Fundamental Studies of Fluoropolymer Photoresists for 157 nm Lithography

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A variety of fluorocarbonol containing polymers have been studied in an effort to identify transparent polymer platforms for use in 157 nm VUV lithography. It was found that a single α -trifluoromethyl substituent renders poly(α -trifluoromethyl vinyl alcohol-co-vinyl alcohol), P(CF₃VA-co-PVA), readily soluble in 0.262 *N* TMAH. The THP-protected polymer can be spin-coated from PGMEA solutions and preliminary studies using 248 nm exposure showed that it undergoes chemically amplified deprotection with a clearing dose of ~ 15 mJ/cm². Using a VUV spectrometer, absorption coefficients of ~ 3 μm^{-1} were observed at 157 nm with P(CF₃VA-co-PVA) and THP protected P(CF₃VA-co-PVA). On the basis of these results, we extended our investigation to a series of fluorocarbonol containing polydienes as aqueous base soluble polymer platforms synthesized by the ene reaction of hexafluoroacetone on the double bond. Fluorine content and glass transition temperature can be well controlled. We will discuss the scope and limitation of fluoropolymers for 157 nm lithography.

Keywords: 157 nm photoresists, fluoropolymers, chemically amplified deprotection

1. Introduction

With recent advances in laser technology and optical materials, photolithography at 157 nm using a F₂ excimer laser has emerged as a major choice for post-193 nm technology to bridge existing optical lithographies with post-optical lithographies such as extreme UV and electron beam projection methods. The most important issue in the resist design for 157 nm application, however, has been the transparency of a polymer platform, since the absorption of organic polymers at 157 nm is dominated by carbon-2p electrons such as the π electrons in carbon-carbon or carbon-oxygen double bonds.[1] Although protected phenols and carboxylic acids are indispensable structural units to induce chemically amplified photolysis and aqueous base solubility in conventional 248 nm and 193 nm resists, Kunz et al. reported that these conventional resists should be less than 60 nm thick in order to achieve an

optical density of 0.4 at 157 nm wavelength.[1] This means known resist materials used at 248 nm and 193 nm are not adequate for single layer resist (SLR) application at 157 nm, and chemical structures must be modified in order to incorporate transparent acidic functions.

It has been reported that fluorocarbonols, 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.[2–4] Przybilla et al. introduced this novel concept in the design of polystyrene-based resists and dissolution inhibitors for 248 nm application,[2] and further extension to the 193 nm resist design has been made by Ito et al. during the preparation of poly(norbornene sulfone)-based resists.[3,4] In both cases, hexafluoroisopropyl alcohol (HFIPA) was incorporated, and this acidic alcohol was protected by *tert*-butoxycarbonyl. If the HFIPA function is

protected by a more desirable protecting groups, such as dihydropyran (DHP) or isobutene, to yield relatively transparent tetrahydropyranyl (THP) or *tert*-butyl ether at 157 nm, it is apparent that this will provide resist chemists with facile routes for the synthesis of 157 nm resists. However, during the synthesis of novel monomers containing HFIPA, we have found that it is extremely difficult, or perhaps impossible under normal conditions, to protect this highly acidic alcohol using DHP. This implies that it is necessary to leverage two of the most important resist properties, i.e., chemical amplification and aqueous base solubility. Therefore, it has been our strategy to incorporate fluorocarbinols within monomer or polymer structures which undergo DHP protection but are still acidic enough to induce aqueous base solubility of the polymer backbone. Our preliminary results indicated that less acidic fluorocarbinols, such as 1,1,1-trifluoroisopropyl alcohol, can be protected using DHP and one trifluoromethyl group is enough to induce aqueous base solubility of the polymer backbone [5]. This design strategy was implemented in the synthesis of THP protected poly(α -trifluoromethyl vinyl alcohol-*co*-vinyl alcohol), P(CF₃VA-*co*-VA). Another key requirement of 157 nm photoresists is a high plasma etch resistance, which typically requires a polycyclic system. The concept of a THP-protected fluoroalcohol was extended to a polycyclic fluoropolymer, which contains the same protecting group chemistry. The basic structure has been derived from a number of polydienes, which were reacted with hexafluoroacetone and subsequently cyclized. These structures provide adjustable fluorine content, higher T_g while maintaining aqueous base solubility and chemically amplified deprotection chemistry. In this report are described our results toward development of SLR for 157 nm lithography.

