Development of Highly Efficient Deep-UV and Electron Beam Mediated Cross-Linkers: Synthesis and Photolysis of Bis(perfluorophenyl) Azides

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The development of bis(perfluorophenyl) azides (bisPFPAs) as a novel class of highly efficient cross-linkers is reported. BisPFPAs **3**, **5**, **7**, and **13** and tetraPFPA **14** were synthesized in high yield from easily accessible materials. Photolysis of bisPFPA **3** in cyclohexane gave bis-CH insertion product **15** in a remarkably high isolated yield of 45%. In contrast, photolysis of the corresponding nonfluorinated bisazide **4** under identical conditions gave no isolable product other than red tar. Polystyrene (PS) mixtures containing bisPFPAs **3**, **7**, and **13** and tetraPFPA **14** and nonfluorinated bisazides **4** and **9** were evaluated as deep-UV and electron beam (EB) resists. Inclusion of as little as 1.2 wt % of bisPFPA **3** in PS led to a film thickness retention of 70% after photolysis and development. The presence of **3** in PS also increased the contrast of the resist. On a molar basis, **3** was about 10 times as effective as the corresponding nonfluorinated bisazide **4** in cross-linking PS while bisPFPA **7** was about 6 times as effective as bisazide **9** under deep-UV exposure conditions. PS containing 2.4 wt % of **3** was found to have a deep-UV sensitivity of 5-10 mJ cm^{-2} and a resolution sufficient to write 0.75 μm lines and spaces. PS containing 3.8 wt % of bisPFPA **7** is about 10 times more sensitive as a negative EB resist than PS itself. On a molar basis, bisPFPA **3** is more than twice as effective as bisazide **4** in cross-linking PS under EB exposure conditions. PS with 3.8 wt % of bisPFPA **7** was found to have an EB sensitivity of 10 μC cm^{-2} and resolution of 0.2 μm.

Introduction

The demands of integrated circuit miniaturization[1] have promoted research in the development of technological alternatives to conventional photolithography.[2-4] Potential alternatives are deep-UV lithography,[5,6] electron beam lithography,[7] and X-ray lithography,[8,9] all of which have been demonstrated to achieve submicron resolution.

Conventional negative resists using cyclized polyisoprene and bisazides as cross-linkers suffer from limitations in resolution imposed by low contrast and the swelling phenomenon.[10] Alternative negative deep-UV resists composed of a polymer such as poly(*p*-vinylphenol),[11] a novolac resin,[12] an acidic resin (30 wt %)[13] or poly(methyl methacrylate) with bisazides (20-30 wt %) have been developed.[14] However, due to the poor cross-linking efficiency of the bisazide,[12] a high percentage of bisazide in the resin has to be used which renders a resist film of 1 μm thickness 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 linewidth and reproducibility.[15]

The photochemistry of aryl azides has been intensively studied in recent years.[16,17] Functionalized perfluorophenyl azides (PFPAs) were recently developed[18-20] as a new class of photolabeling[21,22] and photo-cross-linking agents[23] as well as for photoactivated polymer film and polymer surface modification and enzyme

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immobilization.[24] It has been found that functionalized PFPAs undergo CH insertion efficiently when photolyzed in hydrocarbon solvents such as toluene and cyclohexane.[18] While ring expansion is probably the main wasteful reaction pathway of nonfluorinated aryl nitrenes,[17] the nitrene intermediates derived from photolysis of PFPAs have been found not to undergo ring expansion at ambient temperature.[18] Since the overall cross-linking efficiency of a bisazide depends on the square of the efficiency of the individual azide groups,[25] by taking advantage of the superior CH insertion properties exhibited by nitrenes derived from PFPAs, we[26,27] have developed a new class of highly efficient bis(perfluorophenyl azide) (BisPFPAs)-based[28,29] cross-linkers for lithography.

We have communicated the development of bisPFPAs as efficient cross-linkers for cyclized polyisoprene,[27] polystyrene,[27,30] poly(3-octylthiophene),[31] and polyimide.[32] Herein, we present the details of the synthesis and photolysis of bisPFPAs and discuss the application of bisPFPAs in deep-UV and electron beam lithography. We also report that the deep-UV and electron beam cross-linking properties of bisPFPAs **3** and **7** are superior to those of their respective nonfluorinated analogues **4** and **9** in polystyrene-based resists.

Experimental Section

General Section. ^{1}H NMR spectra were measured at 300 MHz in $CDCl_3$. ^{19}F NMR spectra (C_6F_6, −162.9 ppm as internal standard) were measured on a NT-360 spectrometer. IR spectra were recorded in $CDCl_3$ solution. UV spectra were measured in ethanol solution on a Beckman DU-7 spectrometer or a Perkin-Elmer Lambda UV−vis spectrometer. Melting points are uncorrected. All reactions involving azides were run under subdued light by wrapping the flasks with aluminum foil. Reagent-grade solvents were used without further purification unless otherwise specified. Decafluorobenzophenone and hexafluorobenzene were purchased from Aldrich Co. and used as received. Polystyrene (M_w 125 000−250 000) was from Polyscience Co. Photolyses were carried out in a Rayonet photochemical reactor with either 350 nm lamps or 254 nm lamps at ambient temperature. Solutions were purged with Ar for 1 min before photolysis.

Ethylene 1,2-Bis(4-azido-2,3,5,6-tetrafluorobenzoate) (3). A solution of 278 mg (1.10 mmol) of 4-azidotetrafluorobenzoyl chloride (**1**)[18] in dry ether (3 mL) was added to a solution of 32 mg (0.516 mmol) of ethylene glycol (Aldrich) and 123 mg (1.21 mmol) of Et_3N in dry ether (5 mL). A white precipitate was observed immediately. The mixture was stirred overnight and filtered. The filtrate was evaporated and dried to leave 251 mg (98%) of **3** as a colorless solid, mp 73−74 °C. ^{1}H NMR, 4.680 (s). ^{19}F NMR (AA'XX'), −151.908, −139.362. IR, 2130, 1739, 1648, 1491, 1255, 1008 cm^{-1}. UV, λ_{max} = 264 nm (log ϵ = 4.6). The analytical sample of **3** was obtained by crystallization from $CHCl_3$−hexane as colorless needles, mp 75−76 °C. Anal. Calcd for $C_{16}H_4F_8N_6O_4$: C, 38.73; H, 0.81; N, 16.93. Found: C, 38.60; H, 0.61; N, 17.07.

Ethylene 1,2-bis(4-azidobenzoate) (4) was synthesized from 4-azidobenzoyl chloride (mp 56−58 °C, lit.[33] 57−58 °C) and ethylene glycol in the presence of Et_3N and isolated as a white powder, mp 85−86 °C (lit.[34] 87−88 °C). ^{1}H NMR, 4.647 (s, 4), 7.043 (d, 4, J = 8.7), 8.055 (d, 4, J = 8.7). IR, 2125, 1720, 1604, 1285, 1283, 1175, 1100 cm^{-1}.

