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Synthesis of some onium salts and their comparison as cationic photoinitiators in an epoxy resist

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Several onium salts have been synthesized and compared as cationic photoinitiators in an epoxy resist. 1-(4-Hydroxy-3-methylphenyl)tetrahydrothiophenium hexafluoroantimonate exposed at 365 nm gave the best results, due to its superior absorption at this wavelength. A series of bis-(triphenyl phosphoranylidene) ammonium salts performed poorly with 254 nm, 365 nm and E-beam irradiation even with the addition of photosensitizer. Triphenyl sulfonium hexafluoroantimonate and triphenyl sulfonium triflate formulated the most sensitive epoxy resist materials to both 254 nm and E-beam radiation sources (0.32 mJ cm^{-2} and 0.3 $\mu C\,cm^{-2}$, 59.2 mJ cm^{-2} and 8.0 $\mu C\,cm^{-2}$ at 20 kV, respectively). © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Cationic photoinitiators based on certain sulfonium and iodonium salts[1] are well known for their ability to polymerize efficiently a wide range of epoxy, vinyl ether and propenyl ether monomers and resins. This chemistry has been applied widely, e.g. in the coatings and inks industry[2], for the rapid prototyping of engineering components[3] and for the preparation of advanced composites[4]. Of particular interest to the microelectronics industry are materials that can facilitate the lithographic imaging of intricate structure for both photomask and semiconductor fabrication. In this respect, triphenyl sulfonium hexafluoroantimonate (TPS-SbF6) has, for example, been successfully employed in the deprotection of *t*-butylcarboxylate polymers[5] and in the crosslinking of tetramethoxymethyl glycoluril/poly(hydroxystyrene) mixtures[6]. Both routes have yielded high-performance commercial products. TPS-SbF6 has also been formulated with a fractionated cresol epoxy novolac resin and been demonstrated to have high potential as an E-beam resist[7,8].

Given the continuous search by electronic manufacturers and suppliers to find materials and processes which aid the cost-effective fabrication of ever smaller devices it is not surprising that many other photoinitiator systems have also been studied. These include: arylmethyl sulfones[9], hydroximide sulfonates[10,11], ferrocenium sandwich compounds[12] and a variety of halogenated aromatic compounds[13,14].

The synthesis of a range of onium salts and their comparison in an epoxy resist to determine their suitability for industrial microlithographic operations is reported.

EXPERIMENTAL

Materials

TPS-SbF6 was obtained from GE Corporation. Triphenyl sulfonium triflate (TPS-triflate) was prepared as described in references 15 and 16. Both the *o*-cresol sulfonium and bisphenol-A sulfonium zwitterion precursors were synthesized using methods already described[17,18]. Bis(triphenylphosphoranylidene)ammonium chloride was obtained from Lancaster Chemicals, and all other reagents were used as received from Aldrich Chemical Company.

Equipment

Characterization of compounds and resist formulations was made by n.m.r. (Bruker Cyromagnet 250 MHz in MeOD solvent), i.r. (Nicolet Magna 750), u.v. (Perkin–Elmer 552) and d.s.c. (Mettler DSC30). Broad band filtered 254 nm deep u.v. exposure measurements were performed using an Oriel device, 365 nm exposure with a calibrated and filtered 300 W Hg lamp and E-beam exposure with an IBM Prototype Vs-O operating at 20 kV.