2. Experimental

2.1. Materials

Vinyl acetate (VAc, Aldrich) and α -trifluoromethyl vinyl acetate (CF₃VAc, Aldrich) were treated with aqueous NaOH solution to remove the inhibitor, then distilled twice from CaH₂. All solvents were dried and distilled prior to use. 3,4-Dihydro-2H-pyran (DHP) and 1-aminopropane were obtained from Aldrich and used as received. Acetonyl triphenylphosphine bromide (ATPB) was obtained from Lancaster Chemicals and used as received. The standard

developer CD26 (Shipley) was used for solubility studies and development of the patterns.

2.2. Synthesis of Poly(α -trifluoro-methyl vinyl acetate-*co*-vinyl acetate), P(CF₃VAc-*co*-VAc)

The random copolymers of CF₃VAc and VAc (P(CF₃VAc-*co*-VAc)) were prepared using a similar procedure reported by Haas et al.[6,7] After three cycles of freeze and thaw, the reaction flask, containing equimolar amounts of CF₃VAc and VAc and AIBN (2 mol-%), was sealed and heated to 80 °C. After 17 h, the polymerization was stopped and the polymer was purified by precipitation from acetone into hexane three times. After purification, the polymer was dried in vacuum.

¹H-NMR (CDCl₃, δ in ppm): 5.55–4.7 (CH), 3.2–1.6 (CH₂), 2.1 (CH₃, CF₃VAc), 2.0 (CH₃, VAc). ¹³C-NMR (CDCl₃, δ in ppm): 170.4–168.7 (C=O), 128.2–119.7 (CF₃), 81.6–80.5 (C_{quart.}), 65.7–64.3 (CH), 41.8–37.9 (CH₂), 22.1–20.9 (CH₃). ¹⁹F-NMR (CDCl₃, δ in ppm vs. CFCl₃): -69.1 - -70.7, -71.2 - -77.0, -78.4 - -79.3 (all CF₃). GPC (THF, PS-standards): M_n = 19500 g/mol; M_w/M_n = 1.95.

2.3. Synthesis of Poly(α -trifluoromethyl vinyl alcohol-*co*-vinyl alcohol), P(CF₃VA-*co*-VA)

P(CF₃VA-*co*-VA) was prepared by hydrolysis of P(CF₃VAc-*co*-VAc). The copolymer was dissolved in 1-aminopropane and refluxed for 3 days to yield corresponding vinyl alcohol copolymer, P(CF₃VA-*co*-VA). This was isolated and purified by neutralization and precipitation into water. Finally, it was dried in vacuum. Hydrolysis was complete.

¹H-NMR (DMSO-*d*₆, δ in ppm): 6.1 (br, CH), 4.1 (OH), 1.8 (br, CH₃). ¹³C-NMR (DMSO-*d*₆, δ in ppm): 131.2, 128.3, 125.4, 122.6 (CF₃), 74.8 (C_{quart.}), 64.3, 64.0 (CH), 47.7 (CH₂).

2.4. Tetrahydropyranyl (THP) ether of P(CF₃VA-*co*-VA)

THP protection of P(CF₃VA-*co*-VA) was carried out using DHP and a catalyst (ATPB).[8] To a solution P(CF₃VA-*co*-VA) and DHP (4 equiv.) in dry DMSO, was added 0.1 equiv. of ATPB dissolved in dichloromethane. The reaction mixture was stirred for 30 min at room temperature, and the product was isolated by precipitation into water and dried in vacuum.

¹H-NMR (acetone-*d*₆, δ in ppm): 5.8 (br, CH), 4.5 (CH₂-O, OH), 3.0–1.0 (CH₂). Degree of attachment: 70 %.

