Highly Transparent Resist Platforms for 157 nm Microlithography: An Update

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ABSTRACT

Hexafluoroisopropyl alcohol-functionalized acrylate monomers and their (co)polymers were prepared as photoresist platforms for 157 nm imaging. In order to balance transparency with other desirable traits such as etch resistance, we developed several copolymer systems. One is using 2-methyl adamantyl methacrylate as a comonomer, and the copolymer system showed better dissolution contrast compared to the copolymer with tetrahydropyranyl methacrylate without sacrificing transparency. To further improve the absorption properties at 157 nm, monomers having α-trifluoromethyl group were prepared and polymerized in anionic mechanism. The product polymer was unexpectedly transparent at 157 nm (A = 1.6 μm^{-1}) in spite that all the monomers contain carbonyl group. The second system is the copolymer with *p*-*t*-butoxy-tetrafluorostyrene. *p*-Hydroxy-tetrafluorostyrene and *p*-*t*-butoxy-tetrafluorostyrene were polymerized radically using AIBN in good yield, and the two resulting polymers showed distinctive solubility differences in aqueous base solution. Finally, this paper describes the synthesis of new monomers having fluorine (e.g CF_3- group) in the vicinity of the double bond to improve transparency at 157 nm. Due to the lower electron density of the double bond, these monomers can be copolymerized with electron-rich vinyl monomers using radical initiators.

Keywords: 157 nm lithography, hexafluoroisopropyl alcohol, tetrafluorophenol, chemical amplification

1. INTRODUCTION

Building transparent single layer resists for 157 nm photolithography requires a better understanding of how each of the components of the resist work together and how those changes affect lithographic performance. Protected phenols and carboxylic acids have been utilized as indispensable structural units in the design of conventional 248 nm and 193 nm resists.[1,2] Kunz et al. reported that conventional resists containing such acidic functions must be less than 60 nm thick to achieve an optical density of 0.4, which is required to produce a vertical resist wall profile, at 157 nm.[3] Since this is due to the strong absorbance of the acidic functions at 157 nm, the incorporation of transparent acidic functions within a polymer backbone has been an overriding concern in resist design for 157 nm lithography.

It has been reported that fluorine-containing polymers are highly transparent at 157 nm[3] and fluorocarbinols, whose pK_a values are comparable to those of phenols, can be used as acidic functional groups in the design of chemically amplified and aqueous base developable resists. Przybilla *et al.*[4] introduced hexafluoroisopropyl alcohol (HFIPA) as an alternative acidic group in the design of polystyrene-based resists for a 248 nm application, and further extension to the 193 nm resist design was made by Ito *et al.*[5] during the preparation of poly(norbornene sulfone)-based resists. Although poor dry etch resistance of the resists limits their practical use for lithography, it is notable that, when HFIPA-substituted norbornene is used in alternating copolymerization with sulfur dioxide, the resulting copolymer exhibits high transparency at 157 nm

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with an absorbance of ~3 μm^{-1}.[6] Since this unusual transparency arises from the presence of HFIPA, the HFIPA-substituted norbornene monomers have been actively investigated as transparent building blocks in the design of novel resists for 157 nm lithography.[6,7]

In an effort to develop 157 nm single-layer resists, we have exploited a variety of fluorocarbinol containing polymers mainly focusing on non-norbornene backbones.[8,9] In the course of screening conventional resist backbones such as acrylate system for 157 nm applications, it was found that the transparency of even conventional resist platforms can be significantly enhanced at 157 nm by judicious modification of highly absorbing groups such as carbonyl.[9] We showed that the homopolymer of 2-[4-(2-hydroxyhexafluoro isopropyl)cyclohexane]hexafluoroisopropyl acrylate (AF) was unusually transparent at 157 nm showing an absorption coefficient of 1.93 μm^{-1} in spite of having a carbonyl group. Poly(AF-co-THPMA) was prepared as a first test resist platform and an absorption coefficient at 157 nm of the polymer was determined to be 2.4 μm^{-1}. Resists based on the copolymer were found to show promising lithographic performance both on 248 nm and 157 nm exposure, as shown in **Figure 1** and **Figure 2**, respectively[10]. One major drawback of this system, however, turned out to be its poor etch resistance. The etch rate of the resist was measured to be 1.6 times as fast as a typical 248 nm resist (APEX) on poly etch. Takechi et al. showed in 193 nm resist studies that incorporation of an adamantyl group into acrylate systems could be effective in enhancing etch resistance.[11] Adamantyl groups, therefore, were considered in our acrylate polymer system instead of the THP group. We also employed a new carbonyl-free comonomer, *p-t*-butoxy-tetrafluorostyrene (SFOBu). This comonomer has some advantages such as ease of synthesis, easy of copolymerization with acrylate monomers, lower absorbance, improved aqueous base solubility and high etch stability.

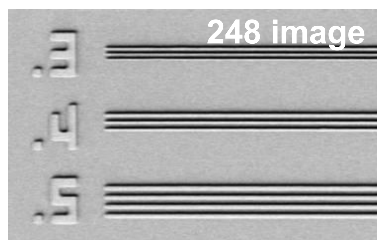


Figure 1. SEM micrograph obtained from poly(AF-co-THPMA): TPSNf (3 wt%), TOA (0.06 wt%); 248 nm exposure.

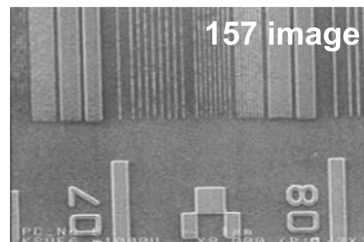


Figure 2. SEM micrograph obtained from poly(AF-co-THPMA): TPSNf (6 wt%), TBAH (0.3 wt%); 157 nm exposure.