Synthesis of cationic photoinitiators

1. Tetrahydrothiophenium salts. The tetrahydrothiophenium salts evaluated were made by utilizing a

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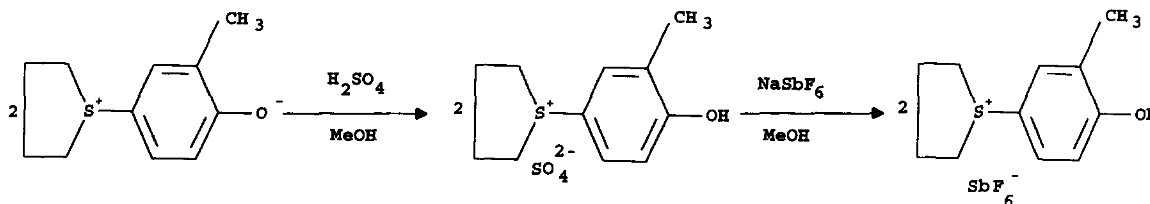
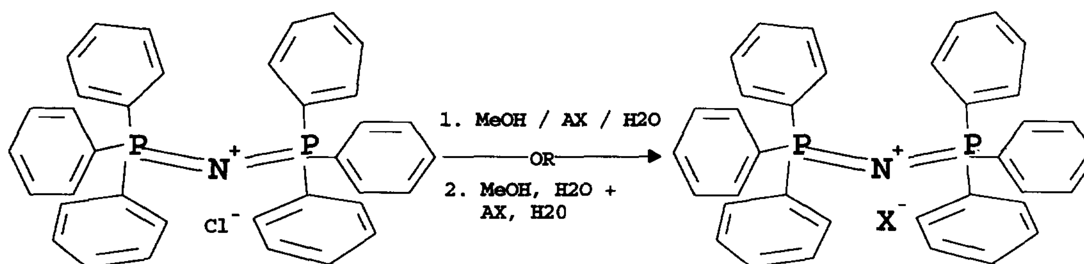
zwitterion precursor to form an immediate sulfate which, through metathesis, is exchanged with the anion of a strong acid. Three sulfonium salts were prepared: 1-(4-hydroxy-3-methylphenyl)tetrahydrothiophenium hexafluoroantimonate (*o*-CS-SbF6), 1-(4-hydroxy-3-methylphenyl)tetrahydrothiophenium triflate (*o*-CS-triflate) and 2,2-bis-(3-tetrahydrothiophenium-4-hydroxyphenyl)-propane triflate (BAS-triflate). Table 1 collates the analytical data.



Preparation example: 25.6 g (0.1113 eq) *o*-cresol zwitterion was dissolved into 125 ml methanol (pH = 11.65). Then 0.5 N H_2SO_4 was added to the zwitterion solution to make a sulfate salt of the zwitterion (pH after addition of acid = 4.94). A small amount of solids present after the addition of acid, was separated from the solution by suction filtration. The intermediate was placed on a rotary evaporator to remove the volatiles (yield: 25.4 g or 93.9%) and an aliquot of sample was titrated with 1 M KOH to determine its activity (2.82×10^{-3} eq g^{-1}). Based on the titration results, the amount of $NaSbF_6$ needed to convert the intermediate compound from the SO_4^{2-} to the SbF_6^- salt was calculated (18.53 g of $NaSbF_6$ was diluted in 150 ml methanol). The remaining dried intermediate was dissolved in 75 ml methanol and to this solution, the methanolic $NaSbF_6$ was added with mechanical stirring. The mixture was allowed to stir for a further 24 h, after which a cloudy (Na_2SO_4) solution was observed. The dispersed Na_2SO_4 was removed by sedimentation with a centrifuge at 6000 rpm for 2 h. The resulting clear solution was devolatilized on a rotary evaporator at 50°C for 3 h. Solid product was collected and weighed (36.8 g, 81.7% yield on the second step, overall yield of 76.7%).

2. *Bis(triphenylphosphoranylidene)ammonium salts.* Two general methods may be employed[19] to derivatize bis(triphenylphosphoranylidene)ammonium chloride (abbreviated to PNP-Cl). These are outlined beneath, each with an example.



A. *Methanolic anion exchange method.* A solution containing PNP-Cl, 1 mmol, and lithium trifluoromethanesulfonate, 3.0 mmol, in 3.0 g of methanol at room temperature was added dropwise to 100 ml of stirred distilled water. The precipitate which formed was collected by filtration and dried under vacuum to yield a white powder product with 93% yield. Elemental analysis for $C_{37}H_{30}F_3N_1O_3P_2S_1$, found (calculated): C 64.31% (64.63), H 4.37% (4.37), N 2.09% (2.04).

