

## Electrophilic Aromatic Functionalization of Phenolic Photoresist Polymers

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### Summary

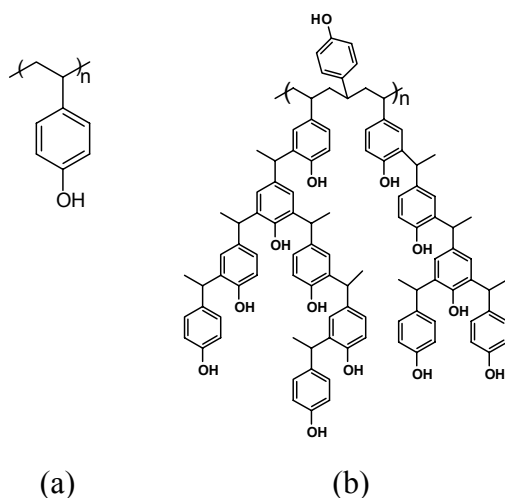
Functionalization of both linear poly(4-hydroxystyrene) (PHS) and branched poly(4-hydroxystyrene) (PHS-B) was accomplished *via* a Reimer-Tiemann electrophilic aromatic substitution reaction. Linear and branched poly(4-hydroxystyrene-*co*-5-vinylsalicylaldehyde) (pHS/5VSA and pHS-B/5VSA) copolymers were observed to undergo acid-catalyzed, novolac type self-crosslinking. Both the pHS/5VSA and pHS-B/5VSA copolymer systems possessed a lower deep ultra violet microlithographic sensitivity compared to linear PHS when formulated in negative photoresists. The sluggishness of the negative photoresists containing 5-vinylsalicylaldehyde functionalized copolymers was attributed to a combination of resonance stabilization and steric hindrance effects.

### Introduction

Development of polymers capable of efficient self-crosslinking is pivotal for paints, adhesives, structural materials, foams and thin film coating applications including microlithographic photoresists. The microlithographic process is *key* to producing miniaturize circuits and substantial continuing efforts exist to reduce the size of elements in microelectronic devices in order to provide improved performance at decreased cost. Hence, more sensitive and responsive polymer systems are required to increase the *non*-linear microlithographic response for increased memory density *via* higher contrast and decreased line width [1]. Radiation-induced covalent crosslinking is used extensively to render polymers insoluble in aqueous base developer for negative tone photoresist applications. Linear poly(4-hydroxystyrene) (PHS) (Figure 1(a)) is the archetypical polymeric component in current negative photoresists used at deep ultra-violet (DUV,  $\lambda=248$  nm) wavelengths [2-3].

Crosslinked PHS networks are preferential for negative photoresist compositions due to the polymer's desirable coating properties as well as its resistance to swelling in aqueous base which can lead to image distortion. Poly(4-hydroxystyrene) (PHS) has also been used as a model synthetic Lewis acidic material for investigating the phase behavior of hydrogen bonded polymer blends and block copolymer systems [4-6]. Branched poly(4-hydroxystyrene) (PHS-B) is patented [7-8] and uniquely produced

by DuPont<sup>®</sup> Electronic Polymers using carbocationic polycondensation copolymerization of 2- and/or 4-hydroxyphenylmethylcarbinol in the presence of oligomeric linear PHS [9] (Figure 1(b)). PHS-B can be tailored to contain a certain concentration of linear PHS on average and its structure is intriguing due to the partial styrenic backbone character as well as novolac-type branches. Hence, the structure of PHS-B is effectively intermediate between linear PHS and a completely branched novolac resin. PHS-B has been shown to possess a thermal resistance and dissolution rate in aqueous base that can be tailored to lie intermediate between linear PHS and conventional novolac binders [7-9].