2. EXPERIMENTAL

2.1 Materials

Materials were obtained from commercial suppliers and used without further purification, unless otherwise noted. α,α'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallizing from acetone. Tetrahydrofuran (THF) was purified as moisture-free by distillation from sodium and benzophenone. 4-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)styrene (StFA) was prepared following literature procedure.[12]

2.2 Instrumentation

IR spectra of samples were measured with a Mattson Infinity Gold series FTIR as thin films coated on silicon wafer. ^{1}H and ^{19}F NMR spectra were measured in $CDCl_3$. Spectra were recorded on a Varian Inova-400 spectrometer. ^{1}H NMR spectra were measured at 400 MHz. Proton decoupled ^{19}F NMR spectra were recorded at 376 MHz. ^{1}H chemical shift (d) was referenced to a selected resonance of residual protons in the solvent employed. Optical spectra of the polymer films were recorded on a VU-301 vacuum ultraviolet variable angle spectroscopic ellipsometer (VUV-VASE) instrument (J. A. Woollam Co.) at International SEMATECH. Samples for VUV-VASE measurements were prepared by spin-coating resists on a silicon wafer, primed with hexamethyldisilazane (HMDS) gas, followed by soft-bake at 115 °C for 120 sec.

2.3 Synthesis

2-[4-(1-ethoxymethoxy-2,2,2-trifluoro-1-trifluoromethyl-ethyl)cyclohexyl]-1,1,1,3,3,3-hexafluoropropan-2-ol (EOM-HF). To a dispersion of sodium hydride (0.96 g) in dry THF (20 mL) was added 15 g of 1,4-bis(2-hydroxyhexafluoroisopropyl)cyclohexane dissolved in dry THF (10 mL) at 0 ^{o}C. After the mixture was stirred for 1 h at room temperature, chloromethyl ethyl ether 3.78 g in 20 mL dry THF was added dropwise over a period of 30 min at 0 ^{o}C. The resulting solution was stirred overnight at room temperature and hydrolyzed by addition of distilled water. The aqueous phase was extracted with ethyl ether and dried over $MgSO_4$. The crude product was purified by column chromatography (60 % yield). ^{1}H NMR: d (ppm) 6.58 (q, 1H), 5.97 (d, 1H), 5.58 (d, 1H), 1.87 (br, -OH).

2-[4-(2,2,2-trifluoro-1-ethoxymethoxy-1-trifluoromethylethyl)cyclohexane]hexafluoroisopropyl(α-trifluoromethyl) acrylate (FAF-EOM). To a solution of EOM-HF 7.16 g in 20 mL dry dichloromethane (DCM) was added 1.5 g of freshly distilled triethylamine (in 5 mL dry DCM) under nitrogen over a period of 30 min at 0 ^{o}C. After 1 h, the resulting solution was treated with 2.4 g of α-trifluoromethyl acryloyl chloride dissolved in 5 mL dry DCM over 30 min at 0 ^{o}C. The resulting solution was stirred overnight at room temperature and hydrolyzed by the addition of 50 mL of distilled water. The aqueous phase was extracted with ethyl ether and the combined organic phase was dried over $MgSO_4$. The crude product was purified by column chromatography (72 % yield). ^{1}H NMR: d (ppm) 6.81 (s, 1H), 6.66 (s, 1H), 5.12 (s, 2H), 3.72 (t, 2H), 3.31 (m, 1H), 2.32 (m, 1H), 1.81-2.24 (m, 4H), 1.62-1.83 (m, 4H), 1.21 (t, 3H). The synthetic scheme is depicted in **Figure 8**.

2-methyladamantyl(α-trifluoromethyl)acrylate (MAdFMA). This monomer was synthesized from 2-methyladamantan-2-ol and α-trifluoromethyl acryloyl chloride using the same procedure described above for synthesis of FAF-EOM. ^{1}H NMR: d (ppm) 6.71 (s, 1H), 6.49 (s, 1H), 2.11-1.68 (m, 17H).

Poly(2-[4-(2,2,2-trifluoro-1-ethoxymethoxy-1-trifluoromethylethyl)cyclohexane]hexafluoroisopropyl(α-trifluorom ethyl)acrylate-co-2-methyladamantyl(α-trifluoromethyl)acrylate). To a 25 mL Schlenk flask containing a stir bar were added 1.7 g FAF-EOM, 0.34 g MAdFMA, 13.2 g 18-crown-6 and 0.0049 g potassium acetate in 1 mL of anhydrous THF. The reaction mixture was stirred at room temperature for 48 h. The polymer is obtained by precipitating into methanol and dried under vacuum. Polymerization was confirmed by ^{1}H-NMR spectroscopy.

***p*-Hydroxy-tetrafluorostyrene (SFOH).** A mixture of 10 g of pentafluorostyrene and 15 g of potassium hydroxide in 200 mL of *t*-butyl alcohol was boiled for 1 h, cooled, diluted with 600 mL of water, and the *t*-butyl alcohol distilled off. The residue was extracted with ether. The aqueous portion was acidified with 10 % HCl, and was extracted with ether. The ether extract was dried and evaporated to remove ether. A distillation under reduced pressure afforded SFOH (yield, 56 %) as a white sticky solid, bp 44 ºC (60 mtorr), which was stored in the freezer until next use. ^{1}H NMR: d (ppm) 6.58 (q, 1H), 5.97 (d, 1H), 5.58 (d, 1H), 1.87 (br, -OH).