B. *Aqueous anion exchange method.* A solution was prepared by dissolving PNP-Cl, 2.87 g, 0.005 mol, in 5.0 g anhydrous methanol, then adding 46.69 g distilled water at room temperature. A salt precipitates on standing, but is easily dissolved by heating to 50°C. A second solution was prepared by dissolving sodium tetrafluoroborate, 0.224 g, 0.002 mol, in 5.0 g of distilled water. An aliquot of the PNP-Cl solution, 10.91 g, 0.001 mol, was added in one portion and agitated. A white precipitate formed immediately, which was separated by vacuum filtration, washed, and dried under vacuum at 80°C for 2 h to produce 3.24 g of material, yield = 53%. Elemental analysis for $C_{36}H_{30}F_4N_1B_1P_2$, found (calculated): C 68.24% (68.89), H 4.90% (4.78), N 2.29% (2.23).

Three PNP-salts were prepared for the study: these are listed in *Table 2*.

Photoinitiator comparison

Thermal stabilities. An important property of photoresists, since pre- and post-exposure bakes can influence the physical state of the material, is the inherent thermal stability of the photoinitiator. This is particularly true for cationic photoinitiator/epoxy blends because crosslinking of unexposed areas must be avoided in order to maximize the photoresist contrast. To assess this likelihood, d.s.c. was employed to measure the onset of thermally initiated polymerization. Samples, 20 mg of epoxy resin (D.E.R.* 330 diglycidyl ether of Bisphenol-A commercially available from Dow Deutschland Inc.), well mixed with 5 weight % cationic initiator, were evaluated and compared over a temperature range between 50°C and 250°C at a heating rate of 10°C min^{-1}; see *Figure 1* for d.s.c. scans and *Table 3* for results summary.

The data indicates that the PNP-salts used do not

Table 1 Analysis of various tetrahydrothiophenium salts

Compound	Melting point (°C)	I.r. bands (cm^{-1})		^{1}H n.m.r. (δ, ppm)	U.v. $\lambda_{max, nm}$ (ϵ_{max}) in MeOH
o-CS-SbF6	>280	O–H	3497	2.26 (s, 3H, CH_3)	
	decomposes	C–H (aromatic)	2997	2.34–2.51 (p, 2H, CH_2)	211 (11.427)
		C–H (aliphatic)	2927	3.57–3.97 (m, 2H, CH_2)	247 (12.432)
		C=C (aromatic)	1591	7.00 (d, 1H, Ph)	297 (1.444)
		C–H (aliphatic)	1503	7.52 (d, 1H, Ph)	
		Sb-F	635	7.58 (s, 1H, Ph)	
o-CS-triflate	107 to 109	O–H	3247	2.26 (s, 3H, CH_3)	
		C–H (aromatic)	3007	2.33–2.56 (p, 2H, CH_2)	206 (14.141)
		C–H (aliphatic)	2947	3.57–3.93 (m, 2H, CH_2)	247 (10.277)
		C=C (aromatic)	1591	6.98 (d, 1H, Ph)	300 (2.525)
		C–H (aliphatic)	1503	7.53 (d, 1H, Ph)	
		S–O	1288	7.57 (s, 1H, Ph)	
		C–F	635		
BAS-triflate	242 to 245	O–H	3457	1.70 (s, 3H, CH_3)	
		C–H (aromatic)	3010	2.34–2.51 (p, 2H, CH_2)	217 (19.386)
		C–H (aliphatic)	2942	3.57–3.97 (m, 2H, CH_2)	294 (6.484)
		C=C (aromatic)	1597	7.00 (d, 1H, Ph)	328 (1.732)
		C–H (aliphatic)	1507	7.52 (d, 1H, Ph)	
		S–O	1290	7.58 (s, 1H, Ph)	
		C–F	635		

