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A comparative study of polystyrene (PS) with bis(perfluorophenyl) azides 1-2 and the corresponding non-fluorinated bisazides 3-4 as deep-UV resists is reported. Inclusion of as low as 1.2 wt-% of 1 in PS led to 70% retention of film thickness after photolysis and development. PS containing 2.4 wt-% of 1 is > 100 times more sensitive as a deep-UV negative resist than PS itself. The presence of 1 in PS also increased the contrast of the resist. On a molar basis, 1 was about 10 times as effective as non-fluorinated bisazide 3 in cross-linking PS while 2 was about 6 times as effective as 4. PS containing 2.4 wt-% of 1 was found to have a deep-UV sensitivity of 5-10 mJ $cm^{-2}$ and resolution of about 0.5 $\mu$m.

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All: Please supply Figure 1 Chemistry

## INTRODUCTION

The miniaturization of integrated circuits in the microelectronics industry[1] has stimulated research in the development of technological alternatives to conventional photolithography.[2,3] Deep-UV lithography,[4] electron beam lithography[5] and X-ray lithography[6,7] all have been demonstrated to give submicron resolution and are undergoing vigorous development.

A negative deep-UV resist composed of poly(*p*-vinylphenol) and a bisazide has been developed.[8] A limitation has been that a high percentage of bisazide (20 wt%) to resin is required such that a resist film of 1 $\mu$m thickness is virtually opaque in the 200-300 nm region. Consequently, undercut profiles are typically observed after development and the processing conditions have to be carefully controlled to maintain line-width and reproducibility.[2] Other negative resists such as novolac resin with a bisazide (15-20 wt%),[9] an acidic resin with a bisazide (30 wt%)[10] and poly(methyl methacrylate) with a bisazide (20-25 wt%)[11] also suffer because of the poor cross-linking efficiency of the bisazide.

We[12,13] and others[14] have developed perfluorophenyl azides (PFPAs) as a new class of photolabeling agents[15] with improved CH insertion efficiency in hydrocarbon solvents over nonfluorinated analogues. The nitrene intermediates derived from photolysis of PFPAs do not undergo ring expansion,[12] which is



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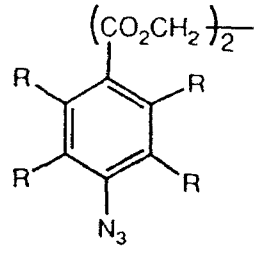
probably the main wasteful reaction pathway of nonfluorinated aryl nitrenes.[16] Since the overall cross-linking efficiency of a bisazide depends on the square of the efficiency of the individual azide groups,[17] bis-PFPAs are expected to be highly efficient cross-linking agents. We have already reported the development of bis-PFPAs as efficient cross-linking agents for cyclized poly(isoprene),[18] polystyrene[18] and poly(3-octylthiophene)[19] and their application in deep-UV and electron beam lithography. Herein, the deep-UV cross-linking properties of bis-PFPAs 1-2 are compared and found to be superior to those of their respective non-fluorinated analogues 3-4.

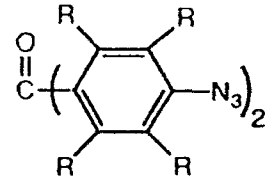
## RESULTS AND DISCUSSION

Bis-PFPA **1**[18] was prepared from 4-azido-2,3,5,6-tetrafluorobenzoyl chloride and ethylene glycol. Bis-PFPA **2**[18] was obtained as a colorless solid from the reaction of decafluorobenzophenone and $NaN_3$. Bisazide **3**[20] was synthesized from 4-azidobenzoyl chloride[21] and ethylene glycol. Bisazide **4**[22] was prepared via diazotization of 4,4′-diaminobenzophenone followed by treatment with sodium azide.

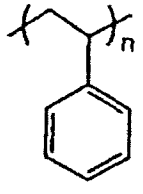
Photolysis of **1** in cyclohexane gave bis-CH insertion product **5** (45%), mono-CH insertion product **6** (21%) and bis-aniline **7**.[18] The isolation of bis-amine **5** appears to be the first instance in which a bisazide has been demonstrated photochemically to give a bis-CH insertion product. In contrast, photolysis of **3** under identical conditions gave no isolable product other than red tar.



