

Bis(fluoroalcohol) Monomers and Polymers: Improved Transparency Fluoropolymer Photoresists for Semiconductor Photolithography at 157 nm

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ABSTRACT: Novel norbornene and [4.2.1.0^{2,5}]tricyclononene monomers bearing two hexafluoro-2-propanol substituents are polymerized with tetrafluoroethylene in solution, giving amorphous, largely alternating copolymers. The norbornene copolymer shows excellent transparency at 157 nm and a dissolution rate in aqueous tetramethylammonium hydroxide that is 100 000 times faster than the corresponding polymer with a single hexafluoro-2-propanol substituent on the norbornene ring. Intermediate dissolution rates are readily obtained using mixtures of the mono- and disubstituted norbornenes. The tricyclononene copolymer is obtained in higher conversion and molecular weight but has a higher absorbance at 157 nm and a slower dissolution rate. Partial protection of the fluoroalcohol groups as their methoxymethyl derivatives gives photoresist polymers with absorbance of 1.0 μm^{-1} or less which can be imaged at 157 nm using a photoacid generator.

Introduction

The design of organic polymers for use as imaging layers in the manufacture of computer chips has become more challenging as feature sizes decrease. Among the required polymer properties are transparency at the imaging wavelength and high resolution and resistance to the ion etching process which will drive the image into the underlying substrate.^{1,2} Most modern photoresists use a chemically amplified imaging process in which a photogenerated acid deprotects a latent acidic functional group on the polymer backbone, allowing the imaged areas to be removed by development with aqueous base.³

Smaller feature sizes are enabled, in part, by decreasing the wavelength of imaging light, but this has required introduction of new polymers for each imaging wavelength in order to meet the transparency requirements. Thus, poly(hydroxystyrene)-based polymers typically used for imaging at 248 nm have been replaced by methacrylate polymers at 193 nm due to the strong absorption of aromatic groups at the shorter wavelength.⁴

For imaging at 157 nm, which had been proposed as the next wavelength node, both aromatics and aliphatic carbonyl groups absorb,⁵ leading to a search for other polymer backbones and latent acid functional groups which could be incorporated into a photoresist. It was known that hexafluoro-2-propanol (HFIP) groups have acidity comparable to that of phenols⁶ and so will ionize for development in aqueous base, and we and others demonstrated that they have high transparency at 157 nm.^{7,8}

Polycyclic units, such as norbornene, have been incorporated into photoresists in order to supply etch resistance and high glass transition temperature, and some years ago we proposed use of tetrafluoroethylene (TFE) as a comonomer for preparation of 157 nm photoresist polymers.⁹ TFE allows radical polymerization of olefins such as norbornene, and the resulting, nearly alternating TFE-*co*-norbornene was found to have both good transparency at 157 nm and good etch resistance.⁹ Then HFIP groups were incorporated as side chains (Figure 1, TFE/NB-F-OH) to provide solubility in aqueous base while retaining good transparency, the idea being that the HFIP could be

(partially) protected by transparent, acid-labile groups such as methoxymethyl for imaging.

In practice, the TFE/NB-F-OH copolymer does dissolve in aqueous base but at a rate far too slow for practical use in a chemically amplified imaging, aqueous tetramethylammonium hydroxide developer system. We then incorporated *tert*-butyl acrylate (*t*-BuAc) into the polymer backbone as the solubility switch.¹⁰ On imaging, the acrylate esters are converted to the corresponding acids which, together with the fluoroalcohol groups, allows rapid dissolution in aqueous base.¹¹

Although the TFE/NB-F-OH/*t*-BuAc system was recognized as the first fully functional 157 nm photoresist,¹² the need for the acrylate component does increase the absorbance at 157 (ca. 1.3 μm^{-1} at 17 mol % acrylate) to above the desired level (<1 μm^{-1}). We now report the incorporation of a second fluoroalcohol group into the polycyclic segment, in the form of novel monomers NB-di-F-OH and TCN-di-F-OH, results in a remarkable increase in dissolution rate, thus allowing removal of the acrylate component and providing a functioning resist with 157 nm absorbance at or below 1 μm^{-1} .

Results and Discussion

Monomer Syntheses. We found in earlier work that the facility of copolymerization of a norbornene with TFE is a sensitive function of the type and orientation of substituents at the 5- and 6-positions.¹⁰ In particular, monomers with *exo* substituents are better behaved than those with *endo* groups, presumably due to steric effects on accessibility of the double bond. Thus, we aimed to prepare the NB-di-F-OH monomer with both fluoroalcohol groups on the *exo* face. This was accomplished as shown in Scheme 1. Norbornadiene is oxidized using a carefully controlled amount of 4-methylmorpholine-*N*-oxide and a catalytic amount of osmium tetroxide to give the diol with 97% *exo/exo* orientation of the hydroxyl groups.¹³ The hydroxyl groups are then converted to the sodium alkoxides using excess sodium hydride and treated with hexafluoroisobutylene oxide (HFIBO).¹⁴ The latter reagent reacts regiospecifically

