Dissolution Inhibitors for 157 nm Photolithography

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ABSTACT

The focus of 157 nm lithographic research is shifting from materials research to process development. Poly (2-(3,3,3-trifluoro-2-trifuoromethyl-2-hydroxypropyl) bicyclo[2.2.1]heptane-5-ene) (PNBHFA) has received a great deal of attention as a possible base resin for 157 nm lithography. The Asahi Glass RS001 polymer, which was introduced at SPIE in 2002, has also shown promise as a 157 nm base resin due to its low absorbance. Partial protection of either polymer with an acid labile protecting group is a common design for functional photoresists. We previously reported the blending of the carbon monoxide copolymers with PNBHFA copolymers to achieve the critical number of protected sites for optimum imaging performance and contrast.[1,2] Our group has since studied the use of the unprotected base resin with an additive monomeric dissolution inhibitors (DIs) and a photoacid generator (PAG) to form a three component resist. Surprisingly unprotected PNBHFA was discovered to have dissolution inhibition properties that are far superior to the dissolution inhibition properties of novolac. Several DIs were prepared and tested in PNBHFA to take advantage of the resins dissolution inhibition properties. We have also recently explored the performance of a two-component resist using PAGs that also function as DIs.

**Keywords:** Dissolution inhibitor, DI, photo acid generator, PAG, 157 nm photoresist

1. INTRODUCTION

Fluorine containing polymers appear to be the most promising resins for 157 nm photoresists. Polymers prepared by anionic, free radical, and metal-catalyzed addition reactions have yielded polymers from which positive-tone 157 nm resists can be formulated. The polymer that has received the most attention for use at 157 nm (polymer **1**) is prepared by the metal-catalyzed addition polymerization of 2-(3,3,3-trifluoro-2-trifuoromethyl-2-hydroxypropyl) bicyclo[2.2.1]heptane-5-ene) (PNBHFA). This polymer must have a critical number of acidic sites blocked by an acid labile protecting group (i.e., acetal or *t*-butyl carbonate) to render the polymer insoluble in standard aqueous tetramethyl ammonium hydroxide developer. The protecting groups can either be incorporated during or after polymerization of PNBHFA.

R = acetal or *t*-boc

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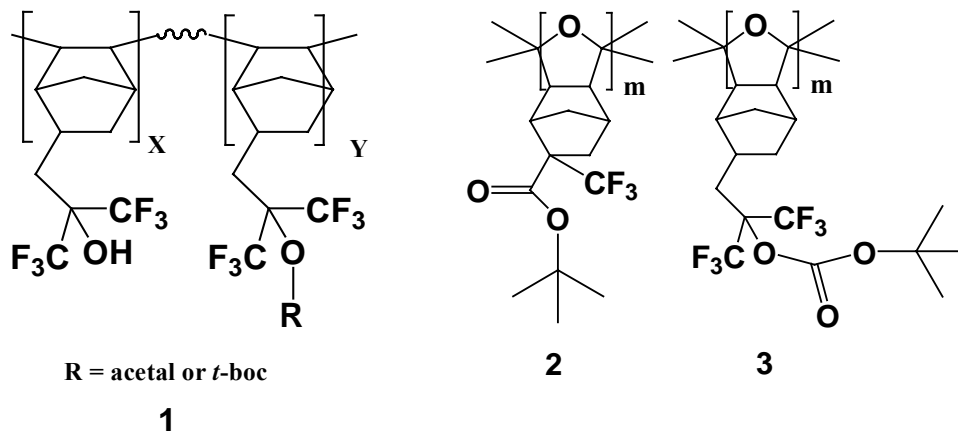
The use of carbon monoxide copolymers (polymer **2** and **3**) as dissolution inhibitors (DIs) has been previously reported.[1,2] The carbon monoxide copolymers were blended with polymer **1** to adjust the percentage of protected sites in the resist formulation. Blending the carbon monoxide copolymers with unprotected PNBHFA provided an attractive way to adjust the critical number of protected sites for optimum imaging performance and contrast. Unfortunately, the carbon-monoxide copolymers have an absorbance of greater than 2.3 μm^{-1} and the images were achieved using 30 wt% of the carbon-monoxide copolymers.[3] Vacuum UV data show that the hydrogenated norbornene monomers used in the preparation of the carbon-monoxide copolymers are more transparent than the resultant polymer. This led to the conclusion that monomeric DIs, based on more transparent monomers, were an attractive alternative to the carbon-monoxide copolymers. In order to simplify the formulation process further, we decided to investigate the use of monomeric DIs in completely unprotected polymer **1**. In the process of testing the dissolution inhibition properties of polymer 1, it was discovered, to our surprise, that polymer **1** has dissolution inhibition properties similar to those of novolac. In fact, the dissolution inhibition response of polymer **1** to a DI was typically an order of magnitude better than the response of novolac to the same DI.