3,3'-Bis(4-azido-2,3,5,6-tetrafluorobenzamido)-*N*-methyldipropylamine (5). A solution of 342 mg (1.39 mmol) of **1**[18] in dry $CHCl_3$ (3 mL) was added to a solution of 159 mg (1.09 mmol) of 3,3'-diamino-*N*-methyldipropylamine and 230 mg (2.27 mmol) of triethylamine in $CHCl_3$ (4 mL). It was heated at 50 °C overnight and evaporated to leave a mixture of solid and liquid which was treated with CH_2Cl_2 (10 mL), water (5 mL), and 20% aqueous NaOH (2 mL). The mixture was extracted with CH_2Cl_2 (3 × 5 mL), and the extract was dried ($MgSO_4$) and evaporated to leave 349 mg (89%) of **5** as a colorless solid. ^{1}H NMR, 2.06 (bm, 4), 2.572 (s, 3), 2.90 (bm, 4), 3.59 (m, 4), 7.59 (m, 2). IR, 3000, 2127, 1675, 1650, 1528, 1487, 1283, 997 cm^{-1}. UV, λ_{max} = 255 nm (log ϵ = 4.6). The analytical sample of **5** was obtained by crystallization from $CHCl_3$−hexane as cubic crystals, mp 109−110 °C. Anal. Calcd for $C_{21}H_{17}F_8N_9O_2$: C, 43.53; H, 2.96; N, 21.76. Found: C, 43.16; H, 2.85; N, 21.39.

4,4'-Diazidooctafluorobenzophenone (7). A mixture of 418 mg (1.15 mmol) of decafluorobenzophenone (**6**) and 156 mg (2.40 mmol) of NaN_3 in acetone (7 mL) and water (2 mL) was refluxed for 4 h. The mixture was added to well-stirred water (20 mL), and the precipitate was filtered, washed with water, and dried to leave 451 mg (96%) of **7** as a colorless solid, mp 134−135 °C. ^{19}F NMR (AA'XX'), −151.368, −142.736. IR, 2134, 2119, 1687, 1644, 1491, 1403, 1334, 1251, 1000 cm^{-1}. UV, λ_{max} = 249 nm (log ϵ = 4.1) and λ_{max} = 293 nm (log ϵ = 4.5). MS, 408 (6, M$^+$), 380 (28), 352 (3), 218 (10), 190 (8), 162 (100). High-resolution MS calcd for $C_{13}F_8N_6O$ 408.0007, found 408.0010.

4,4'-Diazidobenzophenone (9). To a stirred suspension of 613 mg (2.89 mmol) of 4,4'-diaminobenzophenone (**8**) in 3 mL of concentrated HCl (36−38%) kept at 0 °C was added dropwise a solution of 622 mg (9.01 mmol) of $NaNO_2$ in 1 mL of water. The suspension was stirred for 15 min; then a solution of 568 mg (8.74 mmol) of NaN_3 in 2 mL of water was added dropwise (caution, gas evolved). The mixture was stirred for 10 min, filtered, washed with water, and dried to leave 750 mg (98%) of **9** as yellow solid, mp 145−146 °C (lit.[35]

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146–147 °C). ^{1}H NMR, 7.124 (d, 4, J = 8.5 Hz), 7.805 (d, 4, J = 8.5 Hz). IR, 2127, 2095, 1652, 1599, 1279.

1,4-Diazidotetrafluorobenzene (11). (*Caution*: Potentially explosive multiazide side products may be produced in this reaction.) A mixture of 690 mg (3.71 mmol) of hexafluorobenzene (**10**) and 490 mg (7.54 mmol) of NaN_3 in DMF (5 mL) was stirred at 60 °C for 5 h. The mixture was diluted with water (10 mL) and extracted by $CHCl_3$ (3 × 10 mL). The extract was washed with water (3 × 5 mL), dried ($MgSO_4$), and evaporated to leave a red liquid which was separated by chromatography (silica gel, $CHCl_3$–hexane = 1:20) to give 478 mg (55%) of **11** as a solid, mp 65–66 °C (lit.[36] 68–69 °C). ^{19}F NMR, −152.779. IR, 2158, 2117, 1502, 1493, 1309, 1216, 1016 cm^{-1}. UV, λ_{max} = 270 nm (log ϵ = 4.3).

(4-Azido-2,3,5,6-tetrafluorobenzyl) 4-Azido-2,3,5,6-tetrafluorobenzoate (13). To a stirred solution of 221 mg (1.00 mmol) of 4-azido-2,3,5,6-tetrafluorobenzyl alcohol (**12**)[18] and 103 mg (1.02 mmol) of Et_3N in 10 mL of anhydrous ether was added a solution of 276 mg (1.09 mmol) of **1**[18] in 5 mL of anhydrous ether. After being stirrred at 25 °C for 12 h, the mixture was filtered, and the filtrate was washed with aqueous 5% Na_2CO_3 (2 × 5 mL) and H_2O (2 × 10 mL), then dried ($MgSO_4$), and evaporated to leave 437 mg (99%) of **13** as a white solid, mp 69–70 °C. ^{1}H NMR, 5.457 (s, 4). IR, 2124, 1742, 1648, 1493, 1328, 1254, 1191, 1009 cm^{-1}. Anal. Calcd for $C_{14}H_2F_8N_6O_2$: C, 38.37; H, 0.46; N, 19.18. Found: C, 38.21; H, 0.28; N, 19.19.

Pentaerythritol Tetrakis(4-azido-2,3,5,6-tetrafluorobenzoate) (14). To a stirred solution of 15.4 mg (0.113 mmol) of pentaerythritol in pyridine (2 mL, distilled) was added 122 mg (0.481 mmol) of **1**[18] with formation of precipitate. The mixture was stirred at 25 °C for 48 h and poured into aqueous 2 N HCl (20 mL) and then it was extracted by $CHCl_3$ (3 × 10 mL). The extract was dried ($MgSO_4$) and evaporated to leave 168 mg of solid which was dissolved in acetone (1 mL). The acetone solution was added dropwise into hexane (10 mL) to give a crystalline precipitate which was centrifuged and dried to leave 92 mg (81%) of **14** as an almost colorless solid, mp 150–151 °C. ^{1}H NMR, 4.554 (s). IR 2130, 1746, 1646, 1603, 1490, 1473, 1252 cm^{-1}. MS (Fab), 1005 (9, M$^+$ + H) 770 (60), 162 (100). High-resolution MS calcd for $C_{33}H_8F_{16}N_{12}O_8$ + H, 1005.0398, found 1005.0370.

Photolysis of 3 in Cyclohexane. A solution of 52.3 mg of **3** in 120 mL of cyclohexane (8.8 × 10^{-4} M) was photolyzed (350 nm) for 4 h. The mixture was evaporated to leave 73 mg of solid which was separated by preparative TLC (1:2 acetone–hexane) to give 28.6 mg (45%) of bisamine **15**, 12.0 mg (21%) of aniline **16**, and 2.0 mg (5%) of bisaniline **17**. When photolysis of **3** in cyclohexane was carried out at 254 nm, the ^{1}H NMR of the crude mixture was essentially identical with those obtained at 350 nm photolysis.

