Trans. Nat. Acad. Sci. Technol. 14:149-166.1992

MODIFICATION OF CONDENSATION POLYMERS FOR SOFT X-RAY LITHOGRAPHY

by

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ABSTRACT

The semiconductor industry has steadily moved towards a continuous reduction in circuit size. The development of microlithography and synchrotron technologies have pushed the production of devices with feature sizes as small as a micron or less. The processing of this new generation of integrated circuits (VLSI) has opened up a new challenge in all areas of the microelectronic processing. This research deals with the preparation of photoresists sensitive enough to soft x-ray and at the same time resistant enough to dry etching processes.

Poly (arylene ether) sulfones belong to a group of an all-aromatic condensation polymer which has been found to be resistant to conditions of dry etching processes. The sensitivity of these polymers to x-ray was improved by the modification of sulfones through the introduction of silyl groups.

1. Introduction

The growth of polymer science and technology in the last 50 years has been phenomenal. Advances in the field of natural polymers such as celluloses, proteins, starches, rubbers, gums and their derivatives have led to a better understanding of the functions of these polymers in animals and plants. As the needs of mankind increased and became more sophisticated, these natural polymeric materials were augmented by synthetic polymers. Synthetic polymers may be rigid, semirigid or soft. Based upon their specific frameworks, they may be used as fibers, thermoplastics, or elastomers. The ease of synthesis and extended application of synthetic polymers has allowed the production of synthetic materials to dwarf the production of natural polymers. In this electronic age, synthetic polymers have become an integral part of both simple and intricate materials (43), such

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as membranes, foams, medicinals, conductors, insulators, fibers, and films, which are required either in mundane day-to-day activities or in the operation of highly sophisticated devices. The quality of life would never be as good without them.

To further enhance and improve the properties of commercially available polymers, physical and chemical modifications of polymers are performed. This art of modifying polymers for a specific purpose has now been elevated to a science which requires extensive technical skills, since the scope of polymer modifications cuts across the traditional boundaries of both applied and basic sciences. The need to duplicate and to improve the properties of natural materials has always been the motivation in the preparation and modification of synthetic polymers.

Reactions of macromolecular precursors are often the key step in the synthesis of sophisticated materials. Applications of these materials include: linear or crosslinked polymeric reagents and catalysts (20, 28), synthetic membranes, polymers with enzyme-like properties (24, 45), polymeric drugs (3), resins, and photoresists. An active area of research in microelectronic technology is the use of polymers as photoresists for lithographic purposes. Lithography is based on radiation-induced chemical changes in photosensitive polymeric films, known as photoresists. Photoresists are materials that undergo chemical changes upon exposure to radiation. Exposure to radiation can either lead to degradation or crosslinking of the polymeric chains. Degradation of polymeric chains increases solubility of the polymer in a given solvent (positive resist), while crosslinking decreases solubility of the polymer (negative resist). In addition to applications in resist technology, polymers are used as materials for intermetallic dielectrics and packaging of integrated circuits. The ease of processing, light weight and durability of polymers as dielectrics and packaging materials have allowed them to replace ceramics for these applications. Related areas of potential polymer applications which are currently under active research are as matrices for optical storage, semi-conducting and conducting organic substrates, and optical analogs of active electrical elements for computers (46).

Device miniaturization has always been the aim of the integrated circuit industry. Achievement of this aim has led to the development of the small-scale (SSI), medium scale (MSI), large scale (LSI), very large scale (VLSI), and ultra large scale (ULSI) integrated circuit boards. ULSI packs as much as 10^5 or more components per chip. The key to further miniaturization of integrated circuits can be narrowed down to the wavelength of the energy used in exposure techniques.

At present, conventional photolithography used to generate high resolution IC's for commercial purposes utilizes 365-436nm UV radiation (42). Typical critical geometries are 2 to 3 µm for most devices in production, while in state-of-the-art processes 1.25 to 1.5 µm features are common (24). As the state-of-the-art shifts towards the sub-micron level (ULSI), alternative photolithographic approaches are needed to satisfy the demand for higher resolution, higher aspect ratio and smaller linewidth variations. Technology on deep UV systems with resolution

capability of 0.45 μm will be available in the production line by either mid or late 1990 (29). E-beam and X-ray lithography are considered to play more significant roles in the production of devices with feature size of 0.25 μm or less by the end of the century (53). As the shift from the convention UV towards other photolithographic technologies occurs, demand for alternative materials which can be used as masks, substrates, photoresists, and contrast enhancement substances will follow. A majority of experts in this field believe that an alternative' to optical lithography is the only way to a sub-micron linewidth.