**1** R = F
**3** R = H



**2** R = F
**4** R = H



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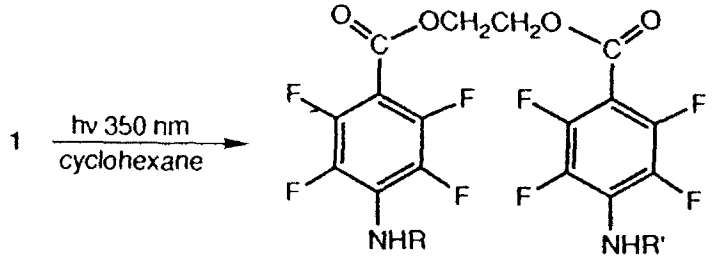

**5** R = R′ = cyclohexyl
**6** R = cyclohexyl, R′ = H
**7** R = R′ = H

Polystyrene (PS) is a negative deep UV[23] and electron beam resist showing high resolution[24] but low sensitivity.[25] Apparently no attempt has been made to improve the sensitivity of PS by addition of a bisazide. We expected that addition of bis-PFPA to PS should result in a deep-UV resist with increased sensitivity. Thus, various amounts of bis-PFPA **1** or **2** and the corresponding nonfluorinated bisazide **3** or **4** were separately added to PS. The resist solutions were then spin-coated on NaCl discs, baked, photolyzed and developed. The intensity of the IR CH stretching absorption at 2924 $cm^{-1}$ before and after development was used to estimate the retention of film thickness.

Table I shows that as low as 1.2 wt-% of **1** (#4) in PS is enough to retain 70% of film thickness after complete decomposition of the azido group. In comparison, about 15 wt-% of the corresponding non-fluorinated bisazide **3** (#3) was needed to retain a similar film thickness. Thus on a molar basis, bis-PFPA **1** is about 9-14 times as effective as its non-fluorinated counterpart **3** in cross-linking PS. Also, a longer photolysis time was needed to decompose bisazide **3** (#3) compared to **1** (#3). Bis-PFPA **2** is less effective on a molar basis than bis-PFPA **1** in cross-linking PS (**2** #3 vs **1** #3). On a molar basis, bis-PFPA **2** is about 6-7

Table 1. Bisazides in Polystyrene as Negative Deep-UV Resists

| bisazde | # | wt-%[a] | mmol/g[a] | $h\nu$(min)[b] | retention[c] |
|---|---|---|---|---|---|
| **1** | 1 | 7.0 | 0.14 | 1 | 0.94 |
| **1** | 2 | 4.6 | 0.092 | 2/3 | 0.83 |
| **1** | 3 | 2.3 | 0.046 | 1/3 | 0.74 |
| **1** | 4 | 1.2 | 0.024 | 1/3 | 0.70 |
| **1** | 5 | 0.6 | 0.012 | 1/3 | 0.08 |
| **1** | 6 | 0.0 | 0.0 | 1 | 0.0 |
| **3** | 1 | 27.5 | 0.78 | 3 | 0.97 |
| **3** | 2 | 19.3 | 0.55 | 3 | 0.83 |
| **3** | 3 | 14.7 | 0.42 | 2 | 0.78 |
| **3** | 4 | 9.7 | 0.27 | 2 | 0.16 |
| **3** | 5 | 5.0 | 0.14 | 1 | 0.0 |
| **2** | 1 | 5.7 | 0.14 | 1 | 0.87 |
| **2** | 2 | 3.8 | 0.093 | 1 | 0.63 |
| **2** | 3 | 2.0 | 0.049 | 1 | 0.0 |
| **4** | 1 | 14.6 | 0.55 | 4 | 0.58 |
| **4** | 2 | 11.4 | 0.43 | 2 | 0.24 |
| **4** | 3 | 7.6 | 0.29 | 2 | 0.12 |
| ~~**4**~~ | ~~3~~ | ~~7.6~~ | ~~0.29~~ | ~~2~~ | ~~0.12~~ |
| **4** | 4 | 3.7 | 0.14 | 1 | 0.0 |