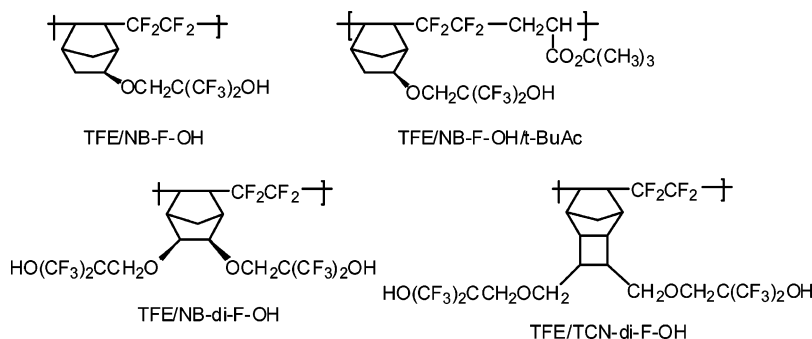
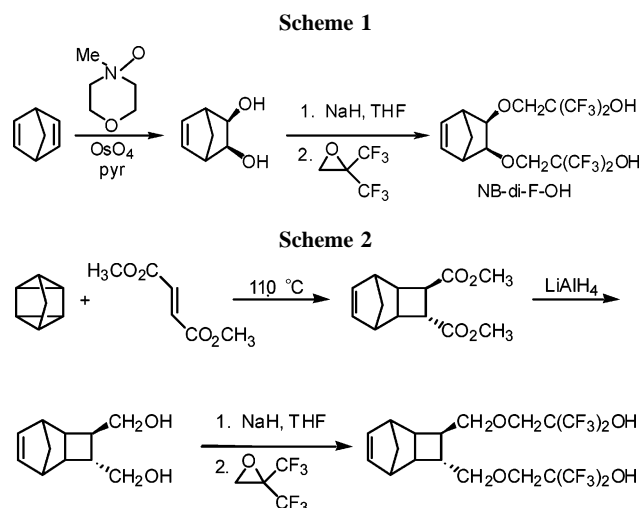


Figure 1. Structures of 157 nm photoresist polymers.



cally with nucleophiles to give the desired bis(hexafluoro-2-propanol) derivative in good yield. NB-di-F-OH is isolated as a crystalline solid.

The 3,4-disubstituted-[4.2.1.0^{2,5}]tricyclononene derivative, TCN-di-F-OH, is prepared as shown in Scheme 2. Cycloaddition of quadricyclane with dimethyl fumarate proceeds readily at 110 °C to give the cycloadduct in high yield.¹⁵ Reduction of the ester groups with lithium aluminum hydride affords the corresponding diol which reacts as described above with HFIBO to afford TCN-di-F-OH. Because of the *exo* orientation of the four-member rings, orientation of the bulky substituent groups appears to have little impact on polymerization.

Polymer Syntheses. Copolymers of TFE and the NB-di-F-OH or TCN-di-F-OH are generally prepared in a stirred metal autoclave using bis[2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-1-oxopropyl] peroxide (HFPO-dp) as initiator.¹⁶ Other low-temperature proxy radical initiators such as *tert*-butylcyclohexylperoxydicarbonate (Perkadox) can be employed, but use of the fluorinated acyl peroxide initiator results in a 0.2–0.3 μm^{-1} improvement in transparency relative to the peroxydicarbonate initiators.¹¹ This is due to the carbonate end groups left on the polymer chains by the latter initiator. A partially fluorinated solvent, 1,1,1,3,3-pentafluorobutane, dissolves the monomers and polymers and should have little chain transfer activity. Polymerizations are conducted in a semibatch mode in which a constant pressure of TFE is maintained by feeding the monomer during polymerization or in a batch mode in which a fixed amount of TFE is charged to the reactor while still cold. In either case, a substantial excess of TFE is present during polymerization. Terpolymers of TFE, NB-F-OH, and NB-di-F-OH are obtained simply by including the third monomer in the polymerization recipe. Polymers are isolated as white solids by precipitation in the nonsolvents hexane or heptane.

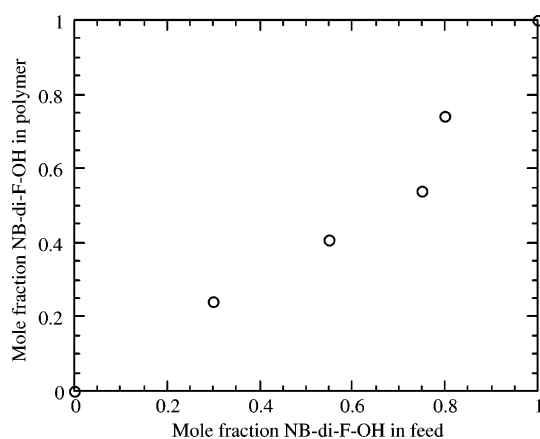


Figure 2. Relative reactivity of NB-F-OH vs NB-di-F-OH in polymerizations with TFE.

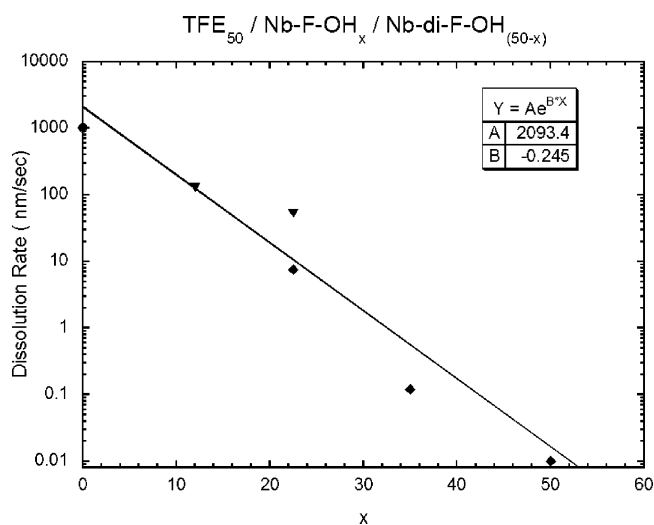


Figure 3. Polymer dissolution rate of TFE₅₀/NB-F-OH_x/NB-di-F-OH_(50-x): (◆) Luzchem TFA-11 measurements; (●) value extrapolated from TFA-11 measurements using dilute developer; (▼) TDS 420-L measurements.