X-ray lithography is a relatively new experimental technique aimed at achieving higher resolution. Advantages of this technique over optical lithography are as follows: the ability to achieve finer resolution than optical method, a higher tolerance to defects caused by organic dust particles, less stringent processing requirements, and the ability to achieve linewidth less than 0.25 μm 1. Major practical problems of x-ray lithography which have to be resolved are high costs, development of x-ray sensitive photoresists, and mask fabrication.

Organic resists in photolithography can be used in either single or multicomponent processes. Regardless of exposure technology used, the role of polymeric resists is twofold. First, it must be radiation-sensitive so it can form a latent image of the circuit pattern in the mask. Second, the areas of resist remaining after development must be able to protect the underlying substrate during subsequent processing. Subsequent processing of photoresists could involve wet or dry treatment. Wet processing involves the use of solvents, whereas dry processing utilizes either plasma or reactive ions to vaporize the exposed resists.

A study (56) suggested that the basic radiation chemistry in electron lithography can be applied to x-ray lithography, e.g., resists that are sensitive to electron beams would respond the same way to x-rays. Although this study showed a strong correlation between sensitivity of resist systems to both types of exposures, the resist sensitivity was insufficient for practical x-ray lithographic applications. The best approach to improve sensitivity is to enhance the absorption of x-rays in the resist either by inclusion of heavy metal atoms or the incorporation of atoms such as chlorine (49), sulfur (50), fluorine (22), bromine (51), and silicon (52).

State-of-the-art technology requires resolution patterns that can be generated only in thin layers. Attempts to generate submicron patterns with single-layer resists are hindered by reflectivity, back scatter, low aspect ratios, and with uneven topography. These difficulties can be resolved by using multi-level resists (MLR) (27). MLR consists of either double layer (bi-level) or triple layer (tri-level) polymeric coatings. Bi-level resists consist of a planarizing layer and thin imaging top layer, while the tri-level configuration introduces an additional layer between the imaging and planarizing layers.

The shift towards multi-level processing requires increased use of dry developing and etching processes, (36) such as plasma or reactive ion etching. Dry developed resists are not subject to pattern distortion induced by polymeric swelling or shrinking which accompanies solvent development of resists. Similarly, dry

etching processes are not subject to typical isotropic profiles that are usually formed when wet etching techniques are used. Thus, our initial research focus is the development of commercially viable polymeric resists which are both sensitive to x-rays and resistant to plasma or reactive ion etching (RIE).

Polymers have always been used as resist materials for integrated circuit fabrication. Optically sensitive polymers which are currently used for commercial purposes are neither sensitive enough towards x-ray radiation nor stable enough towards plasma or RIE to be used. Research has focused on a group of organometallic polymers containing Si due to their potential for bi-level processing and resistance to RIE. The majority of new silicon-containing materials have silicon incorporated in the polymer backbone, such as the polysiloxanes (47, 48) and polysilanes (32). Incorporation of the silicon in polymers increases significantly the resistance of polymers to plasma or reactive ion etching. Some of the disadvantages of this approach are reduction in photo-sensitivity, lowering of Tg and increased hydrophobicity of the polymer layers. Poly (olefin sulfones) are considered to be the most sensitive e-beam resists (50). The first self-developing resist used in e-beam lithography (5) was poly (1-butene sulfone). Its application in X-ray lithography is limited, however, due to a low resistance to various plasma environments. A study done on the incorporation of silicon-containing moieties into the chain of poly (1-butene) sulfone showed a dramatic increase of resistance of the polymer in O_2 RIE environment (6). Clearly, facile incorporation of silicon substituents is a key requirement for useful barrier polymers.

Poly (arylene ether) sulfones are used commercially as engineering resins (21). These polymers, commonly known as "polysulfones" were first introduced in 1965 as a component of electronic and electrical systems (15). These polymers are tough, rigid materials with good mechanical properties over a wide temperature range (41). They are used primarily for applications that require resistance to heat and radiation degradation, such as appliances and electronic parts, films, slabs, reinforced copper clad laminates for printed wiring boards, and as parts of spacecrafts.

2. Approaches to Synthetic Silylation of Poly (arylene ether) sulfones.

2.1 Silylation by Directed Lithiation

Silyl groups were first used for the preparation of volatile derivatives for gas chromatographic purposes. Their roles as protecting agents, precursors in synthetic preparations, and other technological applications have driven the development of a wide variety of reagents and procedures for introducing silicon functional groups; initially on heteroatoms and eventually on suitably activated carbon atoms. The facile transfer of silyl groups has led to a new type of polymerization, i.e. group transfer polymerization, (GTP) (55). An exponential growth of patents and literature on silicon has accompanied an ever evolving list of commercial applications of silicones.