While testing the inhibition properties of new DIs in polymer **1**, it was observed that the photoacid generator (PAG) had a substantial effect on the dissolution rate of the PNBHFA. It has been previously reported that PAGs have an effect on the dissolution rate of 248 nm resist polymers[4], but the effect on polymer **1** is far more dramatic. The dissolution inhibition properties of several PAGs were therefore examined in both polymer **1** and the more transparent polymer **4**.

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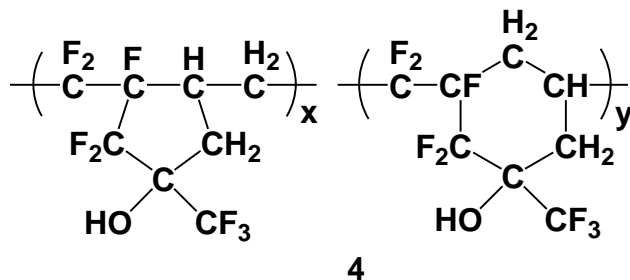
2. EXPERIMENTAL

2.1 Materials
Unprotected PNBHFA was received as a gift from AZ Clariant. Polymer **4** was purchased from Asahi Glass. The novolac used was a Shipley G2 resin and a gift from IBM. The poly(p-hydroxystyrene) was purchased from Hoechst Celanese. DI **5** was a gift from IBM. PAGs **11**, **15** and **16** were purchased from Aldrich. PAGs **12** and **13** were gifts from 3M.

2.2 Synthesis
The synthesis of all other DIs and PAGs will be reported elsewhere.

2.3 Dissolution Rate Measurements
The formulated resists were spin coated on 2 inch hexamethyldisilazane treated silicon wafers. The coated wafers were baked for 90 s at 90 °C. All films were approximately 1 μm thick. The wafers were then cleaved in half. Half of the wafer was exposed to 200 mJ at 248 nm using a mercury arc lamp. All formulations involving novolac were exposed to 200 mJ at 365 nm. The high exposure dose was used to ensure the complete reaction of all photoactive compounds. The exposed half of the wafer was then baked for 90 s at 90 °C. The dissolution rates of the exposed and unexposed films were measured in 0.26 N tetramethylammonium hydroxide.

2.4 Imaging Conditions
The following imaging conditions were used unless otherwise noted. Wafers were pre-treated with either hexamethylsilazane (HMDS) or 80 nm of AR-19 antireflective coating (ARC). The wafers are then coated with 150 nm of photoresist and baked at 90 °C for 90 s. Imaging was performed using a binary mask, with numerical aperture

of 0.6 and partical coherence of 0.6 on a MicroScan3 248 nm full field step and scan tool at SEMATECH. Imaging at 157 nm was performed using a binary mask on a Exitech 157 nm Microstepper at SEMATECH, with a numerical aperture of 0.85 and partial coherence of 0.7 over a range of doses. Wafers were then post-exposure baked at 90 °C for 90 s and puddle-developed for 12 s in 2.38% tetramethylammonium hydroxide (TMAH). Top down scanning electron microscope (SEM) images were obtained using a JEOL 7550 and cross-sectional micrographs were collected on a Hitachi 4500 SEM.