The fluoroalcohol groups in the polymers can be partially protected as their methoxymethyl (MOM) derivatives by reaction of the polymer in acetonitrile solution with potassium carbonate and chloromethyl methyl ether. A careful isolation, as detailed in the Experimental Section, is required to eliminate base from the partially protected polymer because residual base can interfere with the imaging process. The degree of protection can readily be determined by ¹⁹F NMR due to the distinct change in the CF₃ chemical shift on protection.¹⁴

Polymer Properties. Polymers and their properties are summarized in Table 1. TCN-di-F-OH gave significantly higher molecular weight and somewhat better conversion than NB-di-

Table 1. TFE Copolymers of Polycyclic Monomers

monomer (mol % in feed)	conversion ^a (%)	T_g (°C)	M_n/M_w	composition ^b	Ab ^c
NB-di-F-OH (100)	48	151	9000/19600	54/46	0.47
TCN-di-F-OH (100)	72	107	21400/48500	54/46	1.30
NB-F-OH (70)	44	149	12400/19400	55/34/11	
NB-di-F-OH (30)					
NB-F-OH (45)	43	149	12600/19900	55/26/18	0.55
NB-di-F-OH (55)					
NB-F-OH (25)	54	137	6800/18000	54/21/25	
NB-di-F-OH (75)					
NB-F-OH (20)	60	153	16100/22700	54/12/34	
NB-di-F-OH (80)					

^a Of the polycyclic monomer(s), calculated from the isolated yield of polymer and composition from NMR. ^b Mole % as determined by NMR, first number is TFE. ^c Absorbance at 157 nm

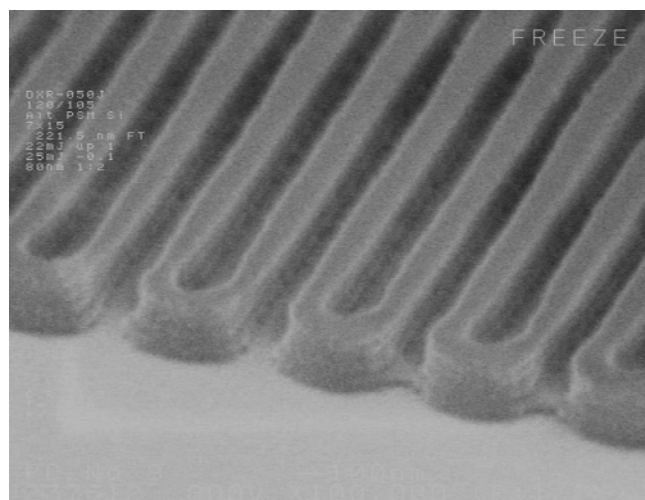


Figure 4. SEM of TFE/NB-di-F-OH copolymer with 39% MOM protection showing 80 nm 1:2 lines: spaces in 221.5 nm thick film. Imaging was created using an alt-PSM mask and illumination optics having NA = 0.85 and $\sigma = 0.7$.

F-OH, a phenomenon we have observed with other 3- and/or 4-substituted tricyclononene monomers.¹⁷ This may be related to isolating the bulky and electronegative substituent groups further from the double bond or to an increase in strain energy in the tricyclic system. The polymers are soluble in moderately polar organic solvents such as THF, acetone, and methylene chloride and in typical photoresist spinning solvent such as 2-heptanone. Glass transition temperatures are in the range 137–153 °C for the norbornene-based copolymers and at 107 °C for the TCN composition. We have observed many cases in which TCN-based polymers have higher T_g 's than norbornene analogues,^{10,17} but in the present case the longer flexible side chains in the TCN polymer may be dominating T_g behavior.

Polymerizations of NB-F-OH and NB-di-F-OH with TFE have not been run under condition which would allow rigorous determination of reactivity ratios, but inspection of the data in Table 1 and Figure 2 suggests that the former is only slightly more reactive.

Absorption data determined on the dipolymers and one of the terpolymers indicate that TFE/NB-di-F-OH polymers are highly transparent at 157 nm with absorptions well below the target of 1.0. In contrast, the TFE/TCN-di-F-OH copolymer is significantly more absorbing, to the point that this system has not been considered further for 157 nm lithography.