**Figure 1.** Chemical repeat structure of (a) linear poly(4-hydroxystyrene) (PHS) and (b) branched poly(4-hydroxystyrene) (PHS-B)

Synthetic placement of a *non*-interacting moiety that is merely sterically hindering, such as an alkyl group, *ortho* to the phenolic hydroxyl group in both PHS and PHS-B would allow investigation of the interplay between local steric as well as global macromolecular architectural and conformational effects. Nevertheless, electrophilic aromatic substitution of a Lewis basic group capable of interacting *via* hydrogen bonding with the *ortho*-phenolic hydroxyl group would allow additional investigation of the intriguing thermodynamic competition between chelation (*intra*-monomer), *intra*-molecular and *inter*-molecular hydrogen bonding. A variety of electrophilic aromatic substitution reactions are capable of placing a complimentary hydrogen bonding (*i.e.* Lewis basic) functional group *ortho* to the polymer's phenolic hydroxyl group [10]. Nevertheless, judicious choice of synthetic transformation was required due primarily to the selective solubility of 4-hydroxystyrene based polymers in either aqueous base or polar organic solvents. The Reimer-Tiemann formylation reaction involving a reactive dichlorocarbene species created from heating chloroform ( $\text{CHCl}_3$ ) in concentrated aqueous base was chosen [11]. Formylation *ortho* to the  $-\text{OH}$  group on the PHS aromatic ring was used to produce a moiety that was not only sterically hindering but also Lewis basic, capable of hydrogen bonding and potentially reactive for covalent, acid-catalyzed self-crosslinking in negative photoresist formulations [2-3].

## Experimental

### *Materials*

Reagent grade chloroform, propylene glycol methyl ether acetate (PGMEA), and ethyl lactate solvents as well as sodium hydroxide and concentrated sulfuric acid were obtained from Aldrich Chemical Company (Milwaukee, WI) and used as received. Perfluoro-1-octane sulfonic acid (PFOS) was purchased from TCI America (Portland, OR) and used as received. Poly(4-hydroxy styrene) linear electronic grade (PHS;  $M_w = 8000$ ,  $DP = 70$ ;  $M_w/M_n = 2.24$ ;  $T_g = 171^\circ\text{C}$ ) and poly(4-hydroxystyrene) branched grade (PHS-B;  $M_w = 4500$ ;  $DP = 3$ ;  $T_g = 113^\circ\text{C}$ ) were donated by DuPont Electronic Polymers (Dallas, TX) and used as received.

### *Infrared Spectroscopy*

All infrared spectra were recorded on either a Thermo Nicolet® Avatar 360 E.S.P. or Nicolet® Impact 400 Fourier transform infrared spectrometer operating at a resolution of  $2\text{ cm}^{-1}$  in transmission using dried polymer samples crushed in infrared grade potassium bromide (KBr).

### *Elemental Analysis*

Elemental analyses for carbon (C), hydrogen (H) and nitrogen (N) were done in the microanalytical laboratory of the Department of Chemistry at Michigan State University, East Lansing. CHN as well as elemental analyses for chlorine (Cl) and oxygen (O) were also done at the QTI Company (Whitehouse, NJ).

### *NMR Spectroscopy*

High resolution  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of 30% (wt/vol) polymer solutions in either acetone- $d_6$  or DMSO- $d_6$  solvent were recorded on a 500 MHz Varian FT-NMR spectrometer operating at  $21^\circ\text{C}$  using at least 128 and 4000 transients respectively.

### *Reimer-Tiemann Reaction*

In a typical reaction, a 3-necked 500 ml flask was charged with 20 g of either PHS or PHS-B and 100 ml of 25% (wt/vol) NaOH (aq). The homogeneous red-brown solution was heated to  $70^\circ\text{C}$  and 50 ml of  $\text{CHCl}_3$  was subsequently added dropwise over a period of 45 minutes while stirring. The solution was gently refluxed at approximately  $70^\circ\text{C}$  for an additional 3 hours and then gradually cooled to  $10\text{--}15^\circ\text{C}$  using an ice water bath. The polymer was precipitated by slow addition of 6M  $\text{H}_2\text{SO}_4$  (aq) to  $\text{pH} = 1\text{--}2$  while stirring. The tan colored polymer precipitate was filtered, washed with DI water and dried in air. The solid polymer was purified by slowly pouring a 20% (wt/vol) solution of the dried precipitate in methanol into at least a 20-fold excess of rapidly stirred DI water. The resulting polymer precipitate was filtered, washed with DI water, dried *in vacuo* and denoted as either poly(4-hydroxystyrene-co-5-vinyl salicylaldehyde) (pHS/5VSA) or branched poly(4-hydroxystyrene-co-5-vinyl salicylaldehyde) (pHS-B/5VSA) respectively. *Structural elucidation of pHS/5VSA*: IR (KBr,  $\text{cm}^{-1}$ ): 3407 (vs, br), 2963 (s), 2927 (s), 2870 (s), 1652 (vs), 1612