2.5. Flood Exposure Experiments

THP protected P(CF₃VA-co-VA) was dissolved in propylene glycol methyl ether acetate (PGMEA) (10 wt.-% of polymer). Triarylsulfonium hexafluoroantimonate was added (1 wt.-% of polymer) as a photoacid generator. The solution was filtered through a 0.2 μ m membrane filter. The photoresist was deposited at 2000 rpm for 60 sec. Resist films, approximately 0.25 μ m thick, were post-apply baked at 90 °C for 60 sec. Wafers were patterned with a test mask at 75 dosages ranging from 5 mJ/cm² to 30 mJ/cm² using a Nikon EX7 DUV 248 nm excimer laser stepper, after which films were post-exposure baked at 110 °C for 60 sec and developed for 60 sec in 0.262 N TMAH solution.

2.6. Living Anionic Polymerization

Monodisperse polydienes were prepared by the living anionic polymerization of 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene using a standard high vacuum technique. These monomers were purified by successive distillation from calcium hydride and dibutylmagnesium. Cyclohexane and THF were dried by distillation from 1,1-diphenylhexyllithium and a sodium-benzophenone complex, respectively. PBD, PIP, and PDMB, with 1,4-enchainment higher than 90 %, were prepared in cyclohexane at 40 °C using *sec*-butyllithium. PDMB, with 66 % 1,2- and 34 % 1,4-enchainments, prepared in THF at -40 °C according to the procedure reported by Yuki et al.[9]

2.7. Ene Reaction of Polydienes with HFA

The ene-reaction of polydienes with HFA was carried out in a pressure vessel using a similar procedure to those reported by Snow et al.[10] and Coleman et al.[11] A typical example is described as follows: 4.79 g of PBD, dissolved in 50 mL of toluene, was charged into a pressure reactor and 29.1 g of HFA (2 equiv) was distilled into the reactor. The mixture was then heated at 180 °C for 24 h. The crude product was purified by precipitation in petroleum ether and then by freeze-drying to yield 13.2 g of hexafluorohydroxypropyl-(HFHP) modified PBD as powder. FT-IR: 3594, 3491, 3011, 2938, 2861, 1656, 1620, 1509, 1367, 1210, 1131, 994, 849, 718 cm⁻¹. Elemental analysis: C, 44.53%; H, 3.76%, F, 48.54%.

2.8. Cyclization of PIP

5 g of PIP ($M_n = 26,000$ and $M_w/M_n = 1.03$) and 0.1 g of trichloroacetic acid were dissolved in 100

mL of anhydrous toluene. Cyclization reaction was started by injecting 0.2 g of SnCl₄ to the reactor kept at 80 °C and continued for 15 ~ 30 min. The reaction mixture was quenched by slow addition of methanol and the product was recovered by precipitation into methanol. After freeze-drying, 4.21 g of white powder was obtained with $M_n = 19,100$ and $M_w/M_n = 1.21$.

2.9. Protection Reaction of HFHP-Modified Polydienes

The HFHP group in the modified polydienes was protected by acid-labile groups such as trimethylsilyl (TMS) or ethoxymethyl (EOM) group. TMS protection was carried out using a similar procedure to that reported by Sprague et al.[12] and EOM protection was carried out as reported by Patel et al.[13]

3. Results and Discussion

3.1. Photoresists based on poly(α -trifluoromethyl vinyl alcohol) copolymer

3.1.1. Photoresist design

The synthesis of the initial 157 nm photoresist platform focussed on three key issues which are important for imaging and development of a 157 nm SLR. We designed our resist material in order to obtain a positive tone pattern, which can be developed in aqueous base, using the industry standard developer (0.262 N TMAH). The key issue of this work was to provide a material, which shows a high transparency at 157 nm. Furthermore it should undergo a chemically amplified solubility change through a deprotection reaction followed by development in aqueous base. It has been well established that fluorinated polymers exhibit several properties which favor application for a 157 nm photoresist. Fluorocarbons are highly transparent at 157 nm [1] and the presence of fluorinated alkyl groups in the α -position of an alcohol decrease the pK_a of the hydroxy function substantially. During our studies of fluorinated poly(vinyl alcohol)s (PVA), we observed that a PVA containing a trifluoromethyl group on every second unit can induce aqueous base solubility of the polymer backbone. This feature is in agreement with early reports on similar polymers,[6,7] but we have demonstrated that the polymer is also soluble in the standard photoresist developers. The synthetic scheme is shown in Scheme 1.