Dissolution. Dissolution rates of the dipolymers and the TFE/NB-F-OH/NB-di-F-OH terpolymers were made on thin films of the polymer solution that had been spin-coated on Si wafers as described in the Experimental Section. Results are shown in Figure 3. These data show that the replacement of NB-F-OH

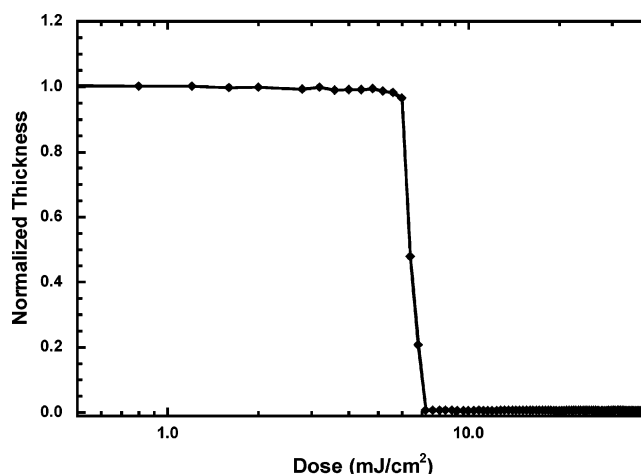


Figure 5. Contrast curve for a TFE/NB-di-F-OH copolymer with 39% MOM protection showing normalized resist thickness as a function of imaging dose in mJ/cm².

with NB-di-F-OH can increase the developer solubility of this system by a factor of 10⁵ and that one can use an appropriate ratio of NB-F-OH to NB-di-F-OH to tune the dissolution rate to any value between 0.01 and 1000 nm/s.

Imaging. Although imaging with this system is still at an early stage, Figure 4 does show clear pattern formation in 220 nm thick film of a 39% MOM-protected TFE/NB-di-F-OH copolymer when the system is formulated with a triarylsulfonium nonaflate photoacid generator. Imaging was performed at International Sematech using the Exitech stepper equipped with Tropel optics. Images were collected with 0.6 or 0.85 numerical aperture (NA) optics using a binary (partial coherence $\sigma = 0.7$) or alternating ($\sigma = 0.3$) phase shift mask. Development used a standard aqueous tetramethylammonium hydroxide solution. The polymer itself has an absorbance of 0.59 μm^{-1} and the formulated resist 1.059 μm^{-1} at 157 nm. The contrast curve for this system (Figure 5) shows good contrast (abrupt onset of solubility with dose, high slope of the thickness/dose curve continuing to zero thickness).

Conclusions

Incorporation of a second acidic hexafluoro-2-propanol group onto each repeat unit in the TFE/norbornene copolymer backbone is a very effective method for increasing the polymer dissolution rate in aqueous base to the point where an acrylate component is no longer required for image development. This affords a base polymer with absorbance well less than 1.0 μm^{-1} which becomes imagable in a chemically amplified system by partial protection of the fluoroalcohols with transparent, acid-labile methoxymethyl groups. The dissolution rate of the fully deprotected polymer is readily controlled simply by varying the ratio of NB-F-OH to NB-di-F-OH in the polymer backbone.

Experimental Section

Caution. Tetrafluoroethylene (TFE) is a deflagrating explosive and a cancer suspect agent. All work with TFE is conducted in barricaded facilities which would contain an explosion of this monomer. Reactor controls are located outside the barricade, and no one is permitted to enter during operations when TFE is present. Chloromethyl methyl ether is a volatile liquid and human carcinogen. Osmium tetroxide is also highly toxic, and quadricyclane is among the more toxic hydrocarbons.¹⁸ These reagents must be handled with special care to avoid exposure or environmental release.

Instrumentation. Glass transition temperatures (T_g) were determined by DSC (differential scanning calorimetry) using a heating rate of 20 °C/min. Data are reported from the second heat. The DSC unit used is a model DSC2910 made by TA Instruments, Wilmington, DE.

Assessment of 157 nm imaging sensitivity was done using a Lambda-Physik Compex 102 excimer laser configured for 157 nm operation. Vacuum-ultraviolet transmission measurements are made using a McPherson spectrometer equipped with a D₂ light source. Samples are spin-coated at several thicknesses on CaF₂ substrates, and the contribution of the substrate to the transmission is approximately removed by spectral division.

More specifically, all absorption coefficient measurements for polymers can be made using the following procedure:

1. Samples are first spin-coated on silicon wafers on a Brewer Cee (Rolla, MO) spin-coater/hot plate model 100CB.

(a) Two to four silicon wafers are spun at different speeds (e.g., 2000, 3000, 4000, 6000 rpm) to obtain differing film thickness, and the coated wafers are subsequently baked at 120 °C for 30 min. The dried films are then measured for thickness on a Gaertner Scientific (Chicago, IL) L116A ellipsometer (400–1200 Å range). Two spin speeds are then selected from these data to spin the CaF₂ substrates for the spectrometer measurement.

(b) Two CaF₂ substrates (1 in. diameter × 0.80 in. thick) are selected, and each is run as a reference data file on a McPherson spectrometer (Chelmsford, MA), 234/302 monochromator, using a 632 Deuterium Source, 658 photomultiplier, and Keithley 485 picoammeter.

(c) Two speeds are selected from the silicon wafer data (a) to spin the sample material onto the CaF₂ reference substrates (e.g., 2000 and 4000 rpm) to achieve the desired film thickness. Then each is baked at 120 °C for 30 min, and the sample spectra are collected on the McPherson spectrometer; the sample files are then divided by the reference CaF₂ files.

(d) The resulting absorbance files are then adjusted (sample film on CaF₂ divided by CaF₂ blank) for film thickness to give absorbance per micron (abs/micron), which is done using GRAMS386 and KALEIDAGRAPH software.

The term “clearing dose” indicates the minimum exposure energy density (e.g., in units of mJ/cm²) to enable a given photoresist film, following exposure, to undergo development.

Materials. The polymerization initiator HFPO-dp [bis[2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-1-oxopropyl] peroxide] (CAS no. 56347-79-6) was prepared in the polymerization solvent as described.¹⁶ Typically, it was prepared within 24 h of the polymerization and stored in solution in a freezer until use. NB-F-OH was prepared as described.¹⁰ Other materials were obtained from commercial sources and used as received.

