equimolar to the base in the resist composition. To justify the titration approach to determine the Dill C parameter and Φ_{H^+}, we consider the kinetics of photoacid formation. Integrating the kinetic equation (2) yields equation (3):

$$G = G_0 e^{-CIt} \tag{3}$$

for the given PAG concentration. Subtracting the last from the initial PAG concentration (G_0) yields formula (4):[12,18]

$$[\text{H}^+] = G_0(1 - e^{-CIt}) \tag{4}$$

for the acid concentration generated during exposure at time t. Here, $[\text{H}^+]$ is the concentration of generated acid, G_0 is the starting concentration of PAG, It is the exposure dose, and C is the rate constant of acid formation (Dill parameter C). In previous work,[18] the low-dose approximation was used to simplify the calculations, when the fraction of the PAG remaining after exposure e^{-CIt}, is taken as $1 - CIt$. Then, for low doses, concentration of generated acid can be calculated as

$$[\text{H}^+] \approx G_0(CIt) \text{ or } [\text{H}^+]/G_0 \approx CIt. \tag{5}$$

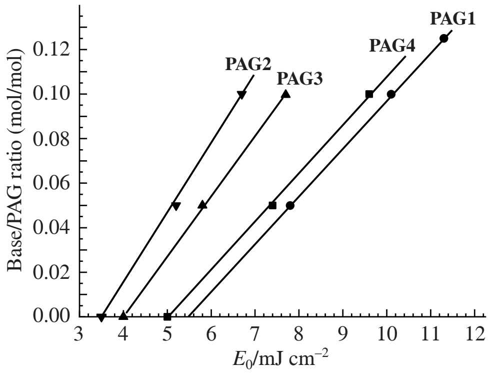


Figure 3 Dependence of the base/PAG ratio (mol/mol) relative to E_0.

If we use in equation (5) the concentration of the base corresponding to the neutralization of acid instead of [H$^+$], the Dill C parameter can be determined from the dependence of the ratio (moles of base/moles of the PAG) on the exposure dose It. The approximation method with small doses can be used up to a value of the ratio moles of base/moles of the PAG of 0.12. Figure 3 shows the results obtained for resists with four synthesized PAGs. The slope of lines was used to determine the Dill C parameter.

The maximum Dill C and the minimum threshold dose E_0 for samples without base (Table 1) imply that the resist with **PAG2** is the most sensitive to radiation exposure. Compositions with **PAG1** and **PAG4** do not differ in the rate of photoacid generation in the film since the same cation of non-substituted triphenylsulfonium is responsible for the spectral sensitivity and quantum yield of the acid. The difference in photosensitivity for samples with **PAG1** and **PAG4** (E_0 of 5.5 and 5.0 mJ cm^{-2}) is due to the fact that it depends not only on the rate of acid formation in the film, but also on the rate of the chemical reaction of unblocking the protected groups in the polymer.

The rate of unblocking depends on the strength of the acid and its diffusion rate. Obviously, the diffusion rate is higher in the case of TfOH. We note that at an exposure dose of E_0, the acid is formed in the resist film in a threshold quantity. Below this quantity or concentration, the unblocking of the protected groups in the polymer under the baking and development conditions is not effective enough, and the resist is not developed. The point of intersection of the lines with the ordinate axis allows one to estimate the threshold concentration of free acid, which is needed for full development of the resist film. The threshold concentrations of perfluorobutane sulfonic acid obtained for **PAG1** and **PAG2** differ from the average value of 5.5 μmol cm^{-3} within experimental error. For TfOH, the threshold value was 5 μmol cm^{-3}. It should be noted that the Dill parameter C characterizes the resist film, in which all components absorb the exposure radiation. Under given experiment conditions, the polymer is transparent to the exposure radiation. The light is absorbed only by the photogenerator, which allows one to determine, along with the Dill parameter C, the quantum yields Φ_{H^+} for the PAGs using the method given previously.[13,19] To determine Φ_{H^+}, we used simplified calculation by introducing the Dill parameter C:

$$\Phi_{H^+} = \frac{C[\mathrm{PAG}]d}{N(1-T)},$$

where C is the Dill parameter (cm^2 mJ^{-1}); [PAG] is the concentration of the PAG in the resist (cm^{-3}); d is the thickness of the resist film (cm); $N = \lambda/(hc)$ is the number of photons with $\lambda = 0.257\times10^{-4}$ cm, equivalent to energy of 1 J (J^{-1}); h is the Plank constant (6.626×10^{-34} J s); c is the speed of light (3×10^{10} cm s^{-1}); and $(1-T)$ is the dose of the light absorbed. The Φ_{H^+} value of 0.59 obtained for **PAG4** matches good with the value of 0.63[13] upon excitation by light with $\lambda = 248$ nm. A decrease in Φ_{H^+} upon the introduction of *tert*-butyl substituents into the triphenylsulfonium cation can be seen.