***p-t*-Butoxy-tetrafluorostyrene (SFOBu).** Potassium *t*-butoxide (0.56 g) was added to a stirred solution of 0.97 g of pentafluorostyrene in 60 mL of THF at 0 ºC. The reaction temperature was increased to room temperature slowly, and 100 mL of aqueous saturated sodium chloride solution was added. The mixture was extracted with chloroform (3 × 100 mL), and the combined extracts were washed with water (5 × 100 mL), dried, and evaporated. A distillation under reduced pressure afforded SFOBu (yield, 89 %) as a colorless liquid, bp 40 ºC (60 mtorr), which was stored in the freezer until next use. ^{1}H NMR: d (ppm) 6.63 (q, 1H), 6.04 (d, 1H), 5.63 (d, 1H), 1.38 (s, 9H).

Polymerization. To a 25 mL Schlenk flask were added monomer, AIBN (1 mol % to monomer), and toluene (in case of the polymerization of SFOH; 50 % solution in v/v). The reaction tube was degassed by the freeze-thaw method (3 times), sealed under nitrogen, and then immersed into the oil bath thermostated at 90 °C. After a suitable time, the polymerization was quenched by immersing in liquid nitrogen. THF was added to dissolve the resulting polymer, and the polymer was precipitated from a suitable non-solvent.

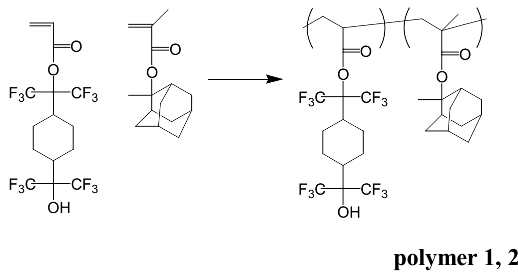
Hydrolysis of Poly(α-trifluoromethyl vinylacetate-co-StFA (Poly(CF_3VA-StFA)). To a solution of copolymer in methanol was added a catalytic amount of sodium methoxide. The mixture was refluxed for 50 h and the product was isolated by precipitation into water. The polymer was then dried under vacuum, and the extent if hydrolysis was determined using ^{1}H-NMR spectroscopy.

Tetrahydropyranyl (THP) ether of Poly(CF_3VA-StFA). THP protection of Poly(CF_3VA-StFA) was carried out using 3,4-dihydro-2H-pyran (DHP) and a catalyst (acetonyltriphenylphosphine bromide; ATPB).[13] To a solution of Poly-(CF3VA-StFA) and DHP in dry dimethyl sulfoxide was added 0.1 equiv. of ATPB dissolved in dichloromethane. The

reaction mixture was stirred for 1 h at room temperature, and the product was isolated by precipitation into hexane and dried under vacuum.

2.4 Lithographic evaluation

Exposure on 248 nm was carried out using a Nikon 248 nm stepper (NA = 0.42, σ = 0.5) equipped with a KrF excimer laser (Cymer CX-2LS). Copolymers were dissolved in propylene glycol methyl ether acetate, added triphenylsulfonium perfluoro-1-butanesulfonate (TPSNf), and trioctylamine (TOA) or tetrabutylammonium hydroxide (TBAH). The resist solution was filtered through a 0.2 μm membrane filter and spin-coated onto silicon wafers that are either primed with HMDS gas or treated with antireflective coatings. Post-apply bake (PAB) and post- exposure bake (PEB) was carried out at 90~130 °C, and development was conducted in 0.262 N tetramethylammonium hydroxide (TMAH) solution. The film thickness was measured on a Tenkor P-10 Surface Profiler and developed patterns were imaged with a Leo 982 (Zeiss) scanning electron microscope (SEM). Imaging experiments at 157 nm were carried out at International SEMATECH using an Exitech 157 nm Microstepper (NA = 0.6, σ = 0.7).



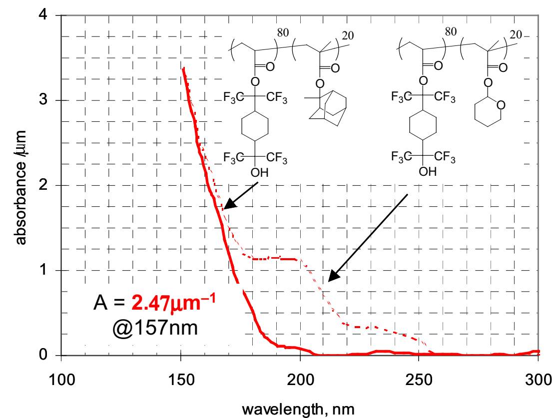


Figure 3. VUV-VASE spectrum of **polymer 1**.

3. RESULTS AND DISSCUSSION

3.1 Acrylate system

AF was copolymerized with 2-methyl adamantyl methacrylate (MAdMA) to form **polymer 1** (20 mol%) and **polymer 2** (40 mol%). The VUV-VASE spectrum of **polymer 1** is shown in **Figure 3**. The absorbance coefficient of **polymer 1** at 157 nm was determined to be 2.4 μm^{-1}, which is comparable to that of poly(AF-co-THPMA) (2.5 μm^{-1}) and means that etch resistance of the resist can be enhanced by an introducing adamantyl group without sacrificing transparency.

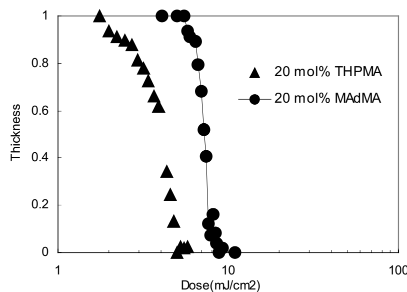


Figure 4(a). Contrast curves obtained with **polymer 1**-based resist and poly(AF-co- THPMA)-based resist: TPSNf (3 wt%), TOA (0.06 wt%), PAB (115 °C for 60 sec), PEB (90 °C for 60 sec).