Synthesis of *exo,exo*-2,3-Dihydroxynorborn-5-ene. A 1 L round-bottom flask was charged under nitrogen with 450 mL of *tert*-butyl alcohol, 30 mL of pyridine, 92 g (1 mol) of norbornadiene, 257.4 g of a 50% aqueous solution of 4-methylmorpholine-*N*-oxide (Sigma-Aldrich Chemical Co., Milwaukee, WI), and 6 mL of a 4% aqueous solution of osmium tetroxide (Sigma-Aldrich Chemical Co.). This mixture was heated at reflux overnight. The solution was cooled to room temperature and treated with 3 g of sodium hydrosulfite and 30 g of Florisil. The pH of the solution was adjusted to 7 by addition of aqueous HCl. The mixture was stirred and filtered through Celite. The filtrate was concentrated on a rotary

evaporator to remove most of the organic solvents. The remaining solution was acidified to pH 1–2 and extracted with ether. The ether extracts were washed with saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and concentrated to give 65.3 g (52%) of the desired product as a white solid judged sufficiently pure for subsequent transformation. ¹H NMR (ppm, CDCl₃, major isomer): δ 1.60 (1H, dp, *J* = 9.5, 2.0 Hz), 1.87 (1H, d, *J* = 9.0 Hz), 2.67 (2H, p, *J* = 2.0 Hz), 3.68 (2H, d, *J* = 2.0 Hz), 6.01 (2H, t, *J* = 2.0 Hz). ¹³C NMR (ppm, CDCl₃, major isomer): δ 42.4, 48.2, 69.1, 136.6. (The *exo/exo* isomer to *endo/endo* isomer ratio was 97:3 by ¹H NMR analysis.)

Synthesis of NB-di-F-OH. A 2 L flask was charged with 18 g (0.75 mol) of sodium hydride (95%, Sigma-Aldrich Chemical Co.) and 800 mL of anhydrous THF inside a drybox. A solution of 42 g (0.33 mol) of 2,3-dihydroxynorborn-5-ene (dried under dynamic vacuum at 40–50 °C for 3 h) in 400 mL of dry THF was slowly added to the agitated suspension of NaH in THF over ~2 h to maintain the internal temperature of the reaction mixture at 25–30 °C. After the addition was finished, the reaction mixture was agitated at 30–40 °C for an additional hour, and then a solution of 125 g (0.69 mol) of HFIBO was added slowly dropwise at 30–35 °C over 30 min. The reaction mixture was slowly brought to 60 °C. A slightly exothermic reaction was observed, and the internal temperature of the reaction mixture slowly increased to 68 °C (~2 h). The reaction mixture was kept at reflux until all of the starting diol was consumed (as determined by GC), requiring 4–5 h. After agitating overnight, 20 mL of methanol was added to the reaction mixture, and the solvent was removed under vacuum. 300 mL of dichloromethane was added to the crude solid product (~230 g). The suspension was cooled to 0 °C, and ~300 mL of a mixture of 50 mL of concentrated HCl in 250 mL of water was added dropwise to bring the pH of the reaction mixture to 1–2. The organic layer was separated, washed with water (2 × 500 mL), and dried over MgSO₄. The solvent was removed under vacuum, and the residue was distilled under vacuum using a short path distillation head. The product crystallized on standing. There was isolated 140.7 g (87%) of crystalline material (bp 112–116 at 0.25 mm; mp 51–52 °C), identified by NMR as NB-di-F-OH (>98% purity, mixture of *exo-exo* and *endo-endo* isomers in the ratio 96:4). ¹H NMR (CDCl₃, major isomer): 1.6 (1H, d, *J* = 10 Hz), 1.8 (1H, d, *J* = 10 Hz), 2.7 (2H, pent, *J* = 1.9 Hz), 3.4 (2H, s), 3.8 (2H, dq, *J* = 10.5, 1.6 Hz), 3.9 (2H, d, *J* = 10.5 Hz), 4.7 (2H, br s), 6.0 ppm (2H, t, *J* = 1.9 Hz). ¹⁹F (CDCl₃, major isomer): –76.6 (3F, q, *J* = 9.1 Hz), –77.30 ppm (3F, g, *J* = 9.1 Hz). ¹³C ({H}), neat major isomer): 43.6, 45.5, 66.0, 75.1 (hept, *J* = 29.1 Hz), 77.8, 122.2 (q, *J* = 284 Hz), 122.3 (q, *J* = 284 Hz), 136.7 ppm.

Synthesis of Tricyclo[4.2.1.0^{2,5}]non-7-ene-*trans*-3,4-dicarboxylic Acid Dimethyl Ester. To a 500 mL round-bottom flask equipped with a stir bar, thermometer, reflux condenser, and nitrogen inlet were added dimethyl fumarate (62.0 g, 0.430 mol) and quadricyclane (47.6 g, 0.512 mol). The mixture was heated at 110 °C for 20 h. Dimethyl fumarate completely dissolved in quadricyclane when the temperature reached 80 °C, resulting in a clear yellow solution. GC analysis of the reaction mixture showed no trace of dimethyl fumarate, and excess quadricyclane was evaporated under vacuum and collected in a cold trap (liquid nitrogen). This yielded a white solid (100 g, 98%). The crude material (>98% purity by GC) was used in the next step without further purification. ¹H NMR (ppm, CDCl₃): δ 1.27 (1H, dt, *J* = 10.0, 1.5 Hz), 1.46 (1H, d, *J* = 10.0 Hz), 2.10 (1H, t, *J* = 5.0 Hz), 2.27 (1H, t, *J* = 8.0 Hz), 2.83 (1H, s), 2.87 (1H, dd, *J* = 7.5, 5.0 Hz), 2.88 (1H, s), 3.60 (1H, dd, *J* = 9.5, 7.5 Hz), 3.69 (6H, s), 5.98 (2H, m).