Table 1 Quantum yields of photoacid generation for **PAG1**–**PAG4** and lithographic indices of resists.

PAG	Threshold dose[a] E_0/mJ cm^{-2}	Dill C/ cm^2 mJ^{-1}	Quantum yield Φ_{H^+}	Fraction of light absorbed by the resist[b] $(1-T)$
PAG1	5.5	0.022	0.59 ± 0.03	0.027
PAG2	3.5	0.031	0.30 ± 0.01	0.075
PAG3	4.0	0.027	0.46 ± 0.02	0.043
PAG4	5.0	0.022	0.59 ± 0.03	0.027

[a] For zero content of base. [b] 300 nm thickness.

The photochemistry of triarylsulfonium salts has been well studied.[20,21] The mechanism of the photochemical reaction of acid formation includes the absorption of a quantum of light by the cation and the degradation of the singlet excited state with the cleavage of the S–C bond. The fragments formed from the cation are transformed into neutral molecules that are accompanied by the formation of strong acid. The decrease in the quantum yields when going from **PAG1** to **PAG2** and **PAG3** is probably associated with the appearance of a new channel for the degradation of the excitation energy along the vibrational levels of *tert*-butyl groups. The results obtained are consistent with the decrease in the efficiency of the PAG when introducing the substituents.[22] The equal Φ_{H^+} values for **PAG1** and **PAG4** indicate that the nature of the anion does not affect the photochemical processes occurring in the triphenylsulfonium cation. The sensitivity of resists is estimated by the threshold exposure dose E_0. The lower the E_0, the higher the sensitivity of the material. It can be seen that the decrease in the quantum yield of photogenerators comprising *tert*-butyl groups is not accompanied by deterioration in the sensitivity of resists based on them. On the contrary, the photosensitivity and the rate constant of the photoacid generation (Dill parameter C) increase, since the decrease in Φ_{H^+} is compensated by an increase in the absorption of actinic radiation by the photogenerator $(1-T)$. From a practical point of view, the C parameter and photosensitivity E_0 are more important characteristics of a resist than the quantum yield. Thus, the investigation of the lithographic performance of four PAGs in a polymer matrix upon exposure to light with a wavelength of 257 nm simulating the conditions of a KrF excimer laser (248 nm) shows that tris(4-*tert*-butylphenyl)sulfonium nonaflate is a very promising PAG. The increase in the extinction coefficients of the PAG with *tert*-butyl substituents levels out the negative effect of the drop in their quantum yield. However, when moving to light with $\lambda = 193$ nm, the value of Φ_{H^+} is expected to be of great importance for assessing the photosensitivity of the material since all the studied PAGs absorb in this region almost equally. Here, we did not determine Φ_{H^+} for light with $\lambda = 193$ nm. It is known when going from 248 nm to 193 nm, the quantum yield of acid generation is decreased.[13,19] If we assume that the dependence of Φ_{H^+} on the structure of the PAG at 193 nm will be similar to that found for 257 nm, thus **PAG1** or **PAG4** will be more preferable to **PAG2** when developing resists sensitive to 193 nm radiation.

In conclusion, in the polymer matrix, photoacid generators based on triarylsulfonium salts exist in a monomolecular state and possess close molar absorption coefficients at 193 nm. When going to 248 nm, the spectral sensitivity of the PAGs decreases by 3–5 times. The introduction of *tert*-butyl substituents into the cation leads to different changes in ε at 248 nm and Φ_{H^+}. Particularly, the absorption intensity for PAGs increases while

$\Phi_{\mathrm{H^+}}$ reduces with the growth in a number of alky groups. At the same time, the photosensitivity of the resist with these PAGs increase, since the drop in the quantum yield is compensated by improving the absorption of photogenerators. The best sensitivity to light with $\lambda = 248$ nm was obtained for a resist based on tris(4-*tert*-butylphenyl)sulfonium nonaflate. Since the PAGs exhibit almost the same absorption at 193 nm, the photosensitivity of the corresponding resist will be determined by $\Phi_{\mathrm{H^+}}$ of the photogenerators. In this case, it is preferable to introduce non-substituted triphenylsulfonium salts into the resist composition.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7743.

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