Ethylene 1,2-bis[4-(cyclohexylamino)-2,3,5,6-tetrafluorobenzoate] (**15**): colorless solid, mp 140–141 °C. ^{1}H NMR, 1.1 (m, 6), 1.3 (m, 4), 1.6 (m, 2), 1.7 (m, 4), 2.0 (m, 4), 3.6 (m, 2), 4.0 (m, 2), 4.608 (s, 4). ^{19}F NMR (AA'XX'), −162.419, −141.282. IR, 3419, 2938, 2959, 1725, 1651, 1536, 1502, 1481, 1417, 1320, 1218, 989 cm^{-1}. UV, λ_{max} = 292 nm (log ϵ = 4.6). MS, 608 (20, M$^+$), 318 (70), 290 (5), 274 (48), 236 (50), 192 (100), 83 (42). High-resolution MS calcd for $C_{28}H_{28}F_8N_2O_4$ 608.1914, found 608.1919.

1-[[4-(Cyclohexylamino)-2,3,5,6-tetrafluorobenzoyl]oxy]-2-(4-[amino-2,3,5,6-tetrafluorobenzoyl]oxy)ethane (**16**): colorless solid, mp 139–14 °C. ^{1}H NMR, 1.2 (m, 3), 1.3 (m, 2), 1.6 (m, 1), 1.7 (m, 2), 2.0 (m, 2), 3.6 (m, 1), 4.0 (m, 1), 4.3 (m, 2), 4.617 (4, s). ^{19}F NMR (two AA'XX'), −163.380, −162.435, −141.310, −141.230. IR, 3513, 3415, 2938, 2857, 1727, 1664, 1652, 1529, 1503, 1321, 1219, 989 cm^{-1}. UV, λ_{max} = 285 nm (log ϵ = 4.3). MS, 526 (32, M$^+$), 274 (20), 236 (85), 192 (100), 164 (14), 83 (18). High-resolution MS calcd for $C_{22}H_{18}F_8N_2O_4$ 526.1139, found 526.1134.

Ethylene 1,2-bis(4-amino-2,3,5,6-tetrafluorobenzoate) (**17**): colorless solid, mp 245–246 °C. ^{1}H NMR, 4.384 (sb, 4), 4.640 (s, 4). ^{19}F NMR (AA'XX'), −163.523, −142.215. IR, 3515, 3415, 2912, 1728, 1665, 1527, 1502, 1322, 1217, 1175 cm^{-1}. UV, λ_{max} = 279 nm (log ϵ = 4.6). MS, 444 (18, M$^+$), 236 (50), 192 (100), 164 (20). High-resolution MS calcd for $C_{16}H_8F_8N_2O_4$ 444.0357, found 444.0354. Bisaniline **17** also was prepared by catalytic hydrogenation (H_2/Pd) of **3**.

Table 1. Bis-PFPAs, Bisazides, and MonoPFPA in Polystyrene as Negative Deep-UV and Electron Beam Resists

bisazide	#	wt %[a]	mmol/g[a]	$h\nu$ (min)[b]	retention[c]	EB dose[d]
3	1	7.0	0.14	1	0.94	15
3	2	4.6	0.092	2/3	0.83	15
3	3	2.3	0.046	1/3	0.74	20
3	4	1.2	0.024	1/3	0.70	
3	5	0.0	0.0	1	0.0	100
4	1	27.5	0.78	3	0.97	
4	2	14.7	0.42	2	0.78	50
4	3	9.7	0.27	2	0.16	45
4	4	3.3	0.093	1	0.0	30
7	1	3.8	0.093	1	0.63	10
9	1	14.6	0.55	4	0.58	
9	2	11.4	0.43	2	0.24	
13	1	4.1	0.094	1	0.88	20
14	1	4.4	0.044	1	0.95	15
19	1	5.9	0.24	1	0.10	80

[a] In PS. [b] Exposure time, 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 s and rinsing in isopropyl alcohol for 10 s. [d] Estimated from the lowest dose (μC cm^{-2}) required to give a well-defined 0.1 μm lines.

Photolysis of 4 in Cyclohexane. A solution of 15.6 mg of **4** in cyclohexane (40 mL) was photolyzed (350 nm) for 2 h. A red precipitate was observed. The mixture was evaporated to leave 16.0 mg of a red solid. The ^{1}H NMR spectrum of the crude product showed no signals corresponding to the starting material nor those expected for CH insertion products. Photolysis of **7**, **9**, and **11** under identical conditions gave similar results as that of **4**.

Photolysis of 13 in Cyclohexane. A solution of 30.7 mg of **13** in 30 mL of cyclohexane was photolyzed (350 nm) for 2 h. The mixture was evaporated to leave a solid which was separated by preparative TLC (1:2 hexane–CH_3Cl) to give 9.3 mg (25%) of bisamine **18**. ^{1}H NMR, 1.169 (m, 6), 1.340 (m, 4), 1.650 (m, 2), 1.736 (m, 4), 2.025 (m, 4), 3.637 (m, 3), 4.027 (m, 1), 5.344 (s, 2). MS, 551 (70, M$^+$ + 1), 291 (25), 260 (100), 178 (85), 177 (50).

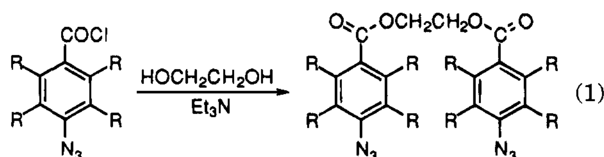
Deep-UV Resists Formulation and Processing. Resist solutions composed of polystyrene (100 mg) containing various amount of bisPFPAs **3**, **7**, and **13**, tetraPFPA **14**, and bisazides **4** and **9** (Table 1) in xylene (2 mL) were prepared. The resist solutions were spin-coated with a spin-coater (Headway Research Inc.) setting at 1000 rpm onto NaCl plates (for IR experiments) or quartz (for UV measurements) or silicon wafers (for lithographic experiments). The resist films were baked at 60 °C for 30 min, and the film thicknesses were measured by ellipsometer (Rodulph Science) to be about 0.7 μm. For resists characterization and evaluation, 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} (azido absorption). The films were developed in xylenes for 25 s and rinsed in isopropyl alcohol for 10 s 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 were measured with a Perkin-Elmer Lambda UV–vis spectrometer. For lithographic evaluation, the resist films on silicon wafer were exposed in a KSM Karl Suss deep-UV contact aligner. The samples were developed in xylene for 30 s and rinsed in isopropyl alcohol for 20 s and air dried. The patterns were observed and photographed under optical microscope.