(s), 1511 (s), 1456 (s), 1374 (m), 1268 (m), 1214 (m), 1172 (m), 832 (w);  $^1\text{H-NMR}$  (acetone- $d_6$ , TMS): 10.82 $\delta$ , 9.76 $\delta$ , 8.05 $\delta$ , 6.62 $\delta$ , 3.04 $\delta$ , 1.90 $\delta$ , 1.49 $\delta$ , 0.60 $\delta$ .

#### *Dissolution Rate Measurement*

Dissolution rate was measured on approximately 3  $\mu\text{m}$  thick films using an aqueous solution of 0.26 M tetramethylammonium hydroxide (TMAH) on a single point/channel dissolution rate measurement (DRM) laser interferometry apparatus [12]. The DRM laser interferometry apparatus was equipped with a Melles Griot<sup>®</sup> HeNe laser ( $\lambda=632.8$  nm, 1 mW max), and a model 101C transimpedance amplifier. Polymer films for DRM were spun from 25% (wt/wt) solutions in PGMEA onto untreated 4 inch diameter silicon wafers at 800 Hz for 30 seconds and soft baked for 2 minutes at 130°C. Film refractive index was measured using a Metricon<sup>®</sup> PC-2000 Prism Coupler (prism crystal code=1023) and film thickness was measured using a Nanometrics<sup>®</sup> model 210 Nanospec/AFT film thickness microscope system with a 10x objective lens.

#### *Thermal Analysis*

Thermal analysis was conducted on a TA Instruments model 2920 Modulated Differential Scanning Calorimeter (DSC) using a heating rate of 20°C/minute under  $\text{N}_2$  (g). All DSC samples were equilibrated at 60°C, heated to 280°C and held isothermally at 280°C for 1 minute. DSC cooling was accomplished using air. All polymer samples were cycled (heat-cool) at least three times and the glass transition temperatures ( $T_g$ ) were determined from the third heating (unless otherwise stated) using the mid-point at half height between the transition's extrapolated onset and endpoint. Curing studies were conducted using multiple (n) heat-cool cycles. The temperature range of the glass transition for the  $n^{\text{th}}$  heating cycle ( $\Delta T_{g,n}$ ) was determined by taking the temperature difference between the extrapolated onset and endpoint. The magnitude of the glass transition for the  $n^{\text{th}}$  heating cycle ( $\Delta Q_n$ ) was determined by calculating the difference between the heat flow (W/g) at the glass transition endpoint and onset on the DSC thermogram.

#### *Deep Ultra-Violet (DUV) Microlithography*

Negative photoresists were formulated using either linear PHS, pHS/5VSA or pHS-B/5VSA with a photoacid generator (PAG), base, surface leveling agent (SLA) and either with or without a tetrafunctional cross-linking molecule in a PGMEA/ethyl lactate solvent mixture. A single puddle of photoresist solution was spun to produce 300 nm film thickness on a 12 inch diameter silicon wafer followed by soft bake. Deep-ultraviolet (DUV,  $\lambda=248$  nm) exposure dose (E) was surveyed on a stepper from 1-100  $\text{mJ}/\text{cm}^2$  in steps of 1  $\text{mJ}/\text{cm}^2$  and contrast curves were obtained to determine the critical exposure dose ( $E_{\text{gel}}$ ).