3. RESULTS AND DISCUSSION

3.1 Functional Group Inhibition Study
Before a monomeric DI for 157 nm could be synthesized, it was necessary to test the effects of different functional groups on the dissolution rate of unprotected polymer **1** and compare those rates with the dissolution rate of the polymer alone. We wanted DIs that were used at 248 and 365 nm to characterize the dissolution inhibition of polymer **1**. Three different DIs based on three different inhibiting functional groups (DIs **5-7**) were prepared and tested in polymer **1** on an equimolar loading of each DI.
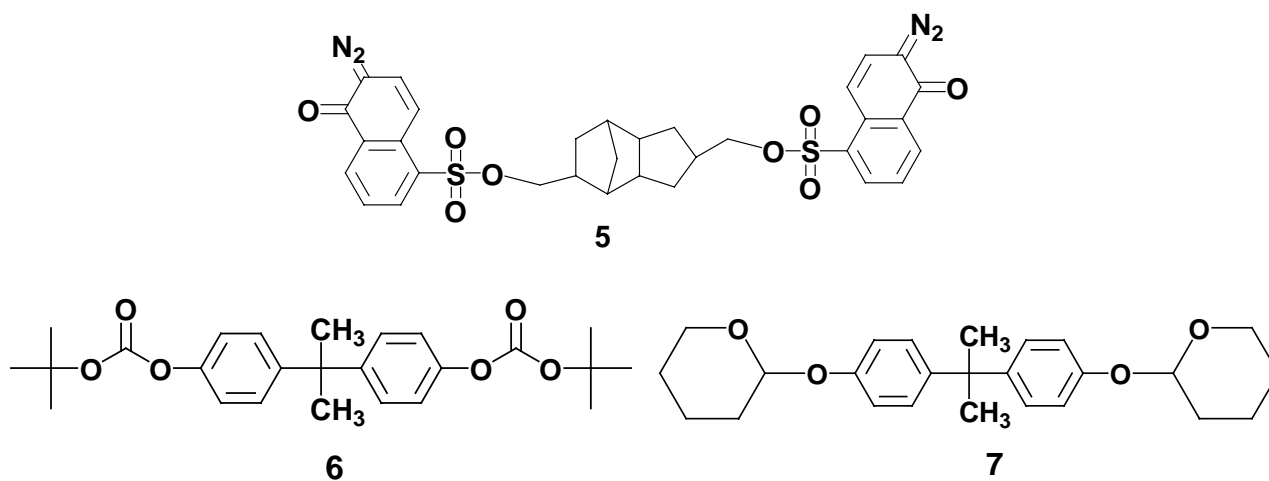
The version of polymer **1** used for these experiments dissolves at a rate greater than 320 nm/s. DI **5**, based on a sulfonate linkage, had the largest impact on the dissolution rate of polymer **1** (0 nm/s). A Meyerhofer plot[5] of DI **5** in Novolac, PHS, polymer **1** and polymer **4** was prepared (**Figure 1**).
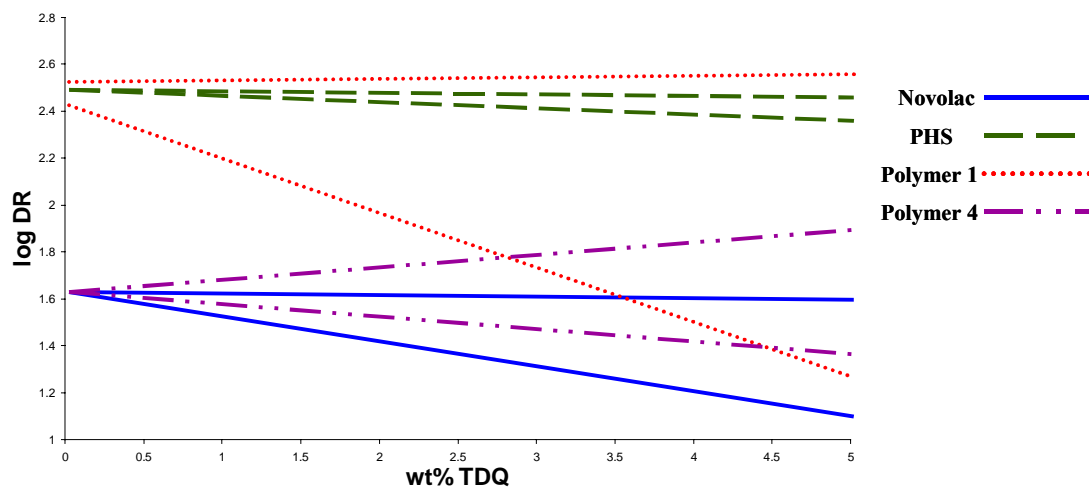

Figure 1: Meyerhofer plot of **5** in novolac, PHS, polymer **1** and polymer **4**.