[a] In PS. [b] Complete decomposition of the azido group was observed by IR at 2123 $cm^{-1}$ after photolysis. [c] The retention (normalized film thickness) was determined by IR at 2924 $cm^{-1}$ (CH absorption) after development in xylene for 25 sec and rinsing in isopropanol for 10 sec.

times (2 #2 vs 4 #1) as effective as its corresponding nonfluorinated bisazide 4 in cross-linking PS. As a control, a resist consisting of 5.9 wt-% of methyl 4-azidotetrafluorobenzoate[12] (a mono-PFPA) in PS was found to retain less than 10% of the film after photolysis and developing. It seems likely that the bis-PFPAs are cross-linking the PS by a bis-CH insertion mechanism similar to that observed in cyclohexane, rather than a polymer radical recombination mechanism.[26]

PS containing 2.4 wt-% and 4.6 wt-% of bis-PFPA **1** and 14.7 wt-% and 19.3 wt-% of bisazide **3** as well as PS itself were evaluated for their sensitivity as deep-UV resists. Figure 1 shows the exposure characteristics for these resists. PS itself is a negative deep-UV resist with very low sensitivity. The sensitivity of PS is remarkably increased by the addition of small amounts of bis-PFPA **1**. PS with 2.4 wt-% **1** is more than two orders of magnitude more sensitive than PS itself. The sensitivity curve also shows that the presence of **1** enhances the contrast of the resist. However, **1** is much more effective than **3** (about 9 times on a molar basis) in crosslinking PS and resists of PS containing **1** are about 5-10 times more sensitive than resists of PS containing 3 (1, 2.4 wt-% vs 3, 14. 7 wt%). From the data shown in Figure 1, we estimate the resist of PS with **1** (4.6 wt-%) has a contrast of about 2.9.

The presence of bisazide 3 in PS also increased the sensitivity of PS.

The UV absorption maximum of **1** in ethanol occurs at 264 nm (log $\varepsilon$ = 4.6, log $\varepsilon_{254}$ = 4.5). PS itself has only weak absorption at 254 nm. UV absorption spectra for the resist film of PS with 4.6 wt-% of **1** before and after photolysis are shown in Figure 2. The low concentration of **1** in the resist resulted in a relatively low absorption at 254 nm, thus allowing homogeneous deep-UV exposure of the resist. The resist is partially bleached at 254 nm by the exposure. This observed partial bleaching is consistent with the observation that the UV absorption maximum of the main photolysis products **5** (292 nm) and **6** (285 nm) of **1** in cyclohexane appear at wavelengths longer than 264 nm.

Lithographic evaluation of the resists was carried out in a KSM Karl Suss deep-UV contact aligner. We find that the sensitivity of the resists of PS with 2.4 wt-% of **1** is 5-10 mJ cm$^{-2}$, while a sensitivity of 30-40 mJ cm$^{-2}$ is found for the resists of PS with 14.7 wt-% of **3**. PS alone has a sensitivity of about 3000 mJ cm$^{-2}$. The smallest feature in the mask (0.5 $\mu$m) could be resolved (Figure 3). Swelling of the polymer was observed under these non-optimized conditions, suggesting that further improvement of the resolution of the resists may be possible.

In conclusion, we have demonstrated that bis-PFPAs **1-2** are about 10 times better than the corresponding non-fluorinated bisazides **3-4** in cross-linking polystyrene. Utilization of the highly efficient cross-linking agents **1-2** significantly reduces the required amounts of cross-linkers in PS-based resists and increases the sensitivities of the resists.

## EXPERIMENTAL

### Resist Preparation and Evaluation

Bis-PFPAs **1** and **2** were prepared as reported.[18,27] Bisazides 3 and 4 were prepared following literature procedures.[20,22] Resist solutions were prepared by