#### *Molecular Modeling*

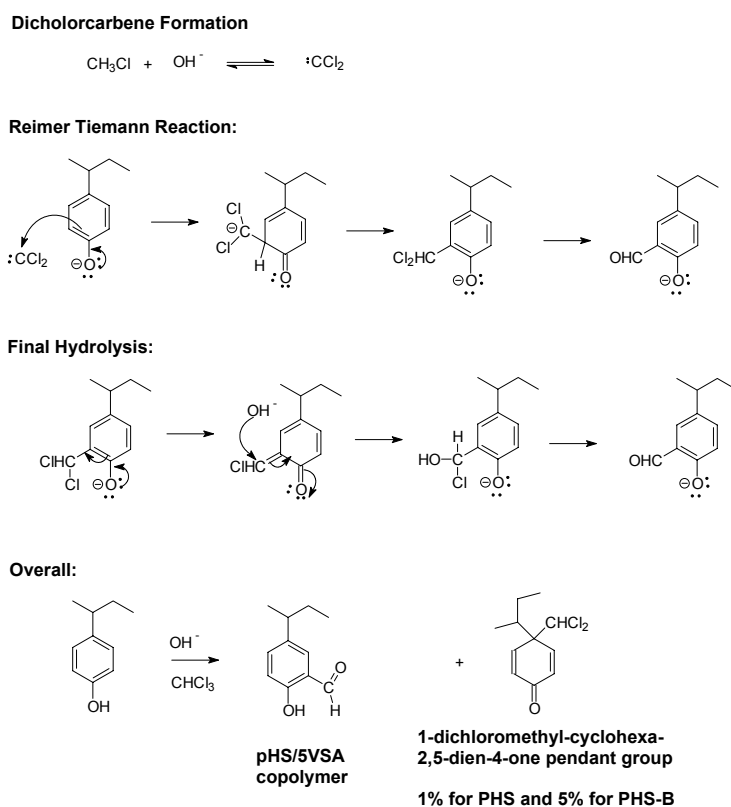
Molecular mechanics energy minimization for chemical structures was accomplished using either Spartan'04<sup>®</sup> for Windows (Wavefunction, Inc., Irvine, CA), with a molecular mechanics force field (MMFF94) or CaChe<sup>®</sup> (Fujitsu Ltd., Chiba City,

Japan) version 6.1 with a molecular mechanics force field (MM2) [13]. Partial charge approximation was accomplished using either Spartan'04<sup>®</sup> or CaChe<sup>®</sup> following *ab initio* energy minimization for equilibrium geometry *via* a Hartree-Fock (HF) wavefunction with a 6-31G\* basis set.

## Results and Discussion

### Reimer-Tiemann Functionalization

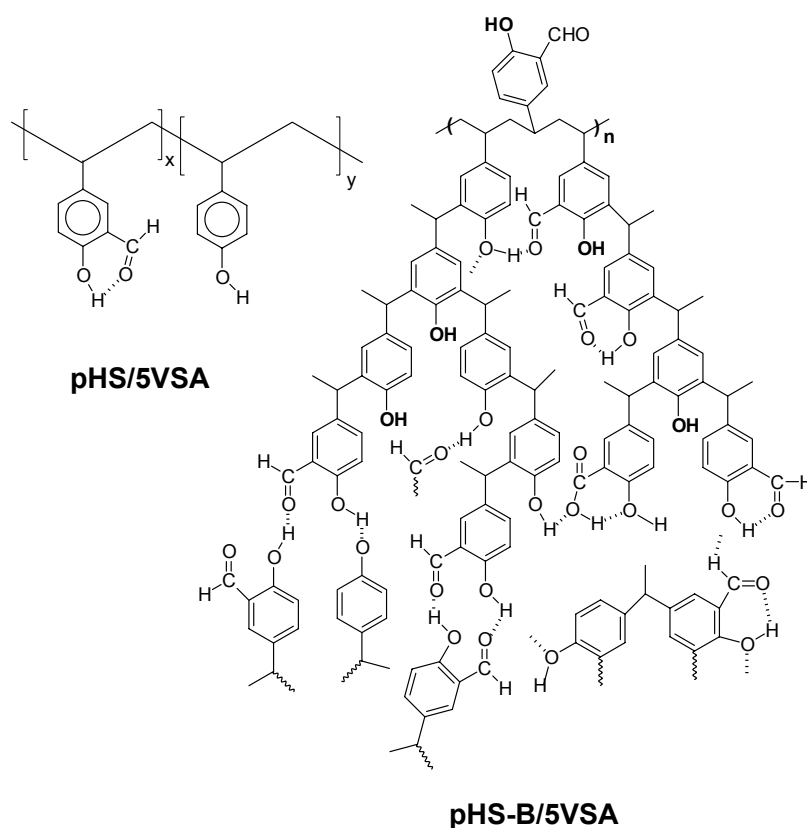
Novel poly(4-hydroxystyrene-*co*-5-vinyl salicylaldehyde) (pHS/5VSA) and branched poly(4-hydroxystyrene-*co*-5-vinyl salicylaldehyde) (pHS-B/5VSA) copolymers were synthesized as shown in Scheme 1.