DI **5** in novolac is an example of a typical I-line resist. Unfortunately, this system is opaque bellow 300 nm. PHS was basically unaffected by the addition of **5**. At 5 wt% loading of **5** in polymer **1**, two orders of magnitude difference between the exposed and unexposed dissolution rates (Δ) was achieved. Novolac, by comparison, requires around 20 wt% of **5** to achieve the same two orders of magnitude rate difference. We have found a transparent resin that has dissolution inhibition properties superior to novolac. Polymer **4** had approximately the same Δ as novolac, but the Δ is due more to acceleration of the dissolution rate after exposure that inhibition of the film before exposure. Unfortunately, **5** is too opaque for use at 157 nm, so we decided to further investigate the carbonate-based DIs. The *t*-butyl carbonate based DI **6** was also efficient at inhibiting the dissolution rate of polymer **1** (7 nm/s). A Meyerhofer Plot of **6** in novolac and polymer **1** (**Figure 2**) was prepared.
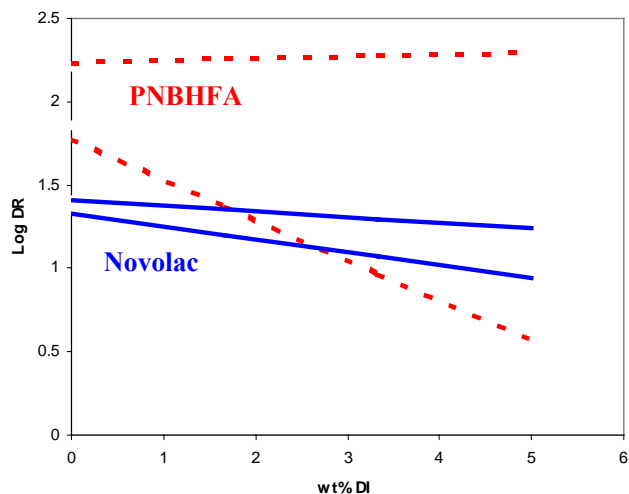

Figure 2: Meyerhofer plot of **6** in novolac and polymer **1** with 1 wt% TPSNf.

 The Δ of **6** in polymer **1** was also orders of magnitude greater than in novolac. Imaging at 248 nm using **6** in polymer **1** is shown in **Figure 3**. Unfortunately, **6** is also too opaque for use at 157 nm, however we now had an idea of how to design a DI for 157 nm. Since the acetal-based DI (**7**) had the least effect on the dissolution rate of polymer **1** (35 nm/s), no other DIs based on acetals were investigated. While all the DIs presented in the rest of this article are carbonate based, we are still investigating ways to take advantage of the inhibition afforded by sulfonate linkages.
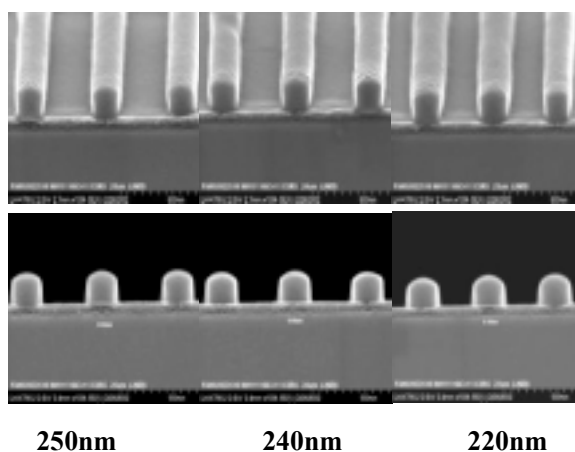

250nm   **240nm**   **220nm**

Figure 3: SEMs of polymer **1** with 10 wt% **6** and 5 wt% TPSNf at 248 nm.

3.2 157 nm Dissolution Inhibitors

The transparency and acidity afforded by the 1,1,1,3,3,3-hexafluoro-2-propanol functional group was used to synthesize a transparent analogue of **6** (**8**) for use at 157 nm. **Figure 4** shows images achieved at 157 nm by substituting the more transparent **8** for **6** in the resist formulation.
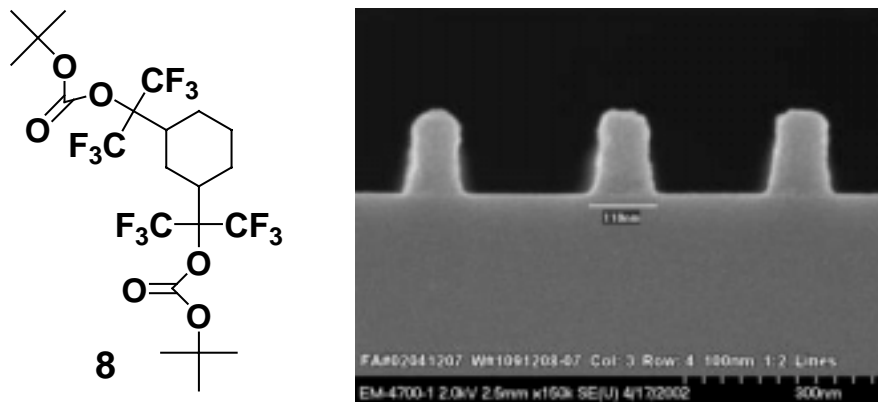

Figure 4: SEMs of polymer **1** with 15 wt% **8** and 5 wt% TPSNf at 157 nm.