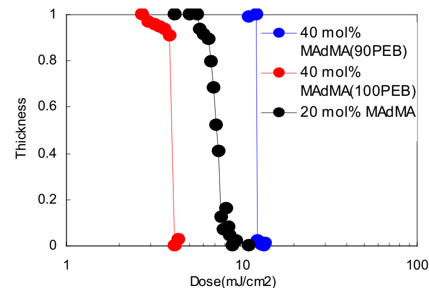


Figure 4(b). Contrast curves obtained with **polymer 2**-based resist: TPSNf (3 wt%), TOA (0.06 wt%).

Figure 4(a) shows the contrast curve of the **polymer 1**-based resist. The resist was found to have much higher dissolution contrast than a poly(AF-co-THPMA)-based resist. Incorporation of 40 mol% adamantyl functionality (**polymer 2**) gave higher contrast (**Figure 4(b)**). Lithographic performance of **polymers 1** and **2** was tested using a 248 nm stepper (NA = 0.42, σ = 0.5). Although the **polymer 1**-based resist was found to show top-rounding and poor resolution (**Figure 5**), **polymer 2**-based resist demonstrated significantly higher resolution up to 0.25 μm L/S (**Figure 6**) without top-rounding. This finding was obtained in the both of bright field (a) and dark field (b) at the same dose. These results suggest that the resist has very high dissolution contrast. In parallel with imaging experiments at 248 nm, lithographic evaluation at 157 nm (NA = 0.6, σ = 0.7) was also carried out with the **polymer 2**-based resist. **Figure 7** shows an SEM image obtained using conventional illumination. The resist produced 130 nm L/S(1/2) patterns. Top-rounding was observed, most probably due to the high absorbance of the resist at 157 nm (3.4μm^{-1}). This suggests that further pursuit of transparency at 157 nm is strongly required to use (meth)acrylate polymers in 157 nm lithography.

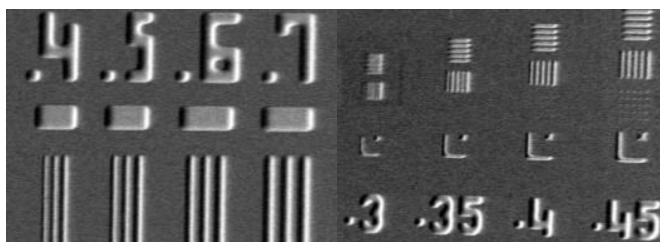


Figure 5. SEM micrographs obtained with **polymer 1**: TPSNf (3 wt%), TOA (0.06 wt%), PAB (115 °C for 60 sec), PEB (90 °C for 90 sec), 10 mJ/cm^2; 248 nm exposure.

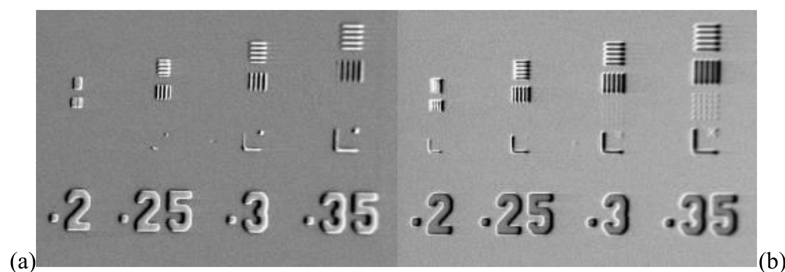
(a)  (b)

Figure 6. SEM micrographs obtained with **polymer 2**: TPSNf (3 wt%), TOA (0.06 wt%), PAB (115 °C for 60 sec), PEB (100 °C for 60 sec); 248 nm exposure; (a) bright field (8.6 mJ/cm^2), (b) dark field (8.6 mJ/cm^2).

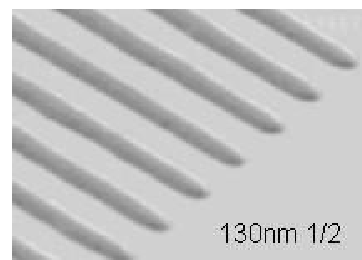
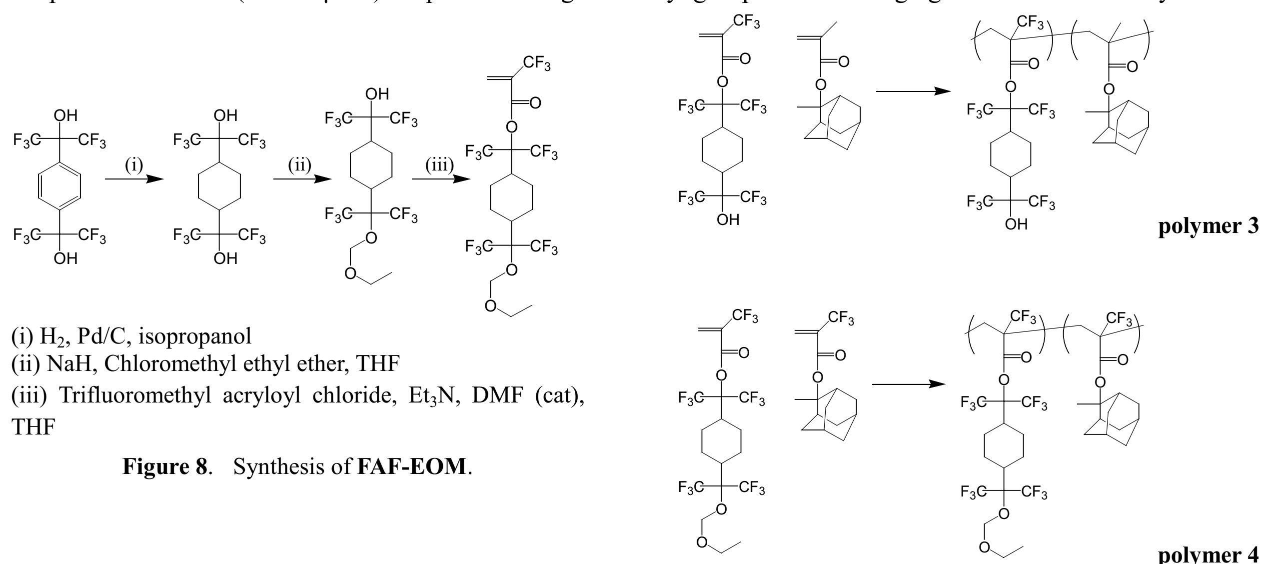