**Scheme 1.** Reimer-Tiemann electrophilic aromatic substitution reaction mechanism with PHS backbone

The structures of these new copolymer systems with potential hydrogen bonded chelation (*intra*-monomer) as well as *intra*-molecular and *inter*-molecular hydrogen bonding interactions are illustrated in Figure 2. Electrophilic aromatic substitution on both PHS and PHS-B allowed tailored adjustment of the unhindered, partially hindered (*ortho*-substituted) and fully hindered (*ortho,ortho*-disubstituted) phenolic

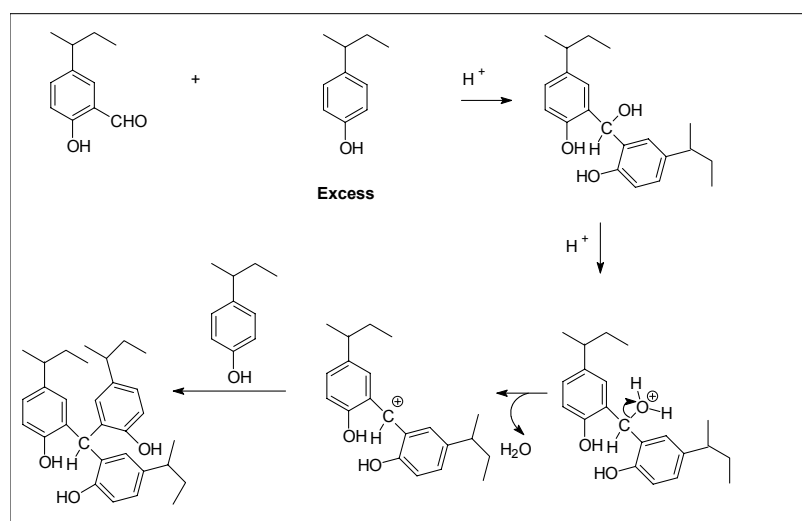
moiety proportions. Reimer-Tiemann formylation reaction produced 30 and 25 mole% *mono*-formylation *ortho* to the phenolic hydroxyl in PHS and PHS-B respectively from both  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR as well as CHN elemental analysis. A small amount (1 mole% for PHS and 5 mole% for PHS-B) of *abnormal* Reimer-Tiemann 1-dichloromethyl-2,5-cyclohexadien-4-one pendant *side*-product was observed using elemental analysis for carbon, hydrogen and chlorine (Scheme 1) [10-11]. For PHS-B it was envisioned that exterior branch aromatic rings would be preferentially formylated over sterically hindered interior phenolic rings [14]. In addition, the potential for autooxidation of the 5-vinylsalicylaldehyde groups to 5-vinylsalicylic acid was noted for pHS-B/5VSA presumably due to oxidized quinoidal structures within the virgin PHS-B sample (Figure 2). Nevertheless, no significant autooxidation was observed from the Reimer-Tiemann reaction on linear PHS to produce pHS/5VSA.



**Figure 2.** Chemical repeat structure for the pHS/5VSA and pHS-B/5VSA copolymer systems

### Crosslinking Chemistry and Dissolution Rate

A dissolution rate (DR) of 2400 angstroms/second was noted for pHS/5VSA with 70/30 mole% composition whereas the DR decreased to 17 angstroms/second with merely 5 wt% added PFOS in 3  $\mu\text{m}$  thin films crosslinked at 130°C for 2 minutes. Novolac *trifunctional* crosslinking chemistry was proposed to ultimately produced methine (CH) bridges *via* an aldehyde-phenol *intermolecular* reaction with a benzylic alcohol intermediate as shown in Figure 3.