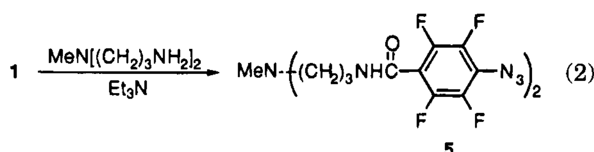
Electron Beam Resists Formulation and Processing. Resist solutions were prepared as above and were spin-coated on silicon wafer with a P-6000 spin-coater (Integrated Technologies Inc.) setting at 4000 rpm (spin time 25 s). The films were baked at 80 °C for 30 min and the film thickness was measured to be about 0.4 μm. Films were exposed in a computer-controlled scanning electron microscope (JSM-840A

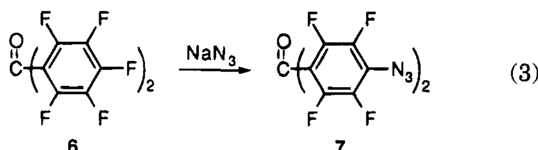
scanning microscope) as an electron beam pattern generator with a test pattern at different doses at 15 keV. The exposed samples were developed by dipping in xylene for 25 s and rinsing in isopropyl alcohol for 10 s. The patterns were observed and photographed under an optical microscope. For observation and photography using SEM, the samples were coated with 20 nm of gold.

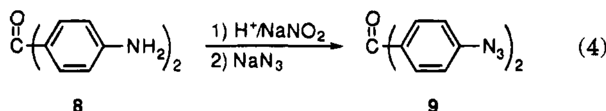
Results and Discussion

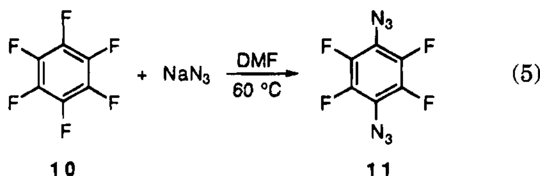
(A) Synthesis. Synthetic routes to a family of bisPFPAs and bisazides are shown in eqs 1–6. BisPF-

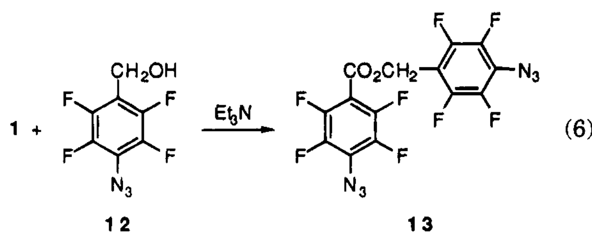




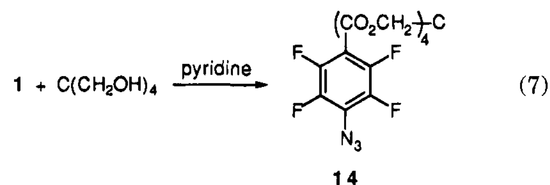






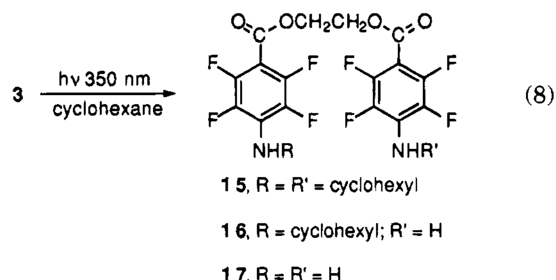


PA **3** and bisazide **4**[34] were obtained as colorless solids by reaction of ethylene glycol with benzoyl chlorides **1**[18] and **2**,[33] respectively (eq 1). BisPFPA **5** was prepared from **1** and 3,3′-diamino-*N*-methyldipropylamine (eq 2). The amide linkage in **5** should render **5** more stable than **3** under basic aqueous developing conditions. The tertiary amino group also provides a site for quaterization, thus allowing the preparation of bisPFPAs with enhanced water solubility. 4,4′-Diazidooctafluorobenzophenone (**7**) was obtained as a colorless solid from the reaction of decafluorobenzophenone (**6**) and NaN_3 (eq 3). Bisazide **9**[35] was prepared by diazotization of 4,4′-diaminobenzophenone (**8**) followed by treatment with NaN_3 (eq 4). 1,4-Diazidotetrafluorobenzene (**11**)[36,37] was synthesized from hexafluorobenzene and NaN_3 (eq 5). BisPFPA **13** was synthesized by the coupling of **1** with alcohol **12**[18] (eq 6). The linker between the two PFPA groups in **13** involves fewer bonds than in **3**; thus the linker in **13** might be more stable under EB exposure conditions than **3**. TetraPFPA **14** was obtained from esterification of pentaerythritol with **1** (eq 7). The UV



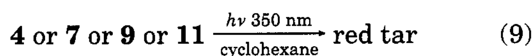
absorption maxima of the bisPFPAs are all in the deep-UV and range from 264 nm for **3** to 270 nm for **11**. Ease of synthesis and the ready availability of the starting materials are important characteristics of bisPFPA chemistry.

(B) Photolysis Studies. To assess the bis-CH insertion capabilities of the bisPFPAs, photolysis of several bisPFPAs was carried out in cyclohexane solution. Photolysis of bisPFPA **3** in cyclohexane at 350 nm gave the bis-CH insertion product **15** in an isolated yield of 45%. This yield corresponds to a CH insertion efficiency of 67% for each individual azido group, which is comparable to the 57% CH insertion yield observed for the monoPFPA methyl 4-azido-2,3,5,6-tetrafluorobenzoate (**19**)[18] when it was photolyzed in cyclohexane under similar conditions. Mono-CH insertion product **16** (21%) and bisaniline **17** (5%) were also obtained (eq 8). The ^{19}F NMR spectra of **15**–**17** all showed the



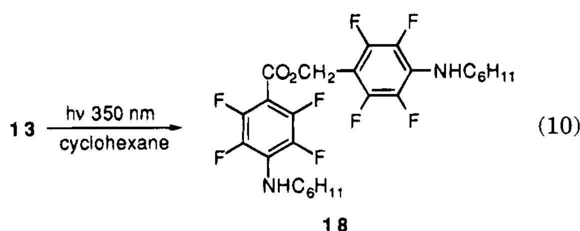
expected AA′XX′ patterns[38] which excluded the possibility of ring expansion. Photolysis of **3** in cyclohexane at 254 nm proceeded similarly, indicating little wavelength dependence of the photolysis reaction. The absorption maximum of the main product **15** (292 nm, $\log \epsilon = 4.6$) as well as that of **16** (285 nm, $\log \epsilon = 4.3$) and **17** (279 nm, $\log \epsilon = 4.6$) are all found at longer wavelength than that of **3** (264 nm, $\log \epsilon = 4.6$). Apparently, the isolation of bisamine **15** is the first instance where a bisazide has been demonstrated photochemically to give an isolated bis-CH insertion product. In contrast, photolysis of the corresponding nonfluorinated bisazide **4** under identical conditions gave red tar as the only isolable product (eq 9). Since the performance of bisazides as cross-linkers

(36) Morse, J. G.; Kuhn, L. P. *U.S. Clearinghouse Fed. Sci. Tech. Inform. AD* **1970**, *70*, 60.
(37) Kashkin, A. V.; Bakhmutov, Yu. L.; Marchenko, N. N. *Zh. Vses. Khim. Obshchest.* **1970**, *15*, 591.
(38) Homer, J.; Thomas, L. F. *J. Chem. Soc. B* **1968**, 141.