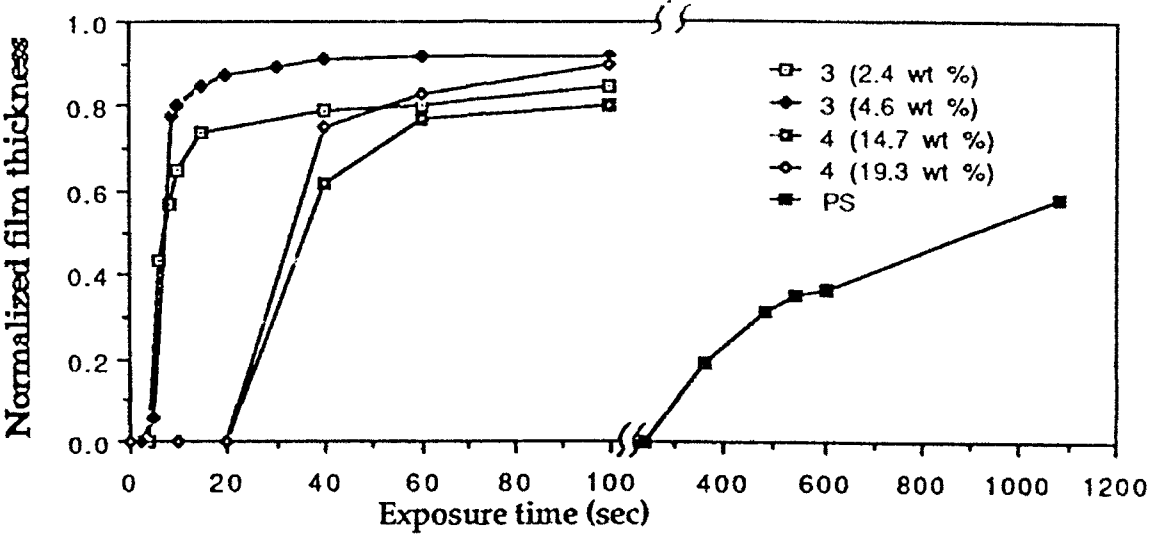


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Figure 1. Effect of concentration on exposure characteristics for resists of PS-bis-PFPA (1), PS-bisazide (3) and PS itself. Resist films were exposed in a Rayonet photoreactor (254 nm) and developed in xylene for 30 sec then rinsed in isopropanol for 10 sec. The normalized film thickness was determined by IR at 2924 $cm^{-1}$ (CH absorption) before photolysis and after development.

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Figure 2

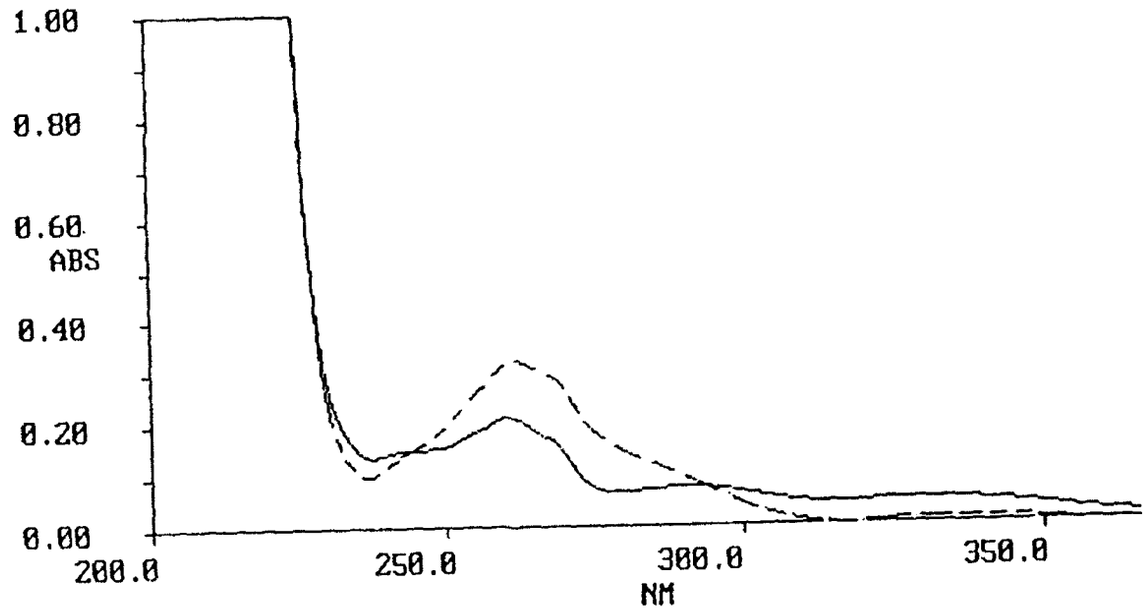


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Figure 2. UV absorption spectra of PS containing 4.6 wt-% of (1) before (- - -) and after (----) photolysis for 20 sec. The film thickness was about 0.7 $\mu$m.