The synthesis was conducted in bulk and gives good yields of the polymer when the feed ratio m/n is ≥ 1 . Under these conditions, both monomers were incorporated into the polymer according to

their feed ratio. For $m/n < 1$, the ratio of units in the polymer is $m'/n' \approx 1$ using these reaction conditions and the yield is also reduced, thereby indicating a substantially lower reactivity for CF_3VAc .

Scheme 1. Synthesis of $\text{P}(\text{CF}_3\text{VA-co-VA})$.

The second step to accomplish our design for a 157 nm resist is the protection of the free alcohol groups with a transparent, acid-cleavable function. Organic protection chemistry provides a limited number of functionalities, which fulfill these requirements. Based on our results for 193 nm photoresists,[14] we chose a THP group as our first candidate. The protection reaction is depicted in Scheme 2.

Scheme 2. Protection reaction of $\text{P}(\text{CF}_3\text{VA-co-VA})$ with DHP.

Early results on the protection reaction revealed that the commonly used reaction with *p*-toluenesulfonic acid as catalyst protects the PVA readily with THP groups, but it only partially converts acidic α -trifluoromethyl alcohol groups, whereas more powerful neutral catalysts like ATPB give high conversion for the protection reaction. With this reaction we were able to get 70% THP attachment on our starting polymer.

Selection of a ratio of repeating units of $m'/n' = 1.22$, is optimal to ensure aqueous base solubility. In summary we developed a three step synthesis of a THP-protected acidic poly(vinyl alcohol) with good yields starting from commercially available monomers.

3.1.2. NMR studies of $\text{P}(\text{CF}_3\text{VAc-co-VAc})$.

Studies on the copolymerization behavior of α -trifluoromethyl vinyl acetate have been performed to investigate the ability to incorporate fluorocarbinols into polymeric systems. A fundamental understanding is necessary to utilize the strategy to incorporate the fluorocarbinol via this monomer. The above mentioned limits on the copolymerization renders the question of the polymerization mechanism. Either random or alternating copolymerization is possible. Sequence analysis of copolymers can provide an answer. We performed ^1H , ^{13}C , ^1H - ^1H and ^1H - ^{13}C correlated NMR spectroscopy to evaluate the sequence of repeating units. The two-dimensional techniques were applied to assign signals via coupling to the adjacent proton. Of particular interest was the question, whether there are two adjacent CF_3VAc units, which would give some indication to the reaction mechanism. Figure 1 shows the ^1H - ^1H -DQCOSY NMR spectrum. This gives $^3J(\text{H,H})$ coupling, which allows the identification of the diads.

Figure 1. ^1H - ^1H -DQCOSY NMR spectrum of

$\text{P}(\text{CF}_3\text{VAc-co-VAc})$ (CDCl_3).

The ^1H -NMR spectrum shows a broad region with methylene peaks ranging from 1.6 to 3.5 ppm depending on the chemical environment. High field peaks (1.6 – 1.9 ppm) indicate two adjacent VAc units (VAc-VAc diad), [15] whereas the region between 2.2 and 3.0 ppm has one vinyl acetate and one α -trifluoromethylvinylacetate peak ($\text{CF}_3\text{VAc-VAc}$ diad). Both areas have cross-peaks due to their neighboring CH group in the ^1H - ^1H -DQCOSY NMR spectrum (5.0 – 5.6 ppm, compare Figure 1), as expected. In contrast to this the CH_2 -peaks between 3.0 and 3.5 ppm do not show any cross-peaks to CH indicating diads of two α -