In order to increase the difference between the exposed and unexposed dissolution rate, a DI with three inhibiting functional groups was synthesized (**9**). A Meyerhofer plot of **9** in polymer **1** was prepared (**Figure 5**). The Δ is greater using **9** than with any other DI investigated.
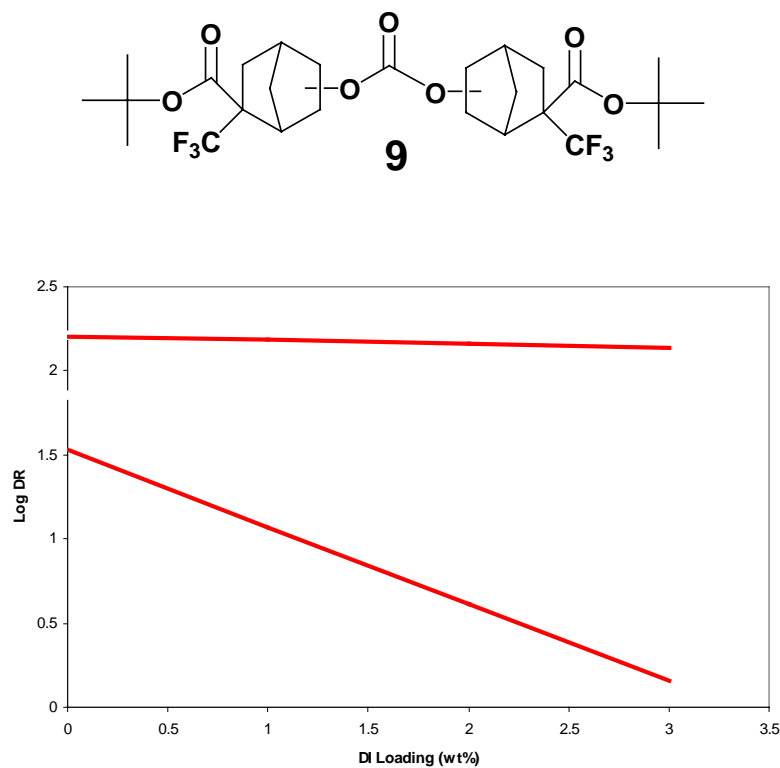

Figure 5: Meyerhofer plot of **9** in polymer **1** with 1 wt% TPSNf.

Imaging with **9** in polymer **1** was problematic. The images had severe top loss, which is an indication that the DI is not completely inhibiting dissolution rate of the film. From a 10 wt% solution in glyme, 5 wt% **9** and 5 wt% polymer **1**, was cast a film on an aluminum backed wafer. The wafer was then baked at 130 °C and reflectance IR was used to monitor the carbonyl signal intensity over time. **Figure 6** shows the carbonyl region of the IR spectrum. The spectrum shows the disappearance of both the ester and carbonate carbonyl peaks. The observed carbonyl loss was likely due to one of two reasons.
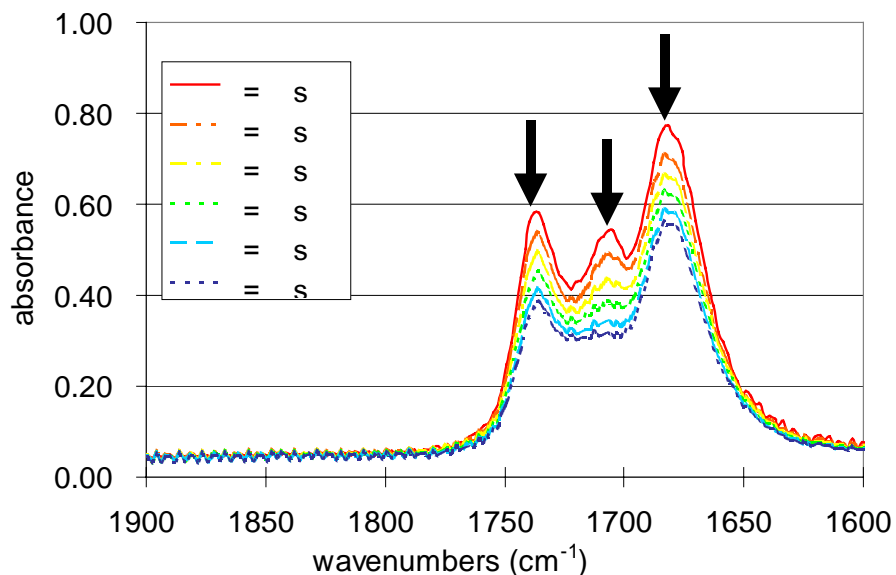