Figure 3

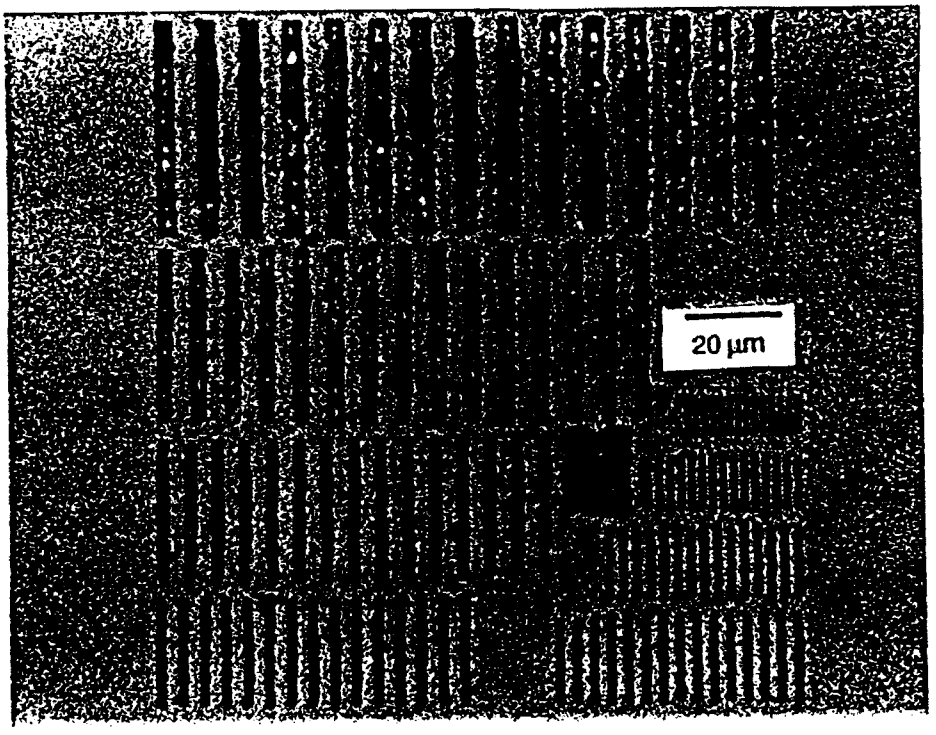


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Figure 3. Optical micrograph of images from a resist of PS containing 2.4 wt-% of (1) The deep-UV exposure dose was 5 mJ $cm^{-2}$. The exposed film was developed in xylene for 30 sec and rinsed in isopropanol for 20 sec.

mixing xylene (2 ml) with 100 mg of polystyrene (MW 125,000-250,000, Polyscience Inc.) and various amounts (Table 1) of bis-PFPA **1** or **2**, or bisazides **3** or **4**. The resist solutions were spin-coated on NaCl discs by a spin-coater (Headway Science Inc.) set at 1000 rpm and the films were baked at 60°C for 30 min. Virgin film thicknesses were measured with an ellipsometer (Rudolph Science) to be about 0.7 $\mu$m. The films were photolyzed at ambient temperature in a Rayonet photoreactor (254 nm). The progress of photolysis was followed by a Nicolet 5DXB FTIR spectrometer at 2123 $cm^{-1}$ (azide absorption). The films were developed in xylenes for 25 sec and rinsed in isopropanol for 10 sec and air dried. The retention of film thickness (normalized) was determined by FTIR at 2924 $cm^{-1}$ for the CH absorption. The UV absorption of the films coated on quartz discs was measured with a Perkin-Elmer Lambda 6 UV/vis spectrophotometer. For lithographic evaluation, resist solutions were spin-coated (1000 rpm) on silicon wafers, baked and exposed in a KSM Karl Suss deep-UV contact aligner. The samples were developed in xylene for 30 sec and rinsed in isopropanol for 20 sec and air dried.

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