trifluoromethyl-vinyl acetate units (CF_3VAc - CF_3VAc diad). The absence of the corresponding $^3\text{J}(\text{H,C})$ cross-peaks in the ^1H - ^{13}C -HMQC-TOCSY spectrum supports this conclusion, but it does not fully prove it because of the low intensity of the signals. Thus a restriction to a 1:1 composition ratio of structural units should result from the low reactivity of the monomer, which can add easily to the highly reactive VAc unit but only poorly to a second CF_3VAc group. From ^1H -NMR diad content was calculated for $\text{P}(\text{CF}_3\text{VAc}(45)\text{-co-VAc}(55))$ as 3 (CF_3VAc - CF_3VAc) : 79 (CF_3VAc -VAc) : 18 (VAc-VAc).

3.1.3. Molecular Modeling studies.

Molecular modeling studies were performed to support our results from NMR spectroscopy. We used the Mac Spartan *Plus* program with a semi-empirical method in geometry optimization.

The electrostatic potentials of the single molecules were calculated using an electrostatic fit after minimizing the structure as shown in Figure 2 for CF_3VAc and VAc. Table 1 shows the charges of some selected atoms at the reaction center.

Figure 2. Semi-empirical molecular modeling on CF_3VAc 1 and VAc 2.

Entries 3 to 6 of Table 1 compare the charges at the same atoms for the corresponding growing radical chain, modeled as a dimeric unit with different penultimate groups (Scheme 3).

The results of Table 1 indicate that the $\text{C}=\text{C}$ bond of CF_3VAc is less polarized due to the electron-withdrawing CF_3 group and therefore it is less reactive in a free radical polymerization. Furthermore, the relative charge at C2 of the growing chain is changed from positive to negative, whereas C1 of both monomers is partially positively charged, which should reduce the electrostatic radical-monomer interaction for the fluorinated unit. These observations are in

agreement with the data gained from NMR measurements, which indicates a general possibility for polymerization but at a strongly reduced reactivity.

Table 1. Calculated charges of selected atoms of CF_3VAc , VAc and four dimer radicals (electrostatic fit).

#		C1 / C1'	C2 / C2'	C3	O4 / O4'
1	1 (CF_3VAc)	-0.22	+0.13	+0.65	-0.49
2	2 (VAc)	-0.35	+0.23	-	-0.51
3	dimer 1-1·	-0.11	-0.04	+0.82	-0.40
4	dimer 2-1·	-0.16	-0.05	+0.82	-0.45
5	dimer 1-2·	-0.20	+0.02	-	-0.42
6	dimer 2-2·	-0.28	+0.07	-	-0.43

Scheme 3. Notation of the four different dimers used in the modeling studies (compare table 1).

3.1.4. Evaluation of Resist Properties

The synthesized THP-protected $\text{P}(\text{CF}_3\text{VA-co-VA})$ shows good solubility in common organic solvents such as acetone or PGMEA, whereas the unprotected $\text{P}(\text{CF}_3\text{VA-co-VA})$ exhibits aqueous base solubility in 0.262 N TMAH. Thus, the polymer can be spincoated from PGMEA and developed in aqueous base, which makes the whole system consistent with standard industry techniques. The second requirement for good resist properties is high transparency at 157 nm. The absorption coefficients are $3\ \mu\text{m}^{-1}$ for $\text{P}(\text{CF}_3\text{VA-co-VA})$ and $3.2\ \mu\text{m}^{-1}$ for the THP-protected $\text{P}(\text{CF}_3\text{VA-co-VA})$. These results would enable a film thickness of $\sim 140\ \text{nm}$ (at OD of 0.4) in lithographic applications. We believe that we can reduce the absorption further by adding more fluorinated alkyl groups to the polymer.

The deprotection mechanism of the THP group has been carried out under chemically amplified conditions. The investigation of the deprotection chemistry was successfully carried out using 248 nm flood exposure with 1 wt.-% of triphenyl sulfonium hexafluoroantimonate as PAG and developing the exposed film in 0.262 N TMAH. A clearing dose of $\sim 15\ \text{mJ}/\text{cm}^2$ was determined and the deprotected polymer dissolved completely in aqueous base within 60 sec at room temperature.