Synthesis of Tricyclo[4.2.1.0^{2,5}]non-7-ene-*trans*-3,4-dimethanol. To a 100 mL three-neck round-bottom flask equipped with a stir bar, thermometer, addition funnel, and nitrogen inlet were added tricyclo[4.2.1.0^{2,5}]non-7-ene-*trans*-3,4-dicarboxylic acid dimethyl ester (5.0 g, 21.2 mmol) and THF (20 mL). The solution was cooled to 0 °C with an ice/water bath, and lithium aluminum hydride (12.7 mL of 1 M solution in THF, 1.2 equiv) was added dropwise. The reaction mixture was warmed to room temperature and stirred for

18 h. The reaction was carefully quenched by adding the reaction mixture to a solution of saturated ammonium chloride in water (50 mL). The pH of the aqueous portion was adjusted to 7. The product was extracted with ethyl acetate (3×20 mL). The combined organics were washed once with water and brine, dried with magnesium sulfate, filtered, and evaporated to yield a yellow oil (3.66 g, 96%). The crude oil (>98% purity by GC) was used in the next step without further purification. ^1H NMR (ppm, CDCl_3): δ 1.27 (1H, dp, $J = 9.2, 1.6$ Hz), 1.63 (1H, m), 1.73 (1H, m), 1.83 (1H, p, $J = 2.0$ Hz), 1.94 (1H, t, $J = 8.4$ Hz), 2.28 (1H, m), 2.52 (2H, bs, OH), 2.69 (2H, s), 3.43 (1H, t, $J = 10.0$ Hz), 3.65 (4H, m), 5.94 (2H, m). ^{13}C NMR (ppm, CDCl_3): δ 36.1, 36.9, 40.0, 41.3, 41.4, 42.9, 44.0, 60.9, 67.1, 135.3, 136.8.

Synthesis of TCN-di-FOH. To a 250 mL three-neck round-bottom flask equipped with a stir bar, thermometer, addition funnel, reflux condenser, and nitrogen inlet were added sodium hydride (1.46 g, 61.0 mmol) and anhydrous THF (30 mL). The mixture was cooled to 0°C with an ice/water bath, and a solution of tricyclo-[4.2.1.0^{2,5}]non-7-ene-*trans*-3,4-dimethanol (5.0 g, 27.7 mmol) and THF (50 mL) was added dropwise. The reaction mixture was maintained at 0°C , and HFIBO (11.0 g, 61.0 mmol) in THF (50 mL) was added dropwise. The reaction mixture was stirred at room temperature for 1 h and then heated to 65°C for 5 h. After heating, the mixture became a homogeneous solution. GC analysis showed complete disappearance of the starting diol and appearance of two peaks for the two product diastereomers. The reaction was carefully quenched by adding 1 M hydrochloric acid until the pH of the aqueous portion was 6. The product was extracted with ethyl acetate (3×50 mL). The combined organics were washed once with water and brine, dried with magnesium sulfate, filtered, and evaporated. The crude oil was vacuum-distilled ($121\text{--}122^\circ\text{C}/0.10$ Torr) to obtain a colorless oil (9.78 g, 65%). ^1H NMR (ppm, CDCl_3): δ 1.33 (1H, d, $J = 8.5$ Hz), 1.55 (1H, d, $J = 10.0$ Hz), 1.57 (1H, s), 1.69 (1H, t, $J = 5.5$ Hz), 1.82 (1H, p, $J = 5.5$ Hz), 1.97 (1H, t, $J = 8.5$ Hz), 2.41 (1H, p, $J = 9.0$ Hz), 2.71 (2H, s), 3.52 (1H, t, $J = 8.5$ Hz), 3.58 (1H, t, $J = 8.5$ Hz), 3.69 (2H, m), 3.81 (3H, m), 4.41 (1H, s), 4.45 (1H, s), 5.97 (2H, m). ^{19}F NMR (ppm, CDCl_3): δ -76.99 (3F, p, $J = 8.7$ Hz), -77.06 (3F, p, $J = 7.9$ Hz), -77.07 (6F, s). ^{13}C NMR (ppm, CDCl_3): δ 35.7, 36.1, 37.7, 38.0, 41.2, 42.6, 43.8, 66.6, 71.9, 77.2, 135.5, 136.6.