Figure 6: Carbonyl region in an IR spectrum of film of **9** in polymer **1** baked at 130 °C.

The first possibility is a carbocation could have formed by the cleavage of the carbonate-oxygen norbornene-carbon bond. Norbornenes are well known to readily form carbocations, which are stabilized through rearrangements. However, since **9** has two strong electron with drawing groups on the norbornene, which would destabilize any carbocation formation making this senario unlikely. The second possibility is that **9** is volatilizing out of the film during the bake step. Since **9** is a high molecular weight molecule, this too seems unlikely. In order to completely eliminate the possibility of carbocation formation, **10** was synthesized. The extra methylene groups in **10** remove the carbonate linkage from the norbornene, thus eliminating the possibility of forming a carbocation that is stabilized by norbornene rearrangements. A Meyerhofer plot of **10** in polymer **1** was prepared (**Figure 7**).
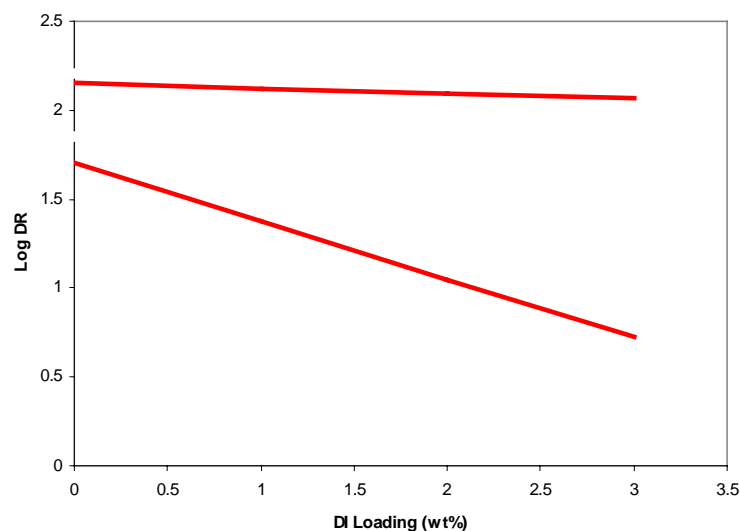

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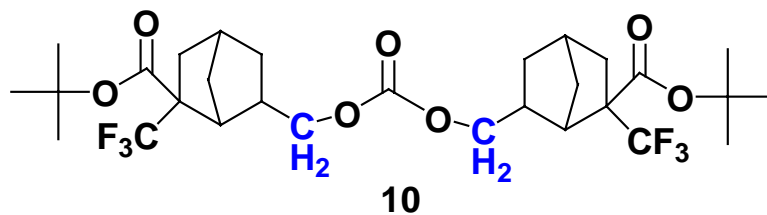
Figure 7: Meyerhofer plot of **9** in polymer **1** with 1 wt% TPSNf.

The Δ was only slightly lower than that observed with **9**. Top loss was again observed when attempting to image using **10** in polymer **1**. This observed top loss using **10** led to further experiments which showed that **9** sublimed, indicate that the imaging problems encountered are a result of the surprising inherent volatility of **9** and **10**.