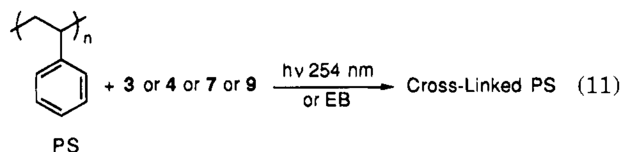
is known to be better in a solid matrix than in solution,[39] these results suggest that the advantage of bisPFPA **3** over bisazide **4** as a cross-linker will extend to deep-UV lithography (see below).

Photolysis of the unsymmetrical bisPFPA **13** in cyclohexane gave bis-CH insertion product **18** in 25% yield (eq 10). Apparently the two different azide groups in



13 behave similarly, suggesting that **13** should be almost as good as **3** when used as a cross-linker. On the other hand, photolysis of 1,4-bisazide **11** gave no isolable CH insertion product. This may be because the two azido groups in **11** are conjugated, thus lowering the reactivity of the corresponding nitrene intermediates. Interestingly, photolysis of bisPFPA **7** in cyclohexane also gave no isolable CH insertion product. This result is somewhat surprising in view of the efficient CH insertion reactions shown by derivatives of **1**[18] and may arise either because of conjugation effects or because the keto group in **7** also undergoes a photochemical reaction. Photolysis of the nonfluorinated bisazide **9** in cyclohexane also gave no isolable product. Reiser et al.[35] reported earlier that photolysis of **9** at 77 K in a matrix fails to give the dinitrene and decomposition of the azide was slow.

(C) Application of bisPFPAs in Deep-UV and Electron Beam Lithography. BisPFPAs **3**, **7**, and **13** and tetraPFPA **14** were next evaluated as cross-linkers for deep-UV and electron beam resists. Polystyrene (PS) is a negative deep-UV[40] and electron beam resist showing high resolution[41] but low sensitivity.[42] Apparently no attempt has been made to improve the sensitivity of PS by addition of a bisazide. We expected that addition of a bisPFPA to PS should result in a deep-UV resist with increased sensitivity. Thus, varying amounts of bisPFPAs **3** or **7** and the corresponding nonfluorinated bisazides **4** or **9** were separately added to PS and evaluated for their abilities to cross-link PS (eq 11). The



resist solutions were spin-coated on NaCl plates, and the progress of photolysis was monitored by the intensity of the azido absorption at 2120 cm^{-1} in the IR

(39) Reiser, A.; Leyshon, L. J.; Johnson, L. *Trans. Faraday Soc.* **1971**, *67*, 2389.
(40) Imamura, S.; Sugawara, S. *Jpn. J. App. Phys.* **1982**, *21*, 776.
(41) (a) Brewer, T. L. *6th Int. Conf. Electron Ion Beam Sci. Tech.*; Bakish, R., Ed.; 1974, p 71. (b) Lai, J. H.; Shepherd, L. T. *J. Electrochem. Soc.* **1979**, *126*, 696.
(42) Reichmanis, E. Thompson, L. F. *Annu. Rev. Mater. Sci.* **1987**, *17*, 235.

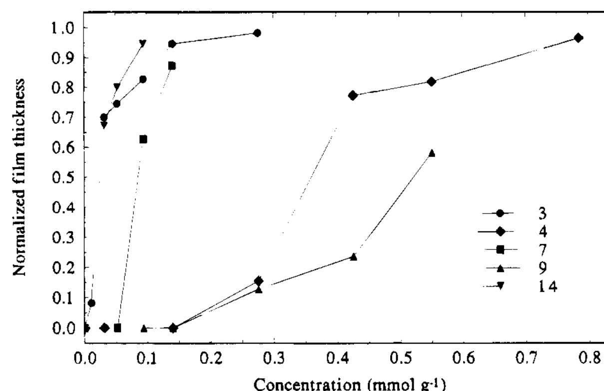
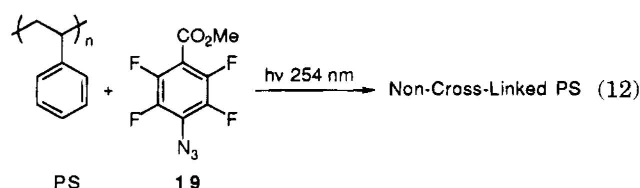


Figure 1. Dependence of the normalized film thickness of resists of PS on the concentration of bisPFPAs **3** and **7**, bisazides **4** and **9**, and tetraPFPA **14** exposed and developed under the conditions given in Table 1.

spectrum. 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. Resists of PS with bisPFPA **13** and tetraPFPA **14** also were evaluated under similar conditions. Selected data are collected in Table 1 and presented graphically in Figure 1.

Figure 1 shows that on a molar basis (counting tetraPFPA **14** as 2 mol of bisPFPA **3**), the ability of the reagents to cross-link PS is **14** $\sim$ **3** > **7** $\gg$ **4** > **9**. Table 1 shows that as little as 1.2 wt % of **3** (#4) in PS is enough to retain 70% of film thickness after complete decomposition of the azido group. In contrast, more than 14 wt % of the corresponding nonfluorinated bisazide **4** (#2) was needed to retain a similar film thickness. Thus, on a molar basis, bisPFPA **3** is about 10 times more effective than the nonfluorinated counterpart **4** in cross-linking PS. Also, a longer photolysis time was needed to decompose bisazide **4** (#2) compared to bisPFPA **3** (#4). On a molar basis, bisPFPA **7** is about 6–7 times (**7** #1 vs **9** #1) as effective as its corresponding nonfluorinated bisazide **9** in cross-linking PS. BisPFPA **7** is less efficient in cross-linking PS than bisPFPA **3** (**3** #2 vs **7** #1), which is in agreement with the photolysis results of bisPFPAs **7** and **3** in cyclohexane. Interestingly, the corresponding nonfluorinated bisazide **9** is also less efficient in cross-linking PS than bisazide **4** (**4** #2 vs **9** #2). As expected from the above photolysis results of **13** and **3**, bisPFPA **13** is about as effective as bisPFPA **3** in cross-linking PS (**13** #1 vs **3** #2). TetraPFPA **14** was found to be somewhat more effective than bisPFPA **3** (counting 1 mol of **14** as 2 mol of **3**) in cross-linking PS (**14** #1 vs **3** #2).