**Figure 3.** Acid-catalyzed novolac-type crosslinking of pHS/5VSA and pHS-B/5VSA copolymer architectures *via* reaction of the aldehyde and phenolic moieties

Covalent crosslinking was observed for both the pHS/5VSA and pHS-B/5VSA systems when heated in the presence of either 5-10% (wt/wt) PFOS catalyst added to copolymer samples purified by reprecipitation from methanol into water. Facile thermal crosslinking was also noted for pHS/5VSA and pHS-B/5VSA samples yet to be reprecipitated containing catalytic quantities of residual  $\text{H}_2\text{SO}_4$  coordinated to the copolymer through hydrogen bonding. Experimental evidence for crosslinking catalyzed by residual  $\text{H}_2\text{SO}_4$  included a gradual monotonic increase of the glass transition temperature ( $T_g$ ), a broadening of  $\Delta T_g$  as well as a suppression of the glass transition magnitude ( $\Delta Q$ ) upon the thermal cycling of PHS/5VSA (70/30) as illustrated in Table 1. Broadening of  $\Delta T_g$  (Table 1) indicated *non-homogenous* acid-catalyzed *self*-crosslinking of the copolymer (*i.e.* no added multi-functional small molecular weight molecule) whereby domains containing a gradient in crosslink density ( $\rho_c$ ) were created.

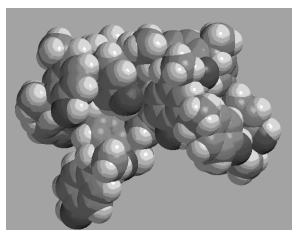
Table 1. Thermal analysis of the PHS/5VSA (70/30) copolymer system crosslinked within the DSC as catalyzed by residual H<sub>2</sub>SO<sub>4</sub> for the n<sup>th</sup> heating cycle

n <sup>th</sup> heating cycle	T <sub>g,n</sub> (°C)	ΔT <sub>g,n</sub> (°C)	ΔQ <sub>n</sub> (mW/g)
1	174	13	90
2	199	21	83
3	212	25	81
4	222	26	72
5	228	27	58
6	231	28	45

The crosslinking reaction was also characterized by following the disappearance of the strong infrared 5-vinylsalicylaldehyde carbonyl band centered at 1650 cm<sup>-1</sup> upon heating pHS/5VSA or pHS-B/5VSA in the presence of catalytic amounts of either added PFOS or residual H<sub>2</sub>SO<sub>4</sub>. Hence, both the pHS/5VSA 70/30 and pHS-B/5VSA 75/25 copolymer systems displayed acid-catalyzed crosslinking and potential use as negative tone photoresist polymers.