3.3 PAGs as Dissolution Inhibitors

While preparing the Meyerhofer plots for DIs **6, 9** and **10**, it was observed that even at 0 wt% loading of the DI there was a difference between the exposed and unexposed dissolution rates of the films. This effect has been reported before in another resin by Ito *et al.*[4] This difference can be attributed to the TPSNf (**11**) used as the PAG in **Figures 2**, **3** and **7**. Meyerhofer plots for several PAGs were prepared. **Figure 8** compares the dissolution rates of several PAGs at 3 wt% loading in novolac, polymer **4** and polymer **1** respectively.
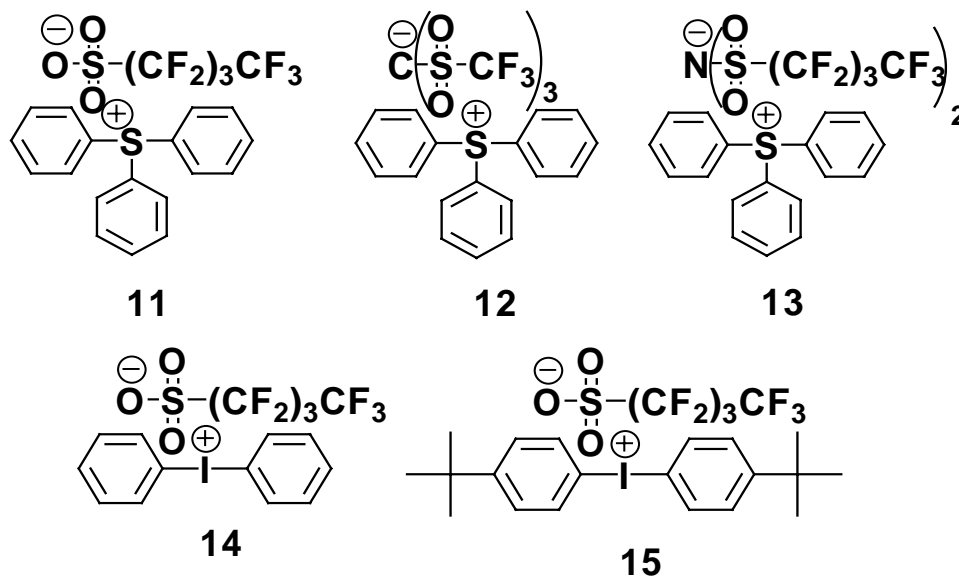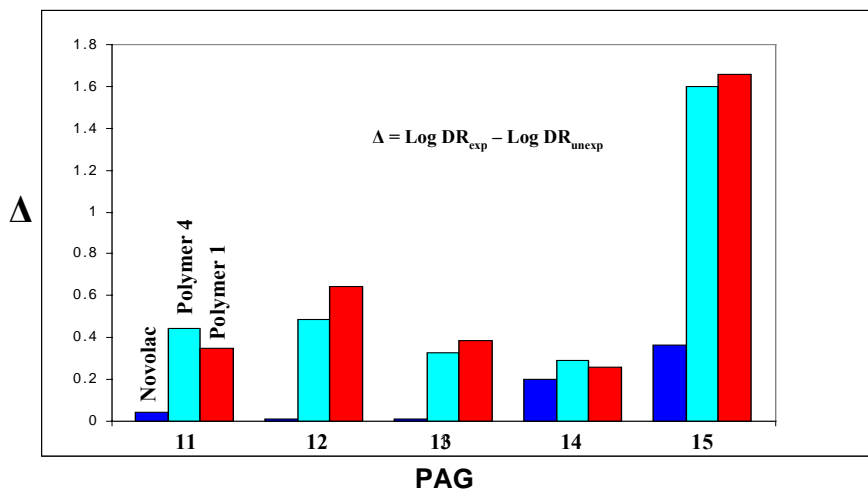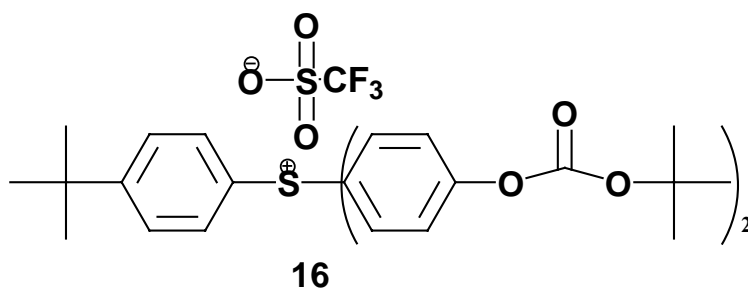
Figure 8: Comparison of PAG's Δ at 3 wt% loading.

The two important conclusions that can be drawn from **Figure 8** are: 1) all the PAGs tested had an inhibition effect on the dissolution rate of all three polymers and 2) the PAGs had different Δ values, which indicates that the structure of the PAG is important in determining a PAG's inhibition effect. PAGs **11-13** are all triphenyl sulphonium salts, however **12** had a larger Δ in both polymers **1** and **4**. Similarly, **14** and **15** are both diphenyl iodonium nonaflates, but **15** has a much higher Δ in polymers **1** and **4**. The relationship between PAG structure and inhibition properties is not fully understood. Screening of different types of PAGs is now underway in an attempt to develop a better understanding of this relationship.