Thus we were able to demonstrate deprotection by a chemically amplified mechanism.

3.1.5. Lithographic Results

We were able to obtain first lithographic results by exposure at 248 nm using the same system as mentioned above (1 wt.-% of triphenyl sulfonium hexafluoroantimonate as PAG, development in 0.262 N TMAH). Figure 3 shows optical micrographs of the developed films. These micrographs clearly demonstrate the lithographic ability of the THP-protected P(CF₃VA-co-VA). To date we were able to resolve 0.55 μ m sized patterns, but the lithographic conditions have not been optimized yet. Therefore, we expect a much higher resolution, when optimizing the exposure and development condition.

Figure 3. Micrograph of the developed film after exposure at 248 nm.

These first experiments have been carried out to show lithographic ability; further experiments are underway in order to reduce the resolved feature sizes.

3.2. Photoresists Using Fluorocarbonol Containing Polydienes

3.2.1. Modification of Linear Polydienes via the Ene Reaction

The fluorocarbonol moiety can also be introduced to a polymer by polymer analogous reaction. Starting from polydienes as double bond-containing polymers one can use the ene-reaction as a very efficient way to add hexafluoroacetone (HFA) to the polymer. As early as the 1960's, HFA was used as a versatile reagent for the modification of saturated hydrocarbon polymers, such as polyethylene and polypropylene, in the presence of a radical initiator.[16] However, only limited information is available for the ene reaction of polydienes with HFA.[10,11] Therefore, in an effort to identify transparent polymer platforms for a 157 nm application, we carried out the ene reaction on various polydienes using HFA. A summary of results is given in Table 2. Most

polydienes exhibited 80 ~ 90 % conversion in the ene reaction, but 1,4-PDMB exhibited considerably lower conversion. The lower reactivity of 1,4-PDMB is presumably due to its semi-crystallinity, and HFHP-modified 1,4-PDMB also exhibited melting endotherm (≈ 139 °C) in its DSC thermogram.

As reported for PIP,[10,11] dramatic changes in solubility and T_g were observed after the incorporation of the HFHP group within polydiene structures. For example, all the products were soluble in methanol after the ene reaction, and most of products exhibited tremendous increase in T_g by 70 ~ 140 °C. Unexpectedly, lower T_g was obtained with 1,2-PDMB which has a relatively high T_g (= 72 °C) before the ene reaction (entry no. 4 in Table 2). This is most probably due to the formation of a longer pendent group (as shown in Scheme 4), compared to other 1,4-polydienes which form an α -HFHP group, and it appears that this long HFHP pendent group causes a large increase in free volume due to a lack of efficient packing.

Scheme 4. Synthesis of Imageable Polymers by Ene Reaction

Table 2. Results in the Ene Reaction of Polydienes with HFA

sample	M_n^a (M_w/M_n^a)	conv., % ^b	T_g
PBD	28,200 (1.04)	89.6	42 (-101 ^{a,c})
PIP	26,000 (1.03)	79.2	53 (-61 ^{a,c})
1,4-PDMB	20,400 (1.07)	58.8	68 (-5 ^{a,c})
1,2-PDMB ^d	16,700 (1.03)	83.9	70 (72 ^a)

^aBefore the ene reaction. ^bFrom elemental analysis. ^cFrom literature. ^d66 % 1,2- and 34 % 1,4-microstructures.

Aqueous base solubility of HFHP-modified polydienes was tested in 0.262 N TMAH solution. Samples were prepared by spin-coating the polymer solution in propylene glycol methyl ether acetate on a silicon wafer at 3000 rpm. After

evaporation of residual solvent at 120 °C for 60 sec, the samples were dipped into 0.262 *N* TMAH solution for 30 sec. Except for HFHP-modified 1,4-PDMB (entry no. 3 in Table 2), the spin-coated samples were readily soluble in 0.262 *N* TMAH solution within 30 sec as confirmed by film thickness measurement using a surface profilometer. Slower dissolution of HFHP-modified 1,4-PDMB can be ascribed to a lower conversion in the ene reaction as well as its semi-crystallinity.