Synthesis of a TFE/NB-di-F-OH Copolymer. A metal pressure vessel of approximate 270 mL capacity was charged with 111.67 g of NB-di-F-OH and 75 mL of Solkane 365 mfc (1,1,1,3,3-pentafluorobutane, Solvay Fluor). The vessel was closed, cooled to about -15°C , pressured to 400 psi with nitrogen, and vented several times. The reactor contents were heated to 50°C . TFE was added to a pressure of 340 psi, and a pressure regulator was set to maintain the pressure at 340 psi throughout the polymerization by adding TFE as required. A 0.21 M solution of HFPO-dp in Solkane 365 mfc was pumped into the reactor at a rate of 1.5 mL/min for 6 min and then at a rate of 0.07 mL/min for 8 h. After 16 h of reaction time, the vessel was cooled to room temperature and vented to 1 atm. The recovered polymer solution was added slowly to an excess of hexane while stirring. The precipitate was filtered, washed with hexane, and air-dried. The resulting solid was twice dissolved in a mixture of THF and Solkane 365 mfc and added slowly to excess hexane. The precipitate was filtered, washed with hexane, and dried in a vacuum oven overnight to give 66.0 g of white polymer. ^1H NMR (ppm, $\text{THF}-d_8$): 1.1–3.2 (m, 6H), 3.3–4.2 (m, 6H, CHOCH_2), 6.7 (s, 2H, OH). ^{19}F NMR (ppm, $\text{THF}-d_8$): -75.60 (s, $\text{C}(\text{CF}_3)_2\text{OH}$), -95 to -125 (m, CF_2); also detected are minor peaks at -128.7 to -129.8 and -74 to -82 assigned to end groups. From integration of the major signals, the polymer is calculated to contain 54% TFE and 46% NB-di-F-OH. GPC: $M_n = 9000$; $M_w = 19\,600$; $M_w/M_n = 2.18$. Anal. Found: C, 34.71; H, 1.96; F, 52.49.

Synthesis of a TFE and TCN-di-F-OH Copolymer. A metal pressure vessel of approximate 270 mL capacity was charged with 124.2 g of TCN-di-F-OH and 75 mL of Solkane 365 mfc (1,1,1,3,3-pentafluorobutane, Solvay Fluor). The vessel was closed, cooled to about -15°C , and pressured to 400 psi with nitrogen and vented several times. The reactor contents were heated to 50°C . TFE was

added to a pressure of 340 psi, and a pressure regulator was set to maintain the pressure at 340 psi throughout the polymerization by adding TFE as required. A 0.21 M solution of HFPO-dp in Solkane 365 mfc was pumped into the reactor at a rate of 1.5 mL/min for 6 min and then at a rate of 0.07 mL/min for 8 h. After 16 h of reaction time, the vessel was cooled to room temperature and vented to 1 atm. The reactor solution diluted with additional Solkane was filter to remove an insoluble white solid believed to be PTFE, and the filtrate was added slowly to an excess of hexane while stirring. The precipitate was filtered, washed with hexane, and air-dried. The resulting solid was dissolved in a mixture of THF and Solkane 365 mfc and added slowly to excess hexane. The precipitate was filtered, washed with hexane, and dried in a vacuum oven overnight to give 109.4 g of white polymer. ^1H NMR (ppm, $\text{THF}-d_8$): 1.5–3.1 (m, 10H), 3.3–3.9 (m, 8 H, CH_2OCH_2), 6.8 (s, 2H, OH). ^{19}F NMR (ppm, $\text{THF}-d_8$): -75.7 (s, $\text{C}(\text{CF}_3)_2\text{OH}$), -95 to -125 (m, CF_2); also detected are minor peaks at -128.7 to -129.8 and -74 to -82 assigned to end groups. From integration of the major signals, the polymer is calculated to contain 54% TFE and 46% TCN-di-F-OH. GPC: $M_n = 21\,400$; $M_w = 48\,500$; $M_w/M_n = 2.27$. Anal. Found: C, 38.84; H, 2.78; F, 48.88.

Synthesis of a TFE, NB-F-OH, and NB-di-F-OH Terpolymer.

A metal pressure vessel of approximate 270 mL capacity was charged with 50.8 g (0.175 mol) of NB-F-OH, 36.5 g (0.075 mol) of NB-di-F-OH, and 75 mL of Solkane 365 mfc. The vessel was closed, cooled to about -15°C , pressured to 400 psi with nitrogen, and vented several times. The reactor contents were heated to 50°C . TFE was added to a pressure of 340 psi, and a pressure regulator was set to maintain the pressure at 340 psi throughout the polymerization by adding TFE as required. A 0.21 M solution of HFPO-dp in Solkane 365 mfc was pumped into the reactor at a rate of 1.5 mL/min for 6 min and then at a rate of 0.07 mL/min for 8 h. After 16 h of reaction time, the vessel was cooled to room temperature and vented to 1 atm. The recovered polymer solution was added slowly to an excess of hexane while stirring. The precipitate was filtered, washed with hexane, and air-dried. The resulting solid was dissolved in a mixture of THF and Solkane 365 mfc and added slowly to excess hexane. The precipitate was filtered, washed with hexane, and dried in a vacuum oven overnight to give 52.6 g of white polymer. GPC: $M_n = 12\,400$; $M_w = 19\,400$; $M_w/M_n = 1.58$. DSC: T_g at 145°C . ^{13}C NMR analysis was used to determine the ratio of NB-F-OH to NB-di-F-OH in the polymer by integration of the peaks at 65.96 ppm (1C, OCH_2 of NB-F-OH) and 67.97 ppm (2C, OCH_2 of NB-di-F-OH). The TFE to norbornene fluoroalcohol ratio was determined from the ^{19}F NMR as described above. These data showed the composition to be 55% TFE, 34% NB-F-OH, and 11% NB-di-F-OH. Anal. Found: C, 37.89; H, 2.58; F, 44.38.