Unfortunately, the iodonium salts are more highly absorbing than sulphonium salts at 157 nm. PAG **16** was synthesized in order to make a sulphonium salt with a Δ similar to that of **15**. The two *t*-boc groups should make the inhibition effect of **16** far superior to the other sulphonium based PAGs tested. The phenolic species generated after exposure should increase the base solubility of the exposed film. **Figure 9** shows that the Δ afforded by **16** is greater than **15** in both polymers **1** and **4**, and **Figure 10** shows preliminary imaging of **16** in polymer **1**.
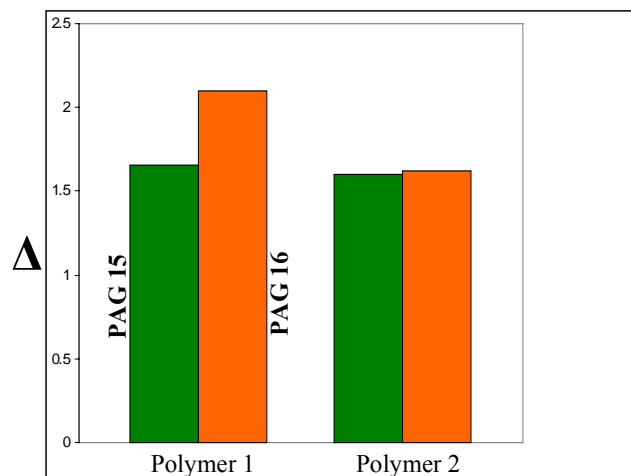

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Figure 9: Comparison of **15** and **16**'s Δ at 3 wt% loading.

The images were achieved using **16** will improve by using the corresponding nonaflate salt, which does not suffer from the volatility and increased diffusion path lenths of **16**.
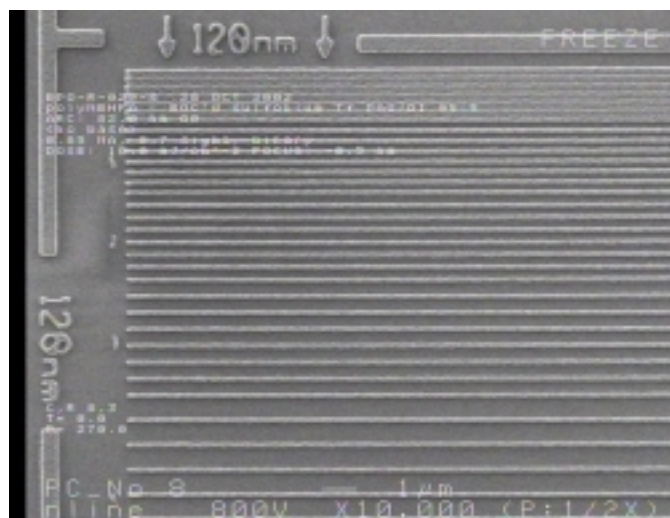

Figure 10: Top down SEM of polymer **1** with 5 wt% **16** at 157 nm.

CONCLUSIONS

PNBHFA (**1**) shows great promise as a resin for 157 nm photoresists due to its transparency and its dissolution inhibition characteristics are similar in nature, yet superior to those of novolac. Dissolution inhibitors show great promise for use at 157 nm and it was demonstrated that the new resist systems are backwards compatible to both 248 and 193 nm. The use of dissolution inhibitors with unprotected homopolymers should greatly ease resist formulation and speed development of highly transparent and etch resistant 157 nm photoresists. The volatility issues of our current DI should be easy to overcome by switching to higher molecular weight DIs with more inhibiting functional

groups. In the future we will also investigate DIs for the highly transparent Asahi polymer (**4**). We are optimistic about the possibility of a two-component resist system with PAGs that also act as dissolution inhibitors. So far all the PAGs tested have shown an effect on the dissolution rate of Novolac, PNBHFA and Asahi polymer. Investigation of the correlation between structure and dissolution inhibition of PAGs is an area of intense interest. Future work will focus on synthesis and testing of PAGs to fully determine what structure types will give the highest Δ values and higher resolution images at 157 nm. It seems clear that a viable 157 nm single layer resist can be formulated from the available matrix resins by judicious combinations of partial blocking of side chains, addition of monomeric or oligomeric DIs and functional PAGs.

ACKNOWLEDGEMENTS

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