#### *Micro lithographic Negative Photoresist*

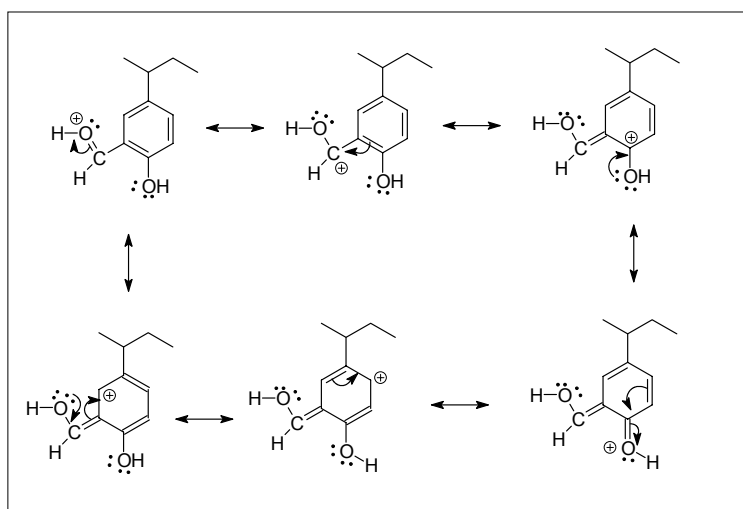
Both the pHS/5VSA 70/30 and pHS-B/5VSA 75/25 systems were observed to be quite sluggish compared to the linear PHS/*tetra*-functional crosslinking molecule system when formulated with a PAG and lithographically characterized at λ=248 nm (DUV). Formulations containing either pHS/5VSA 70/30 or pHS-B/5VSA 75/25 were not observed to effectively crosslink with a DUV exposure dose of up to 100 mJ/cm<sup>2</sup>. When a *tetra*-functional crosslinking molecule was included within formulations containing equal amounts of either linear PHS, pHS/5VSA 70/30 or pHS-B/5VSA 75/25, the critical dose (E<sub>gel</sub>) for linear PHS and pHS/5VSA 70/30 were observed to be 3.3 mJ/cm<sup>2</sup> and 10 mJ/cm<sup>2</sup> respectively. The pHS/5VSA 70/30 system was about 3 times slower than linear PHS when formulated in negative tone photoresists and tested at λ=248 nm. Furthermore, merely a faint latent image was observed for pHS-B/5VSA 75/25 when the small molecular weight crosslinking molecule was included. The slower speed of the pHS/5VSA system was attributed initially to the increasing steric hindrance from *ortho*-aromatic functionalization. In addition, the sluggish behavior of the resist containing pHS-B/5VSA was attributed to the relatively dense packing within the branched material inhibiting crosslinking (Figure 4).



**Figure 4.** Molecular mechanics energy minimized structures for PHS-B indicating a relatively dense, spherical globule whereby the phenolic moieties within the PHS-B interior appear particularly sterically *screened* compared to the relatively *unhindered* phenolic moieties in linear PHS



Very small deviations in electronic charge on the phenolic oxygen atom were observed in preliminary *ab initio* molecular modeling calculations on 5-ethylsalicylaldehyde compared to 5-ethylphenol. The low sensitivity and sluggish nature of the formylated copolymers was prospectively attributed mainly to local steric hindrance of the aromatic aldehyde groups placed *ortho* to the phenolic hydroxyl moieties. However, significant resonance stabilization of the protonated 5-vinylsalicylaldehyde moiety during photolithography was postulated as shown in Figure 5.



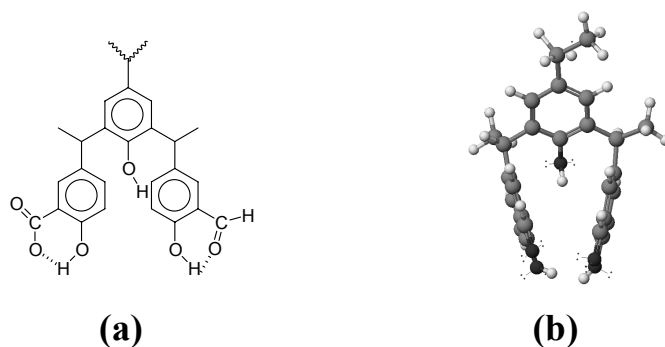
**Figure 5.** Resonance contributors of the polymeric 5-vinylsalicylaldehyde repeat unit protonated intermediate

Hence, the reactivity of the protonated 5-vinylsalicylaldehyde intermediate (Figure 5) was postulated to be less than conventional acid-catalyzed phenol-formaldehyde novolac systems due in part to steric hindrance as well as the following two related electronic effects. (1) The availability of the cyclohexadienyl carbocationic resonance contributors effectively decreasing the electron deficiency of the carbonyl carbon in addition to (2) the electron withdrawing effect of the aldehyde substituent decreasing the Lewis basicity of the aromatic ring (Figure 5). Thus, despite the relatively small oxidation susceptibility of the 5-vinylsalicylaldehyde functionality, the lithographic sensitivity of both the pHS/5VSA 70/30 and pHS-B/5VSA 75/25 salicylaldehyde based negative photoresists presented here were much lower than PHS copolymers containing either *ortho*-benzylic alcohol functionalities, synthesized by hydroxymethylation of the polymer [2-3], or other negative lithographic systems based on electrophilic aromatic substituted PHS [15-17].