Table 2 Analysis of various bis(triphenylphosphoranylidene)ammonium salts

Compound	Method	M.p. (°C)	I.r. bands (cm^{-1})		^{1}H n.m.r. (δ, ppm)	U.v. $\lambda_{max, nm}$ (ϵ_{max}) in MeOH
PNP-triflate	A	212–214	C–H (aromatic)	3052		
			C=C (aromatic)	1438		220 (22.651)
			P=N	1267	7.41–7.69 (m, 5H, Ph)	259 (3.559)
			P–C	1115		267 (3.101)
			C–F	639		
PNP-BF_4	B	217–219	C–H (aromatic)	3050		
			C=C (aromatic)	1438		221 (21.897)
			P=N	1267	7.44–7.69 (m, 5H, Ph)	261 (3.890)
			P–C	1115		238 (3.119)
			B–F	631		
PNP-SbF_6	A	206–209	C–H (aromatic)	3050		
			C=C (aromatic)	1438		224 (22.159)
			P=N	1266	7.44–7.68 (m, 5H, Ph)	262 (3.981)
			P–C	1115		269 (3.005)
			Sb-F	658		

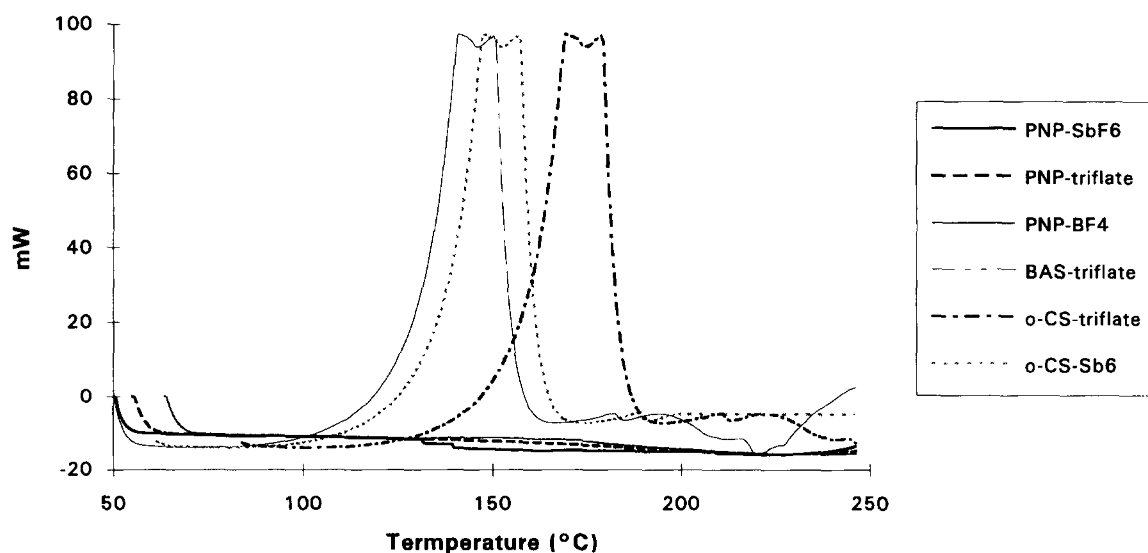


Figure 1 D.s.c. scans from mixtures of D.E.R.* 330 epoxy resin and various cationic photoinitiators

Table 3 Thermal analysis on various onium salts

Compound	PNP-triflate	PNP-BF_4	PNP-SbF_6	BAS-triflate	*o*-CS-triflate	*o*-CS-SbF6
T (onset) (°C)	None	None	None	89.1	110.7	94.3
Enthalpy ($J\,g^{-1}$)	None	None	None	289	294	278