Figure 7. SEM micrograph obtained with **polymer 2**: TPSNf (6 wt%), TBAH (0.3 wt%). PAB (100 °C for 90 sec), PEB (90 °C for 60 sec); 157 nm exposure

3.2 α-trifluoromethylacrylate system

Incorporation of a trifluoromethyl group on the α–position of acrylate polymers has been one of the best ways to enhance transparency of polymers at 157 nm.[14,15] For this purpose, 2-[4-(2-hydroxyhexafluoro isopropyl) cyclohexane] hexa-fluoroisopropyl (α-trifluoromethyl)acrylate (FAF) was synthesized. It was reported that α-trifluoromethylacrylic monomers could undergo copolymerization with acrylates and methacrylates by free radical polymerization using AIBN.[14] Therefore FAF (50 mol%) was copolymerized with MAdMA (50 mol%) to give **polymer 3**. **Polymer 3** was found to form a nice 248 nm image, as shown in **Figure 9**. However the absorption coefficient at 157 nm of **polymer 3** was measured to be 5.0 μm^{-1}. It suggests that FAF was difficult to incorporate into the polymer due to a lower reactivity than MAdMA under free radical polymerization. Therefore anionic polymerization was employed. In order to do this, 2-methyladamantyl(α-trifluoromethyl)acrylate (MAdFMA) was synthesized. As well 2-[4-(2,2,2-trifluoro-1-ethoxymethoxy-1-trifluoromethylethyl)cyclohexane]hexafluoroisopropyl (α-trifluoromethyl)acrylate (FAF-EOM) was synthesized to avoid catalyst decomposition during polymerization. Copolymers of these two monomers (**polymer 4**) were

prepared by anionic polymerization (MAdFMA; 30mol%) using potassium acetate and 18-crown-6 at room temperature. The VUV-VASE spectrum of **polymer 4** is presented in **Figure 10**. It was found that **polymer 4** was unexpectedly transparent at 157 nm (A = 1.6μm^{-1}) in spite of the high carbonyl group content. Imaging studies are underway.



(i) H_2, Pd/C, isopropanol
(ii) NaH, Chloromethyl ethyl ether, THF
(iii) Trifluoromethyl acryloyl chloride, Et_3N, DMF (cat), THF

Figure 8. Synthesis of **FAF-EOM**.

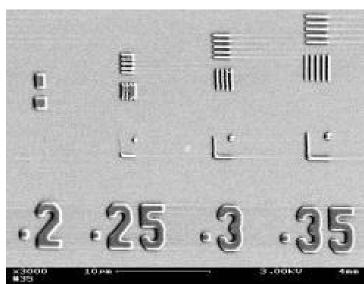


Figure 9. SEM micrograph obtained with **polymer 3**: TPSNf (3 wt%), TOA (0.06 wt%), PAB (115 °C for 60 sec), PEB (100 °C for 60 sec), 11.2 mJ/cm^2; 248 nm exposure.

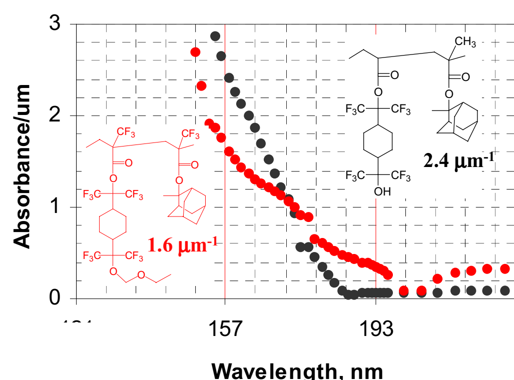


Figure 10. VUV-VASE spectra of **polymer 1** and **polymer 4**.

3.3 *p-t*-Butoxy-tetrafluorostyrene system

In most of the resist systems, a carbonyl group seems indispensable for good performance. Since it is preferred to avoid this group in a resist structure because of its high absorbance at 157 nm, we examined new carbonyl-free functional groups. Tetrafluorophenol was employed for this purpose. The highly electron-withdrawing fluorine atom would be expected to reduce absorbance of the aromatic group. Moreover, the acidity of hydroxyl groups was increased to the level of carboxylic acids, which makes it possible to use a t-butyl function as a protecting group. Among the various polymer structures, we are interested in styrenes as a platform in photoresist applications because of its advantages of ease of polymerization, inherent etch resistance, and ease of incorporating other groups to give better performances.

***p*-Hydroxy-tetrafluorostyrene.** Because of the structural similarity we pursued the possibility of using fluorinated hydroxystyrene in photoresist applications. The syntheses were very simple and the product could be obtained in high yield by two-step reactions from commercial pentafluorostyrene (**Figure 11**). **Figure 12** shows the ^{19}F-NMR spectrum of SFOH. There are only two peaks with the same integration, which indicates that there is only one nucleophilic substitution on the *para*- position to the vinyl group.