As a control, a resist of PS containing 5.9 wt % (0.24 mmol/g) of methyl 4-azidotetrafluorobenzoate (**19**,[18] a mono-PFPA) was found to retain less than 10% of the film thickness after photolysis and developing (eq 12).



In comparison, PS containing about the same molarity of bisPFPA **3** (counting 1 mol of **3** as 2 mol of **19**)

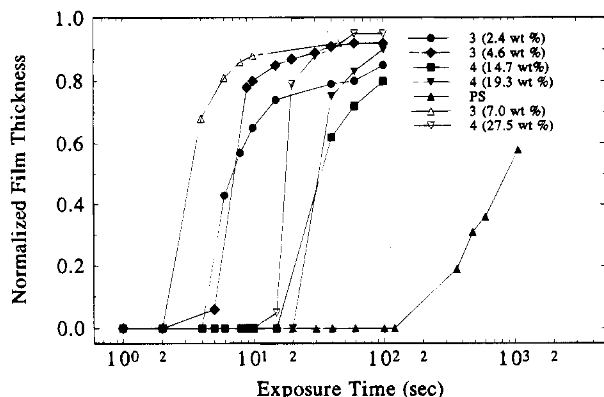


Figure 2. Exposure characteristics for resists of PS with bisPFPA **3**, PS with bisazide **4**, and PS itself. Resist films were exposed in a Rayonet photoreactor (254 nm) and developed in xylene for 30 s, then rinsed in isopropyl alcohol for 10 s. The normalized film thickness was determined by IR at 2924 cm^{-1} (CH absorption) before photolysis and after development.

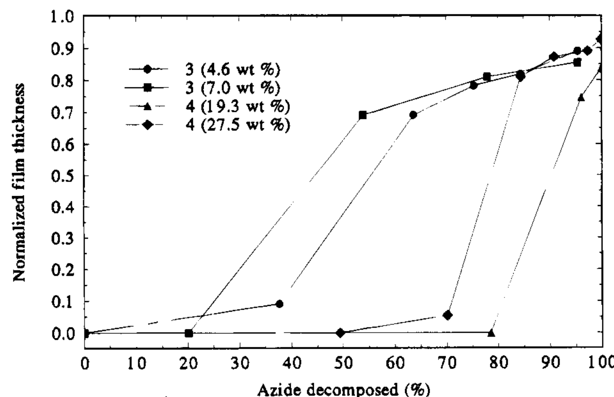


Figure 3. Exposure characteristics for resists of PS with bisPFPA **3** and with bisazide **4**. Resist films were exposed and developed under the conditions given in Figure 2. The percentage of azide decomposition was determined from IR spectra measured before and after photolysis for the azido absorption at 2123 cm^{-1}. The normalized film thickness was determined by IR at 2924 cm^{-1} (CH absorption) before photolysis and after development.

retained more than 80% of the film (**3** #1 and #2) under the same conditions. On the basis of the C−H insertion products isolated from the photolysis experiment of **3** in cyclohexane (see above), it seems likely that the bisPFPAs are cross-linking the PS by a bis-CH insertion mechanism rather than a polymer radical recombination mechanism.[43]

PS containing 2.4 wt %, 4.6 wt %, and 7.0 wt % of bisPFPA **3**, 14.7 wt %, 19.3 wt %, and 27.5 wt % of bisazide **4**, as well as PS itself were evaluated for their sensitivity as deep-UV resists. Figure 2 shows the exposure characteristics for these resists. PS itself is a negative deep-UV resist with very low sensitivity and contrast. The sensitivity of PS is increased considerably by the addition of small amounts of bisPFPA **3**. PS with 2.4 wt % **3** is more than 2 orders of magnitude more sensitive than PS itself. The sensitivity curve also shows that the presence of **3** enhances the contrast of the resist. An increase in the amount of **3** in PS from 2.4 wt % to 4.6 wt % and 7.0 wt % resulted in an improved retention of film thickness as well as increase in the sensitivity of the resist. The presence of bisazide **4** in polystyrene also increased the sensitivity of PS. However, **3** is much more effective than **4** (about 9 times on a molar basis) in cross-linking PS, and resists of PS containing **3** are about 5−10 times more sensitive than resists of PS containing **4** (**3** (2.4 wt %) vs **4** (14.7 wt %)).

The normalized film thickness after development as a function of the percentage of azido decomposed as measured by IR absorption at 2924 and 2123 cm^{-1}, respectively, is shown in Figure 3. For example, in the case of PS containing 7.0 wt % of bisPFPA **3**, a film retention of 68% was observed when about 54% of the total azido groups was decomposed. Assuming that the two azido groups in **3** act independently from each other, this corresponds to about 29% of original bisPFPA molecules in which both azido groups have been decomposed.[44] Because decomposition of both azido groups in one bisPFPA molecule is essential for the formation of one cross-link, only 29% of bisPFPA **3** contributes to the cross-linking of polymers under these conditions. By comparison, for PS containing 27.5 wt % of bisazide **4**,

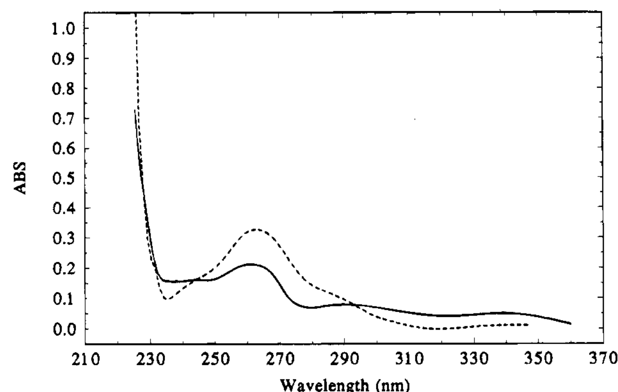


Figure 4. UV absorption spectra of PS containing 4.6 wt % of bisPFPA **3** before (- - -) and after (—) photolysis for 20 s. The film thickness was about 0.7 μm.

about 80% decomposition of the total azido groups (corresponding to 64% of bisazide with both azido groups decomposed, more than 2 times that of bisPFPA **3**), is necessary for retention of 68% of film thickness. Since on the molar basis, 27.5 wt % of bisazide **4** in PS (0.78 mmol/g) contains more than 5 times the number of bisazide molecules as that of 7.0 wt % of bisPFPA **3** in PS (0.14 mmol/g), the efficiency of bisPFPA **3** in cross-linking PS is more than 10 (2 × 5) times of that of bisazide **4**. This is in agreement with the value estimated from Table 1 (see above).

UV absorption spectra for the resist film of PS with 4.6 wt % of **3** before and after photolysis are shown in Figure 4. Because PS itself only has a weak absorption at 254 nm, the low concentration of **3** (λ_{max} = 264 nm) in the resist results 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 partial bleaching is consistent with the observation that the UV absorption maxima

(43) Nonogaki, S.; Hashimoto, M.; Iwayanagi, T. Shiraishi, H. *Proc. SPIE, Adv. Resist Tech Proc. II* **1985**, *539*,189.