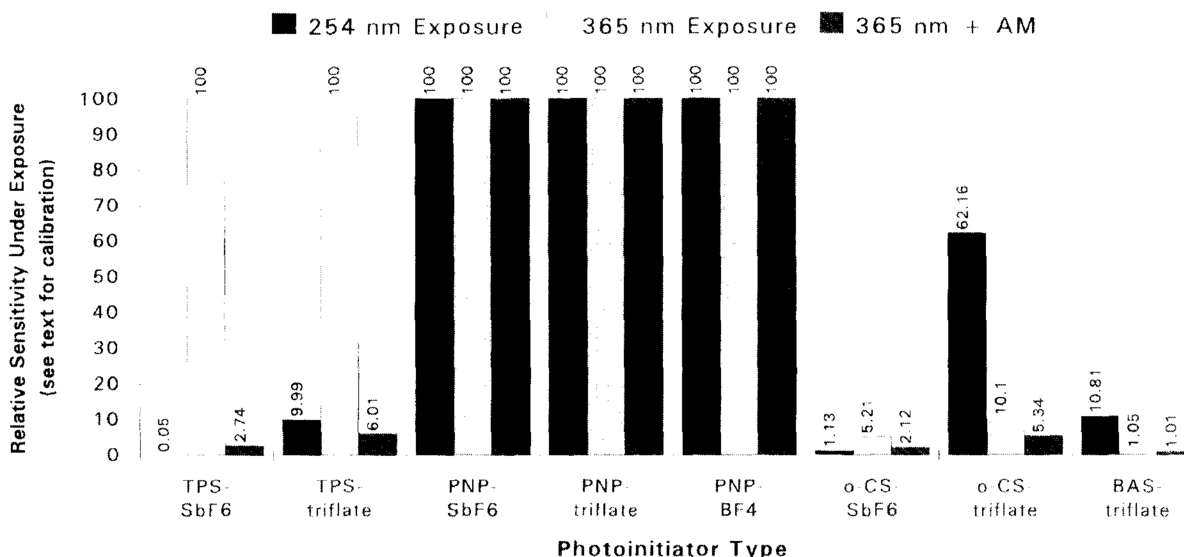


Figure 2 Relative photoinitiator sensitivities under 254 and 365 nm exposure

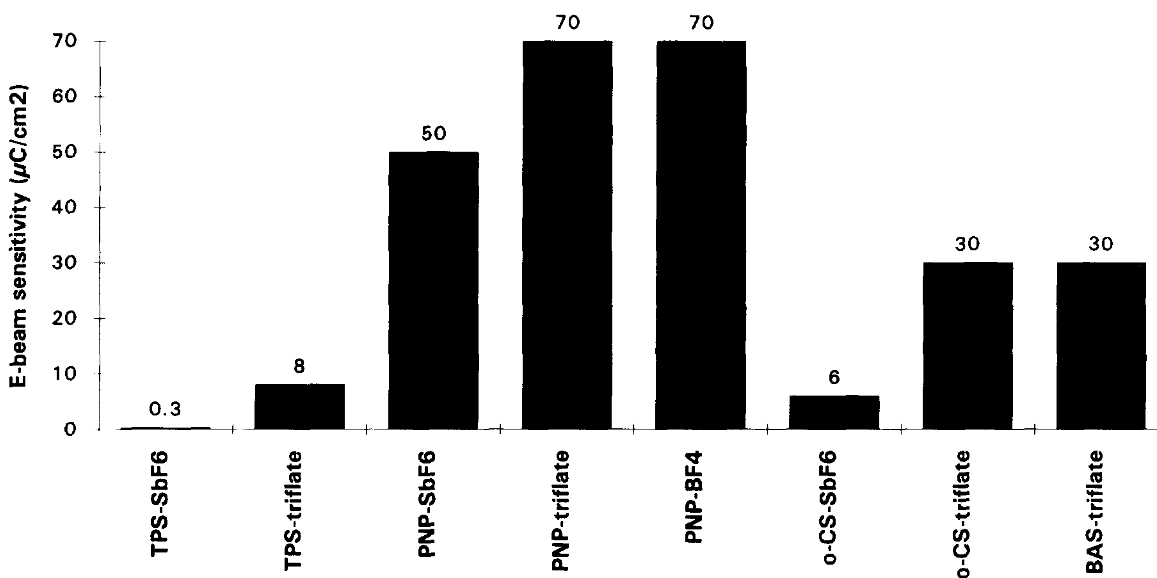


Figure 3 Initiator sensitivities under E-beam exposure

initiate homopolymerization of glycidyl ether based epoxy resins over the temperature range measured, in contrast to one of the patented applications[19]. Also, as implied from the onset of the exotherms recorded for the epoxy/sulfonium blends, temperatures in excess of 90°C should be avoided when processing these materials; results which are reinforced by work with related compounds[20,21].

Lithographic evaluation. Photoresist formulations were prepared in the following general way: a solution of the photoinitiator was predissolved (20% in 2-methoxy-1-methylethylacetate) 1 g of which was subsequently added to 26.67 g of a resin solution (24% fractionated cresol epoxy novolac[7] in 2-methoxy-1-methylacetate). This corresponds to a 30% resin solution with a 2.5% addition of photoinitiator on resin solids. For comparative purposes the formulations were spun on silicon wafers, 5 inch diameter, and pre-baked 3 min at 90°C (final film thickness being ≈9000 Å). After exposure the samples were post-baked for a further 3 min at 90°C and developed using 2-methoxy-1-methylethylacetate and rinsed with isopropanol.

The photoinitiators were soluble in the 2-methoxy-1-methylethylacetate with the exception of the tetrahydrothiophenium and PNP salts, although no indication of solubility difficulties was mentioned in previous work[22].

Instead, blends of diglyme and 2-ethoxyethanol were used to pre-dissolve them before mixing with the epoxy resin solution. For each of the formulations a classical exposure curve (exposure dose required to achieve 90% of imaged thickness) was generated from which the materials relative radiation sensitivity is extrapolated[23].