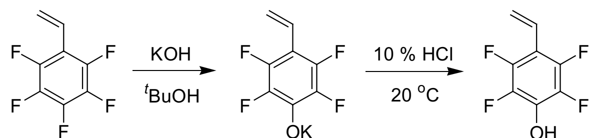


Figure 11. Synthesis of SFOH.

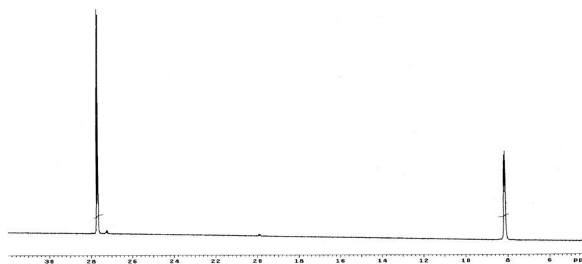


Figure 12. ^{19}F-NMR spectrum of SFOH.

We polymerized SFOH using AIBN as a radical initiator in toluene (50 %, v/v). The polymerization was slow, and it took 90 h at 90 °C to reach 80 % conversion. It is probably due to a chain transfer reaction through free phenol moieties. For the same reason, the hydroxyl groups of the hexafluorocarbinol functionalized-norbornenes were protected with acetyl or *t*-BOC beforehand to accelerate the polymerization in radical mechanism.[16] The resulting poly(SFOH) was freely soluble in 0.26 N TMAH solution.

***p-t*-Butoxy-tetrafluorostyrene.** Since the tetrafluorophenol group is highly acidic, a simple *t*-butyl group was thought to be enough as a protecting group. The *t*-butyl protected SFOH was prepared following a slightly modified synthesis of SFOH. During the synthesis of SFOH, SFOBu was also prepared in low yield (~ 6 %) as a side product. However, using potassium *t*-butoxide, SFOBu was obtained in high yield (89 %). The protected monomer was polymerized under the same condition used for the polymerization of SFOH. Surprisingly, the polymerization rate was very fast, and the reaction mixture was completely solidified after 5 min. This also supports the possibility of chain transfer reactions to the free hydroxyl groups in the polymerization of SFOH. DSC analysis showed the polymer has T_g of 163 °C. In solubility tests, the polymer was practically insoluble in 0.26 N TMAH solution.

One of the possible problems using the tetrafluorophenyl group in photoresist applications is the stability of the C-F bond. The highly polarized C-F bond makes the carbon atom susceptible to a nucleophilic aromatic substitution reaction. Since the photolithography process uses base solutions in the development step, we must check the stability of the polymer in the base developing solution. **Figure 13** shows the IR spectra of the polymer film before and after applying development conditions. It shows no change after the developing process and indicates that the polymer film is stable enough at least in the normal developing solution. These results support the possibility of using tetrafluorophenol-functionalized polymer for 157 nm photoresist applications. The preparation of poly(AF-co-SFOBu) as a photoresist at 157 nm is currently underway.

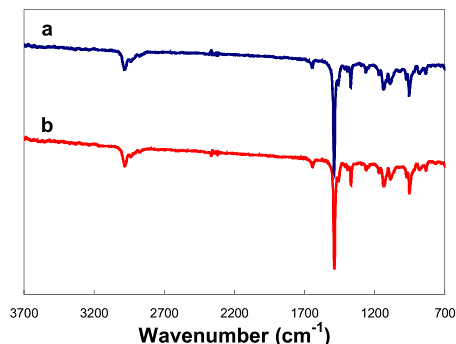
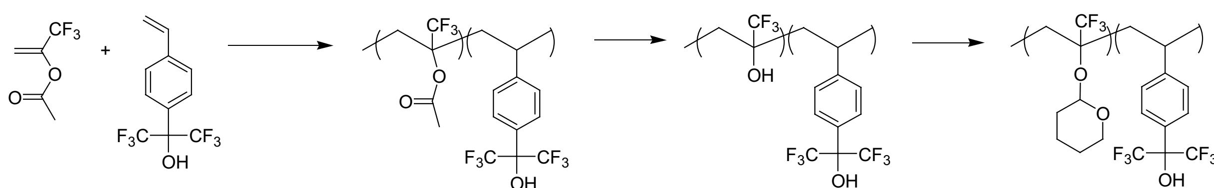


Figure 13. IR spectra of poly(SFOBu) films spin-coated on the Si wafer before (**a**) and after (**b**) applying developer (0.26 N TMAH solution).

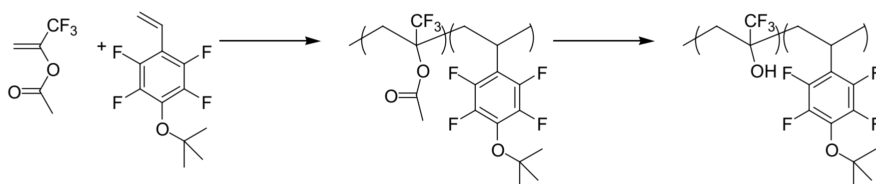
3.4 Copolymerization of trifluoromethyl vinylacetate (CF_3VAc). In our previous studies we identified poly(vinyl alcohol-*co*-α-trifluoromethyl vinyl alcohol) (PVA-*co*-CF_3VA) as a photoresist platform.[17] This polymer has a low 157 nm absorption in the THP-protected state. It can be deprotected by a chemically amplified mechanism and the resulting polymer is aqueous base soluble (0.26 N TMAH). Based on these results we want to extend our strategy to improve our