(44) For example, assuming 60% of the total azide groups have been decomposed and the two azide groups in **3** act independently from each other, then the percentage of bisPFPA molecules in which both azide groups have been decomposed is 60% × 60% = 36%, the percentage of bisPFPA molecules in which one azide group has been decomposed is 2 × 60% × 40% = 48%, and the percentage of bisPFPA molecules in which no azide group has been decomposed is 40% × 40% = 16%.

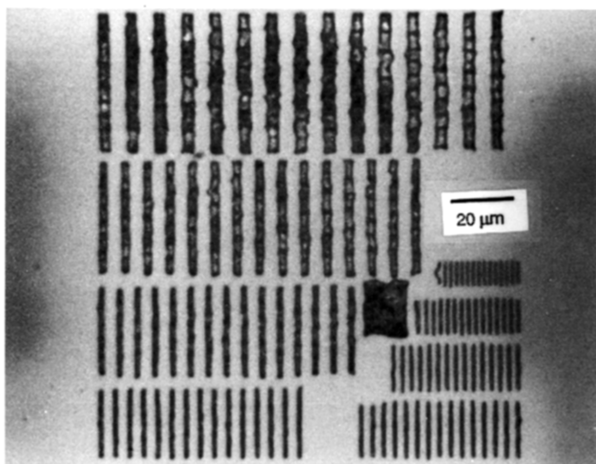


Figure 5. Optical micrograph of patterns obtained from a resist of PS containing 2.4 wt % of bisPFPA **3**. The deep-UV exposure dose was 5 mJ cm^{-2}. The exposed film was developed in xylene for 30 s and rinsed in isopropyl alcohol for 20 s.

of the main photolysis products **15** (292 nm) and **16** (285 nm) of **3** in cyclohexane appear at wavelengths longer than 264 nm.

Evaluation of the resists for lithography was carried out in a KSM Karl Suss deep-UV contact aligner. The exposed sample was developed in xylene for 30 s and rinsed in isopropyl alcohol for 20 s. The sensitivity of the resists of PS containing 2.4 wt % and 4.6 wt % of **3** was determined to be 5−10 mJ cm^{-2}, while a sensitivity of 30−45 mJ cm^{-2} was found for the resists of PS containing 14.7 wt % and 19.4 wt % of **4**. For comparison, PS alone has a sensitivity of about 2000−3000 mJ cm^{-2}. Figure 5 shows that the smallest mask features (0.75 μm lines and spaces) could be resolved without coalescence of the structures. Also, apparent in Figure 5 is some swelling, particularly in the larger features.

Polystyrene mixtures containing various amounts of bisPFPAs **3**, **7**, and **13**, tetraester **14**, bisazides **4** and **9**, and 1,4-diazide **11** were next evaluated as negative electron beam (EB) resists. A modified scanning electron microscope (SEM) equivalent of an electron beam pattern generator[45] was used to provide accurate exposure conditions. A pattern consisting of a group of horizontal lines was reproduced on the resist films many times, each time with a different electron dose. The EB exposed films were developed by dipping in xylene for 25 s and then rinsing in isopropyl alcohol for 10 s. We found that a shorter developing time in xylene and rinsing in isopropyl alcohol significantly reduced the swelling problem.[26] The sensitivity of the resists was estimated from the lowest dose needed to produce the 0.1 μm lines. For example, Figure 6 shows that for PS containing 3.8 wt % of bisPFPA **7**, the sensitivity for the 0.1 μm lines was about 10 μC cm^{-2} under these conditions. Selected results are collected in Table 1.

A resist of PS with 4.6 wt % of bisPFPA **3** (**3** #2) was found to have an EB sensitivity of about 15 μC cm^{-2}, while a resist of PS with the same molar concentration of bisazide **4** (**4** #4) has a sensitivity of about 30 μC cm^{-2}. PS alone has a sensitivity of about 100 μC cm^{-2} (**3** #5). The difference in sensitivity between **3** and **4** is much smaller under EB exposure conditions (about 2-fold)

(45) Nabity, J. C.; Wybourne, M. N. *Rev. Sci. Instrum.* **1989**, *60*, 27.

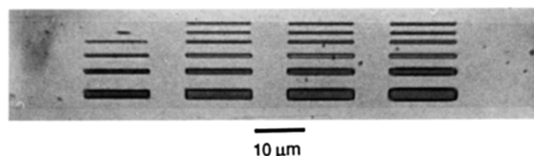


Figure 6. Optical micrograph of patterns obtained from a resist of PS containing 3.8 wt % of bisPFPA **7**. The micrograph consists of four six-line patterns. Within each pattern, the drawn line thicknesses are 0.1 (top), 0.1, 0.2, 0.5, 1.0, and 2.0 μm. The EB doses increased from left to right: 5, 10, 15, and 20 μC cm^{-2}. The exposed film was developed in xylene for 25 s and rinsed in isopropyl alcohol for 10 s.

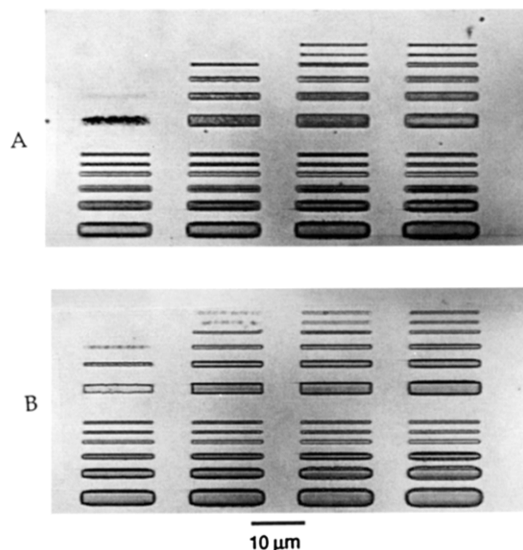


Figure 7. Optical micrograph showing the EB exposure sensitivities of PS containing same molar concentration (0.13 mmol/g) of bisPFPAs **3** and **7**. The micrograph consists of eight six-line patterns. Within each pattern, the drawn line thicknesses are 0.1 (top), 0.1, 0.2, 0.5, 1.0, and 2.0 μm. EB doses increased from left to right: top rows, 5, 10, 15, and 20 μC cm^{-2}; bottom rows, 25, 30, 35, and 40 μC cm^{-2}. The exposed film was developed in xylene for 25 s and rinsed in isopropyl alcohol for 10 s. (A, top) PS containing 6.6 wt % of **3**. (B, bottom) PS containing 5.8 wt % of **7**.

than under deep-UV exposure conditions (about 10-fold). We also observed that the difference in sensitivity between PS containing **3** and PS alone is much smaller under EB exposure conditions (about 10-fold) than under deep-UV exposure conditions (more than 100-fold). Apparently under deep-UV exposure conditions, cross-linkers such as **3** and **4** are responsible for almost all of the cross-linking reaction taking place in the polymer, whereas under EB exposure conditions, both EB radiation itself and cross-linker are responsible for cross-linking the polymer.