Photosensitivities of the formulations recorded under u.v. exposure at both 254 and 365 nm are compared in *Figure 2*. The data are presented as a relative sensitivity at each of the exposure wavelengths, i.e. at 254 nm a relative sensitivity of 1 is calibrated to be 6.4 mJ cm^{-2} and at 365 nm the relative sensitivity of 1 is calibrated to be 23 mJ cm^{-2}. Also shown in *Figure 2* are data comparing the formulations sensitivities towards 365 nm irradiation with the addition of 0.05 weight % of anthracene methanol [AM]. This well known sensitizer[24,25] is commonly added to photoresist formulations to enhance lithographic sensitivity, and during the course of this study all but the PNP-salts were substantially sensitized by the presence of the AM.

Towards E-beam irradiation the pattern of resist behaviour was similar to the 254 nm exposure results. Triphenylsulfonium salts were found to be approximately 10× more sensitive than the tetrahydrothiophenium salts and 100× more sensitive than the PNP-based materials (see *Figure 3*). Indeed formulations with PNP salts were found to have sensitivities of the same order of magnitude as catalyst free epoxy materials (E-beam induced crosslinking of epoxy ring).

CONCLUSIONS

Various new onium photoinitiators were prepared and compared with known materials under different exposure methods. The three tetrahydrothiophenium salts (*o*-CS-SbF6, *o*-CS-triflate and BAS-triflate) gave the best results at higher wavelengths (365 nm) which can be explained by their extended u.v. absorption profile, however, it is not expected that the new compounds presented here will find applications in the microelectronics field. This is because in order to achieve reduction in device dimensions, u.v. with wavelengths <300 nm will be employed, shown by this study to be more suited for TPS-SbF6 and TPS-triflate. The most appropriate area of application for the tetrahydrothiophenium salts might be conventional u.v. cure epoxy coatings, and especially in the 'dual cure' area[26]. For the latter, the combined u.v. and low-temperature initiation capability might be of value in formulated coatings and paints. Finally, further work would be required to understand the poor performance of the PNP-based salts in the epoxy matrix.

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