Protection reactions of HFHP-modified polydienes were also studied using hexamethyldisilazane and 2-chloroethyl methyl ether to yield acid-labile TMS and EOM ethers, respectively. In both cases, the protection reaction of the fluorocarbinols was effectively carried out as confirmed by both ¹H NMR and FT-IR spectroscopies. In Figure 4, are shown FT-IR spectra of 1,2-PDMB (A), after the ene-reaction (B), and after the protection reaction using 2-chloroethyl methyl ether (C). The absence of absorption in the 3680-3140 cm⁻¹ region (O-H stretching) of Figure 4C clearly proves virtually quantitative protection of HFHP-modified 1,2-PDMB with 2-chloroethyl methyl ether.

Figure 4. FT-IR spectra of 1,2-PDMB (A), after HFA reaction (B), and after EOM protection (C).

3.2.1. Ene Reaction of Cyclized Polydienes

In general, the protected polymers exhibited lower T_g 's than unprotected polymers by ~20 °C due to the loss in hydrogen bonding. In order to prepare HFHP-modified polydienes with higher T_g

and built-in etch barriers, we further extended the ene reaction to cyclized polydienes. The cyclization reaction of PIP was carried out using trichloroacetic acid and SnCl₄. Although the cyclization of polydienes can enhance T_g as well as etch resistance of the polymer platform, broadening in the molecular weight distribution was reported to occur due to the presence of the intermolecular cyclization reaction. [17] Since a narrow molecular weight distribution is preferred for better resist performance and higher resolution imaging,[18] we carried out the cyclization reaction under various conditions to find optimal conditions to achieve lower M_w/M_n values. It was found that the broadening in the molecular weight distribution could be minimized using lower concentrations of trichloroacetic acid and SnCl₄. Representative GPC traces of PIP before and after cyclization are shown in Figure 5.

Figure 5. GPC RI traces of 1,4-PIP (A) with $M_n = 26,000$ and $M_w/M_n = 1.03$ and cyclized 1,4-PIP (B) with $M_n = 19,000$ and $M_w/M_n = 1.21$.

A small shoulder at a lower elution volume (high M_n) indicates the presence of intermolecular cyclization. Lower M_n values were always observed after cyclization and, since the polymer chain takes on a more compact conformation after cyclization, this appears to be due to the decrease in hydrodynamic volume. As expected cyclized PIP's exhibited high T_g 's after the ene reaction with HFA, ranging in value from 120 to 170 °C.

4. Conclusion

The design of a 157 nm photoresist material is restricted to a limited number of chemical functions due to the requirements for transparency, solubility, chemically amplified solubility change, development and pattern transfer by etching. Some of these requirements and structural units seem to call for contradictory solutions, e.g. etch resistance and transparency. Thus, one has to carefully balance the properties of the photoresist. With this study we have succeeded in fulfilling three of the key demands of a 157 nm photoresist: transparency at 157 nm, chemically amplified solubility change and aqueous base development using a THP-protected poly(α -trifluoromethyl vinyl alcohol-co-vinyl alcohol). Furthermore, the protected polymer is soluble in PGMEA, which allows standard spincoating techniques for the wafer preparation. A 248 nm exposure demonstrated the lithographic ability of these resists. Presently 157 nm exposure studies and etching studies are underway to evaluate and optimize pattern development and transfer. The ene reaction has been demonstrated to be a powerful tool in order to introduce fluorocarbon groups into polydienes. The choice of different polydienes as well as the possibility to cyclize the polydienes opens a broad spectrum of different polymer structures, which offers the chance to optimize resist requirements such as etch resistance and glass transition temperature while maintaining aqueous base solubility and the chemically amplified deprotection reaction. Furthermore the living polymerization mechanism allows control over molecular weight, which will be important for control over the dissolution rate.

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