For PS containing the same molar concentration (0.13 mmol/g) of bisPFPA **7** and **3**, PS with **7** was somewhat more sensitive than PS with **3** under EB exposure conditions as seen from a comparison of parts A and B of Figure 7. This is opposite to the behavior of these two bisPFPAs under deep-UV exposure conditions where **3** is more efficient than **7**. Possibly the linker between the two phenyl azido groups in **7** is more stable than that in **3** under EB exposure. Another possibility is that the keto group of **7** is also involved in the cross-linking process under EB exposure. Interestingly, bisPFPA **13** (**13** #1) was found to be about as effective as bisPFPA **3** in cross-linking PS under EB exposure, although **13** has a shorter linker than that of **3**. TetraPFPA **14** (**14** #1,

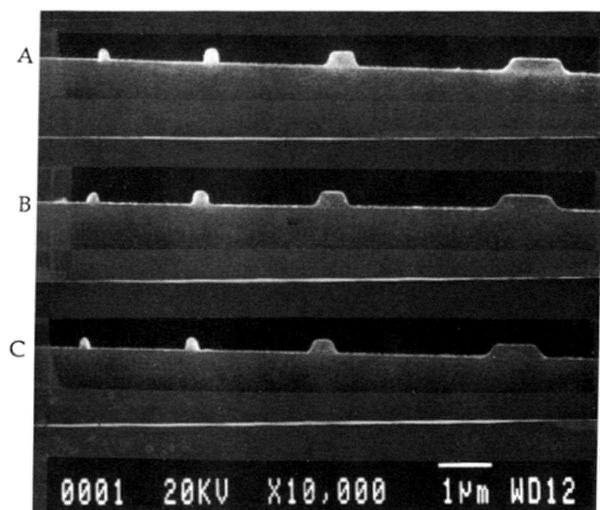


Figure 8. SEM micrograph showing the cross sections of lines drawn on resists of PS containing the same molar concentration (0.092 mmol/g) of bisPFPA **3**, **7**, and bisazide **4**. The drawn line thicknesses from left to right are 0.1, 0.2, 0.5, and 1.0 μm. (A) PS containing 4.6 wt % of **3**, with an EB dose of 15 μC cm^{-2}. (B) PS containing 3.3 wt % of **4** , with an EB dose of 35 μC cm^{-2}. (C) PS containing 3.8 wt % of **7**, with an EB dose of 12 μC cm^{-2}.

counting 1 mol of **14** as 2 mol of **3**) also was found to behave similarly to that of **3**. The sensitivity of a PS containing 1,4-diazide **11** (2.1 wt %, 0.090 mmol/g) was only marginally (about 60 μC cm^{-2}) better than PS itself as an EB resist, probably because the two azido groups are conjugated and do not act independently (see above photolysis experiments). As a control, the presence of monoPFPA **19** (6.7 wt %, 0.27 mmol/g) in PS was shown to have only a small effect on the sensitivity of PS under EB exposure conditions (about 80 μC cm^{-2}), suggesting that the bisPFPAs cross-link the polymer by way of the bis-CH insertion mechanism. Therefore, bis-CH insertion may be responsible for the cross-linking of the polymer under both deep-UV and electron beam irradiation.

The cross sections of EB exposed resists of PS containing the same molar concentration (0.092 mmol/g) of bisPFPAs **3**, **7**, and bisazide **4** after development are compared in Figure 8. The figure shows that bisPFPA **3** is more than twice as efficient at cross-linking PS than bisazide **4** and that bisPFPA **7** is somewhat better than **3** in cross-linking PS. The line designed to be 0.1 μm in width was found to be about 0.2 μm wide. This is probably the resolution limit of the resist under the conditions described.

Finally, a comparative study of EB sensitivities of PS containing various amounts of bisPFPA **3** and bisazide **4** was carried out. The results are presented in Figure 9. An interesting relationship between the concentration of bisPFPA **3** and bisazide **4** in PS and the sensitivities of the resists was observed. As the concentration of **3** or **4** in PS increased, the sensitivity of the resists increased until the resist contained about 0.1 mmol of cross-linker/g of PS. In the case of **4**, further

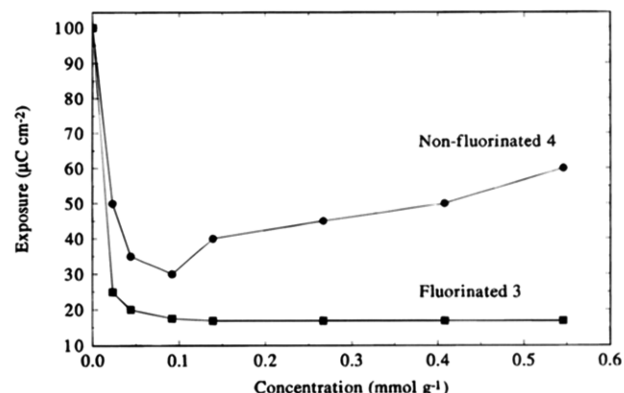


Figure 9. Molar concentration of bisPFPA **3** and bisazide **4** in PS (mmol/g) versus EB sensitivity. The sensitivity of the resists was estimated from the lowest dose required to produce the 0.1 μm lines.

increasing the concentration led to a decrease of sensitivity whereas with bisPFPA **3**, increasing the amounts of **3** did not appreciably change sensitivity. The behavior of **4** may be related to its low efficiency of cross-linking and the need for the increased EB dosage required for the complete decomposition of the azido groups in the resists as the azide concentration is increased. A cross-linking can form only when both azido groups in a bisazide are decomposed.

Conclusion

In conclusion, the convenient synthesis of bisPFPAs **3**, **5**, **7**, and **13** and tetraPFPA **14** provides a new class of efficient cross-linkers for polymers. Photolysis studies of **3** and **13** in cyclohexane demonstrate that bisPFPAs are superior to nonfluorinated bisazides in undergoing bis-CH insertion, suggesting that bisPFPAs function as highly efficient cross-linkers for polymers in lithographic applications. We have found that bisPFPA **3** is about 10 times more efficient than the corresponding nonfluorinated bisazide **4** in cross-linking polystyrene under deep-UV exposure. Utilization of **3** and **7** is shown to significantly reduce the required amount of cross-linkers in PS-based negative deep-UV resists and to increase the sensitivities of the resists. Resists of PS containing 2.4 or 4.6 wt % of bisPFPA **3** have been found to have a deep-UV sensitivity of 5–10 mJ cm^{-2} and a high enough resolution to produce 0.75 μm lines and spaces. A resist of PS containing 3.8 wt % of bisPFPA **7** has been found to have an EB sensitivity of about 10 μC cm^{-2} and resolution of better than 0.2 μm. Further characterization of these new resist systems and application of these new cross-linkers for lithography is currently underway in this laboratory.

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