materials towards a higher glass transition temperature, greater transparency and improved etch resistance. This can be done by utilizing copolymerization of CF_3VAc with different monomers. From the study of copolymerization with various vinyl monomers, the electronic character of the C=C bond of CF_3VAc was found to be electron poor due to the electron-withdrawing CF_3 group, and CF_3VAc was successfully copolymerized with electron-rich vinyl monomers such as vinyl acetate, vinyl ether, or vinyl pyrrolidinone. Based on this, norbornenes and styrenes were chosen as comonomers to provide the higher glass transition temperature and improved etch resistance. Various norbornenes including norbornene, norbornadiene, norbornene-2-(1,1,1-trifluoro-2-trifluoromethylpropan-2-ol), and *t*-BOC protected norbornene-2-(1,1,1-trifluoro-2-trifluoromethylpropan-2-ol) were tested in copolymerizations with CF_3VAc. However, no polymer was prepared in all attempts.

We could obtain copolymers of CF_3VAc with StFA. The radical polymerization of CF_3VAc with StFA using AIBN at 90 °C afforded copolymers with 50 % yield in 50 h. The ^{1}H-NMR shows that the copolymer contains about 30 % of CF_3VAc from the 1:1 initial monomer ratio. The vinyl acetate groups were hydrolyzed to alcohols using sodium methoxide, and the alcohols were then protected with THP. The copolymer was tested in lithography at 248 nm. The polymer film showed a clear latent image after PEB, but the dissolution contrast was too poor to form a nice pattern. We believe it is due to the low level of THP protection. Because the hexafluorocarbinols on the styrenic part are known to resist protection with THP, the CF_3VA groups are the only possible sites for THP protection. Moreover, the THP protection reaction on the trifluoromethyl alcohols is not quantitative. To increase the protection ratio, studies using different protection groups such as ethoxymethyl are currently underway.



SFOBu was also used in the copolymerization with CF_3VAc. One of the advantages of using this comonomer is the higher level of incorporation of a protected group to increase dissolution contrast. In this case, we can use *t*-butoxy moieties as acid cleavable groups. On copolymerization at 90 °C with a 1:1 starting monomer ratio, a copolymer was prepared in 50 % yield after 3 days of reaction, and 15 % CF_3VAc was incorporated in the copolymer.



3.5 Alternating copolymer system

It was reported that electron-deficient olefin tetrafluoroethylene could undergo free-radical copolymerization with norbornene and 1,1,1-trifluoro-2-(trifluoromethylpropan-2-ol), giving copolymers with very high transparency at 157 nm.[18] Many attempts have been made to incorporate functionality in these copolymers by modification of norbornene and terpolymerization. However, any substituent on norbornene will dramatically reduce the yield of polymer. Our approach is makes use of trifluoroacrylate and/or 2,2,3,4,4-pentafluorobut-3-enoic acid ester instead of tetrafluoroethylene to make copolymers (**Figure 14**). The synthesis of monomers is depicted in **Figure 15**.

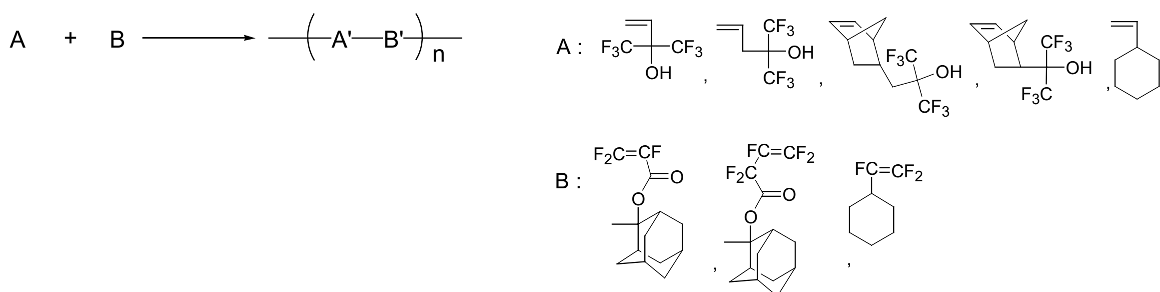


Figure 14. Alternating copolymerization of electron-rich monomers (A) and electron-deficient trifluorovinyl monomers (B).

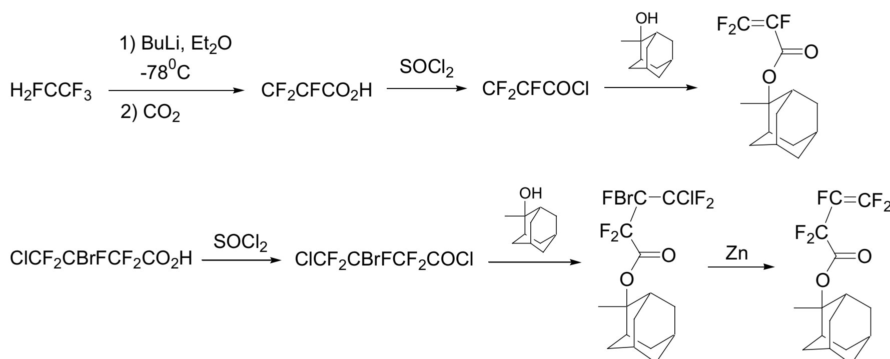


Figure 15. Syntheses of trifluorovinyl monomers.