## Conclusion

An electrophilic aromatic substitution reaction was used to synthetically insert a hydrogen bonding aldehyde moiety *ortho* to a fraction of the phenolic groups in both linear and branched poly(4-hydroxystyrene). Novel linear and branched poly(4-hydroxystyrene-*co*-5-vinyl salicylaldehyde) copolymers with 70/30 and 75/25 molar

compositions respectively performed sluggishly in DUV microlithography compared to linear PHS. This was attributed to resonance stabilization and steric hindrance from *ortho* substituents and macromolecular branching. Synthesis of branched and linear poly(4-hydroxystyrene-*co*-5-vinyl salicylaldehyde) has prompted further investigation of their thermal properties, acid-catalyzed curing kinetics as well as the interplay between local steric screening and macromolecular architectural conformation. Furthermore, linear poly(4-hydroxystyrene-*co*-5-vinyl salicylaldehyde) has provided entree into investigating an intriguing thermodynamic competition between polymeric *inter*-molecular, *intra*-molecular and *intra*-monomer (chelation-type) hydrogen bonding. Preliminary molecular mechanics modeling of the pHS/5VSA system has indicated a strong propensity for *intra*-monomer (aldehyde-hydroxyl) hydrogen bonded chelation with a hydrogen bond distance of  $2.1 \pm 0.1$  angstroms (Figure 6(a) and 6(b)) in addition to *intra*-molecular hydrogen bonding.



**Figure 6.** (a) Triphenyl subunit within the pHS-B/5VSA repeat structure with hydrogen bonded chelation interaction noted. (b) Equilibrium geometry of a selected triphenyl subunit within PHS-B repeat structure energy minimized using molecular mechanics (MM2) force field (CaChe<sup>®</sup>)

Nevertheless, it should be noted that facile thermal crosslinking has made on-going miscibility/hydrogen bonded complexation studies of blends containing either PHS/5VSA or PHS-B/5VSA and poly(2-vinyl pyridine) (P2VP) Lewis basic *homo*- and *co*-polymers increasingly challenging.

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## References

1. Moreau WM (1987) *Semiconductor Lithography: Principles, Practices and Materials*. Plenum Press, New York.
2. Lee SM, Frechet JMJ, Willson CG (1994) *Macromolecules* 27:5154
3. Lee SM, Frechet JMJ (1994) *Macromolecules* 27:5160
4. Moskala EJ, Varnell DF, Coleman MM (1985) *Polymer* 26:228

5. Dai K, Kramer EJ, Frechet JMJ, Wilson PG, Moore RS, Long TE (1994) *Macromolecules* 27(18):5187 (1994)
6. Xu Z, Jandt KD, Kramer EJ, Edgecomb BD, Frechet JMJ (1995) *J Polym Sci, Polym Phys* 33:2351
7. Sounik J (1996) US Patent 5,554,719
8. Sounik J (1996) US Patent 5,565,544
9. Sounik J, Vicari R, Lu PH, Kokinda E, Ficner S, Dammel RR (1996) *SPIE Advances in Resist Technology and Processing XIII* 2724:196
10. Smith MB and March J (2004) *Advanced Organic Chemistry: Reactions, Mechanisms and Structure* 5<sup>th</sup> Edition. Wiley-Interscience, New York
11. Wynberg H, Meijer EW (1982) *Organic Reactions* 28:1
12. Reiser A, (1989) *Photoreactive Polymers: The Science and Technology of Resists*. Wiley, New York
13. Allinger NL (1977) *J Am Chem Soc* 99:8127
14. Pruthikul R, Coleman MM, Painter PC, Tan NB (2001) *J Polym Sci, Polym Phys* 39:1651
15. Beck B, Allen RD, Tweig RJ, Willson CG, Matuszczak S, Stover NHL, Frechet JMJ (1989) *Polym Eng Sci* 29(14):960
16. Frechet JMJ, Matuszczak S, Lee SM, Fahey J, Willson CG, Frechet JMJ (1992) *Polym Eng Sci* 32(20):1471
17. Stover HDH, Matuszczak S, Willson CG, Frechet JMJ (1991) *Macromolecules*, 24(8):1741