Synthesis of a Methoxymethyl Ether Protected TFE/NB-di-F-OH Copolymer. To a 250 mL three-neck round-bottom flask equipped with a magnetic stir bar, thermometer, N_2 inlet, addition funnel, and dry ice condenser were added a TFE/NB-di-F-OH polymer (10.0 g, 34.1 mmol, based on equivalent weight of 293 g/mol per OH), K_2CO_3 (14.1 g, 102 mmol), and acetonitrile (68 mL). This peach-colored mixture was heated to 80°C for 20 min using an oil bath equipped with a thermocouple and remained a heterogeneous mixture. The mixture was then cooled to 45°C , at which time chloromethyl methyl ether (0.82 g, 10.2 mmol) was added dropwise. The milky white heterogeneous mixture was heated at 45°C for 3 h and then stirred at room temperature overnight. The mixture was then precipitated into 700 mL of a 1% HCl solution. The pH of the solution was determined to be slightly acidic (5–6). The precipitate was then vacuum-filtered, washed with water, and air-dried. The dried polymer was redissolved into 50 mL of acetone. This homogeneous solution was then acidified with 0.5 mL of 37% HCl solution. The solution was then vacuum-filtered to remove any precipitated salts. The filtrate was then reprecipitated into 700 mL of 1% HCl solution, vacuum-filtered, and washed with water until the pH of the water filtrate was neutral. The polymer was air-dried and then thoroughly dried in a vacuum oven at 100°C for at least 3–4 h. This procedure afforded a white, fluffy

Table 2

component	wt (g)
TFE/NB-di-F-OH/NB-di-F-OMOM polymer (39% protected)	2.202
2-heptanone	14.741
solution of tetrabutylammonium lactate in 2-heptanone prepared as follows: 2.5 g of aqueous tetrabutylammonium hydroxide (40%, Sigma-Aldrich Chemical Co.) was dissolved in 97.5 g of ethyl lactate (Sigma-Aldrich Chemical Co.); 6.0 g of this solution was later dissolved in 6.0 g of 2-heptanone	0.92
6.82 wt % solution of triphenylsulfonium nonaflate dissolved in 2-heptanone that had been filtered through a 0.45 μ m PTFE syringe filter	1.137

polymer (9.2 g, 40%). The percent of MOM protection was determined via ^{19}F NMR analysis: 23%. The molecular weight and polydispersity were determined by SEC analysis relative to polystyrene standards: $M_w = 19\,400$; PDI = 1.97. DSC analysis showed a T_g of 129 °C. Thermal decomposition temperature at 10 wt % loss was determined to be 362 °C by TGA.

Synthesis of a Methoxymethyl Ether Protected TFE/TCN-di-F-OH Copolymer. A TFE/TCN-di-F-OH copolymer with $M_n = 11\,000$ and $M_w = 20\,000$ (8.0 g) was charged under nitrogen to a 100 mL round-bottom flask equipped with a dry ice condenser. To the flask was added 50 mL of acetonitrile and 10.35 g of anhydrous sodium carbonate. The mixture was heated to 80 °C for 20 min. It was cooled to 40 °C, and 1.006 g of chloromethyl methyl ether (Sigma-Aldrich Chemical Co.) was added dropwise. The resulting mixture was maintained at 40–50 °C for 3 h and stirred overnight at room temperature. The reaction mixture was poured into 700 mL of 1% hydrogen chloride in water. The precipitate that formed was collected and washed with water. It was dissolved in 50 mL of acetone and added to 700 mL of 1% hydrogen chloride in water. The precipitate was collected and dried overnight in a vacuum oven at 100 °C, giving 7.3 g of polymer. The fluorine NMR spectrum indicated that about 44% of the fluoroalcohol groups were converted to methoxy methyl ethers.

Formulation and Imaging of a Photoresist Prepared from a Methoxymethyl Ether Protected TFE/NB-di-F-OH Copolymer. The formulation in Table 2 was prepared and magnetically stirred overnight. A qualitative assessment of the photosensitivity of this formulation was made by using an open-frame 248 nm test tool. In this test the formulation was spin-coated on a hexamethyl-disilazane (HMDS) primed Si wafer. A post-apply bake (PAB) of 150 °C for 60 s was used to remove coating solvent.

The wafer was then exposed to 248 nm light generated by an Oriel solar simulator whose output had been passed through a 248 nm interference filter. Exposure time was 15 s, providing an unattenuated dose of 22.5 mJ/cm². By using a mask with 18 positions of varying neutral optical density, a wide variety of exposure doses were generated. After exposure, the exposed wafer was baked at 105 °C for 60 s.

The wafer was tray developed for 60 s in aqueous 2.38 wt % tetramethylammonium hydroxide (TMAH) solution (Shipley LDD-026W, Marlborough, MA). This test generated a positive image with a clearing dose of ~ 2.2 mJ/cm².

Dissolution Rate. Measurements were made on thin films of the polymer solution that had been spin-coated on HMDS primed Si wafers. After spinning, a post-apply bake (PAB) of 150 °C for 60 s was used to remove coating solvent.

Dissolution rates were measured using both a Luzchem TFA-11 thin film analyzer and a TDS 420-L dissolution rate monitor. Both of these tools use a multiwavelength diode array detector to monitor sample reflectivity as a function of time when developer is applied to the sample. In these tests, a standard lithographic developer

(Shipley LDD26W-0.26N) was used. In instances where development was too fast to be tracked by the analyzer, the developer was diluted to slow development. In these cases, several different dilutions were used to allow an extrapolation to effect of using full strength developer.

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