4. SUMMARY

In order to balance the high transparency of hexafluoroisopropyl alcohol-functionalized acrylate polymers with other desirable traits like etch resistance, 2-methyl adamantyl methacrylate was copolymerized. The resist based on the polymer showed high dissolution rate without sacrificing transparency. To further improve absorption properties at 157 nm, monomers having α-trifluoromethyl groups were prepared and polymerized using an anionic mechanism. This polymer was found to be unexpectedly transparent at 157 nm (A = 1.6 μm^{-1}) despite the fact that all monomers contain carbonyl groups. The second system examined is a copolymer with *p*-*t*-butoxy-tetrafluorostyrene. *p*-Hydroxy-tetrafluoro- styrene and *p*-*t*-butoxy- tetrafluorostyrene were polymerized radically using AIBN in good yield, and the two resulting polymers showed distinctive solubility differences in aqueous base solution. Finally, the synthesis of new monomers having fluorine adjacent to a double bond such as trifluoromethylene group was carried out to improve transparency at 157nm. Due to the lower electron density of the double bond, these monomers can be copolymerized with electron-rich vinyl monomers using radical initiators.

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REFERENCES

1. Reichmanis, E.; Houlihan, F. M.; Nalamasu, O.; Neenan, T. X. *Chem. Mater.* **3**, 394, 1991.
2. MacDonald, S. A.; Willson, C. G.; Frechet, J. M. J. *Acc. Chem. Res.* .**27**, 6, 1994.

3. Kunz, R. R.; Bloomstein, T. M.; Hardy, D. E.; Goodman, R. B.; Downs, D. K.; Curtin, J. E. *J. Vac. Sci. Technol. B*, **17**, 3267, 1999.
4. Przybilla, K. J.; Roschert, H.; Pawlowski, G.; *Adv. Mater.* **4**, 239, 1992: *Proc. SPIE-Int. Soc Opt. Eng.* **1672**, 500, 1992.
5. (a) Ito, H.; Seehof, N.; Sato, R. *Poly. Mater. Sci. Eng.* **77**, 449, 1997: (b) Ito, H.; Seehof, N.; Sato, R.; Nakayama, T.; Ueda, M. *ACS Symp. Ser.* **706**, 449, 1998.
6. Ito, H; Wallraff, G. M.; Brock, P.; Fender, N.; Truong, H.; Breyta, G.; Miller, D. C.; Sherwood, M. H.; Allem, R. D. *Proc. SPIE-Int. Soc. Opt. Eng*. **4345**, 274, 2001
7. (a) Chiba, T.; Hung, R. J.; Yamada, S.; Trinque, B.; Yamachika, M.; Brodsdy, C.; Patterson, K.; Heyden, A. V.; Jamison, A.; Lin, S.-H.; Somervell, M.; Byers, J.; Conley, W.; Willson, C. G. *J. Photopolym. Sci. Technol.* **13**, 657, 2000: (b) Patterson, K.; Yamachika, M.; Hung, R.; Brodsky, C.; Yamada, S.; Somervell, M.; Osborn, B.; Hall, D.; Dukovic, G.; Byers, J.; Conley, W.; Willson, C. G. *Proc. SPIE-Int. Soc. Opt. Eng.* **3999**, 365, 2000: (c) Feiring, A. E.; Feldman, J. WO 00/67072, 2000.
8. (a) Schmaljohann, D.; Bae, Y. C.; Weibel, G. L.; Hamad, A. H.; Ober, C. K. *Proc. SPIE-Int. Soc. Opt. Eng.* **3999**, 330, 2000: (b) Bae, Y. C.; Dai, J.; Weibel, G. L.; Ober, C. K. *Polym. Prepr.* **41(2)**, 1586, 2000: (c) Schmaljohann, D.; Bae, Y. C.; Weibel, G. L.; Hamad, A. H.; Ober, C. K. *J. Photopolym. Sci. Technol.* **13**, 451, 2000.
9. Bae, Y. C.; Ober, C. K. *Polym. Prepr.* **42(2)**, 403, 2001.
10. Bae, Y. B.; Douki, K.; Yu, T.; Dai, J.; Schmaljohann, D.; Kang, S. H.; Kim, K. H.; Koerner, H.; Conley, W.; Miller, D. Balasubramanian, R.; Holl, S.; Ober, C. K. *J. Photopolym. Sci. Technol*. **14**, 2001.
11. Nozaki, K.; Kaimoto, Y.; Takahashi, M.; Takechi, S.; Abe, N. *Chem. Mater.* **6**, 1492, 1994.
12. Snow, A. W.; Sprague, L. G.; Soulen, R. L.; Grate, J. W.; Wohltjen, H. *J. Appl. Polym. Sci*. **43**, 1659, 1991.
13. Hon, Y.-S.; Lee, C.-F. *Tetrahedron Lett.* **40**, 2389, 1999.
14. Ito, H.; Miller, D. C.; Willson, C. G. *Macromolecules* **15**, 915, 1982.
15. Willson, C. G.; Ito, H.; Miller, D. C.; Tessier, T. G. *Polym. Eng. Sci*. **23**, 1000, 1983.
16. Ito, H; Wallraff, G. M.; Fender, N.; Brock, P. J.; Larson, C. E.; Truong, H. D.; Breyta, G.; Miller, D. C.; Sherwood, M. H.; Allen, R. D. *J. Photopolym. Sci. Technol.* **14**, 583, 2001.
17. Schmaljohann, D.; Hamad, A. H.; Weibel, G. L.; Ober, C. K. *PMSE Preprints* **83**, 445,2000
18. M. K. Crawford, A. E. Feiring, J. Feldman, R. H. French, M. Periyasamy, F. L. Schadt III, R. J. Smalley, F. C. Zumsteg, R. R. Kunz, V. Rao, L. Liao, and S. M. Holl, *Proc. SPIE-Int. Soc. Opt. Eng.* **3999**, 357, 2000.