Although the last decade showed an extraordinary growth in this area, the discovery of alternatively efficient synthetic approaches to carbon-silicon bond formation is still a challenge in polymeric silicon research. A common approach to C-silylation reactions employs organolithium reagents to generate carbanions, followed by quenching of the alkyl-aryl lithium derivatives with silyl containing compounds. Direct metalation of polymers usually requires fairly acidic protons, activated by neighboring electronegative groups which by themselves are also reactive. Formation of alkyllithium-amine complexes of TMEDA proved to be a successful approach in directly metalating benzene (10), polystyrene (11), and even diene (33) containing polymers. Extensive investigation on the reactivity of different amine complexes in the metalation process was undertaken by Smith (37). A common conclusion of these studies is chelating with TMEDA enhances the reactivity of organolithium compounds to such an extent that non-activated hydrogen atoms can be abstracted in these reactions.

Calas et al (7) were able to silylate most organic functional groups using $Me_3SiCl/Mg/HMPA$ 38 or $Me_3SiCl/Li/THF$ (25) as silylating agents. Similarly, Chalk and Hay, disclosed in their publications (19), effective metalation of polyphenylene ethers under similar conditions. Guiver and associates (16, 17) investigated the probability of direct metalation on polysulfones in the absence of TMEDA as catalyst. This approach can effectively facilitate aromatic substitution of protons ortho to the aryl sulfones. The reaction is regiospecific and appears to be limited to monoaryl anions, e.g. only one silyl group can be introduced per aromatic ring and only sulfone activated rings can be silylated.

2.2 Silylation by Directed Bromination/Lithiation.

The ortho-directing effect of the methoxy substituent on metalation was first described by Gilman and Bebb (13). In succeeding years, metalation of many monosubstituted benzenes were investigated with respect to their ease of ortho lithiation (4, 57).

Electrophilic aromatic substitution reactions are also regio-selective; ortho substitution is directed by the ether moiety. Among these reactions are bromination, nitration, and phthalimidization. These reactions are often used for the formation of reactive polymeric precursors for further modifications. Electrophilic substitution of aromatic hydrocarbons by bromine is a well-known organic reaction (12). Selective monobrominations of reactive aromatic rings were effected by reagents such as NBS in DMF (34), bromine and thallium (III) acetate (30), and $CuBr_2$ (35). Alternative approaches to conventional bromination of deactivated aromatic systems were also described by Shabbir et al. (44)

Daly et al. (9) worked on bromination of polymers derived from Bisphenol-A in the absence of catalyst with good yields and minimum degradation. Comparable results were obtained by Guiver et al. (18). The bromination was quantitative with a maximum of two bromine atoms substituted per poly (arylene ether) repeat unit. Preparation of aryl lithium salts from aryl halides had been used extensively.

Various organic halides react easily with alkali metals such as lithium, sodium and potassium to yield alkali metal derivatives (54). Factors controlling regioselectivity and efficiency of lithiation of aromatic substrates had also been the subject of considerable research (14, 31). Introduction of electrophiles to aromatic substrates can be easily controlled with the use of aryllithium intermediates.

Among the silyl groups originally used for protection and derivatization of functional groups, the most important is the trimethylsilyl, (TMS) group (39, 23). In gas chromatography and mass spectrometry, the high volatility, thermal and chemical stability of the derivatives has made TMS the best choice for this application. In synthetic chemistry, TMS is widely used as a protecting group (26, 8) particularly for the hydroxyls and the enolisable carbonyls. The TMS group can be easily introduced by choosing the appropriate silylating reagent which can be selective and stable under certain reaction conditions. Some of the disadvantages of the TMS group is moisture sensitivity and tendency to undergo acidic and basic hydrolysis, or solvolysis with an alcohol. The lack of stability to moisture has limited the use of TMS derivatives to groups which are destined to be cleaved in the reaction scheme. Our study would aim to prepare polymers with silyl groups as integral parts of the molecule, with the intent that these groups would contribute to the final properties of the polymer.

3. Experimental

General Information

The polymer used in these modifications was previously prepared in the laboratory (2) and dried in vacuo before use. Bromine and butyllithium were obtained commercially and used without further purification. Chlorotrimethylsilane (TMSO) was dried by refluxing with CaH_2 and distilled before use. THF was refluxed with metallic potassium until the blue color ketyl forms from benzophenone, and fractional distilled before use. All other solvents and reagents used for general syntheses described herein were anhydrous and of reagent grade.

Intrinsic viscosities were determined at 30°C in NMP using a Ubbelohde dilution viscometer, No. 50-M45. The solvent was purified and filtered before use. A plot of η_{sp}/C vs C was extrapolated to zero concentration, to estimate the intrinsic viscosity according to the following equation.

$[\eta]$	=	$\lim (\eta_{sp} / C)$, where $C \rightarrow 0$
η_{sp}	=	$t - t_o / t_o$
t	=	efflux time of polymer solution
t_o	=	efflux time of pure solvent
C	=	concentration (g/dl)
$[\eta]$	=	intrinsic viscosity in dl/g

Nuclear Magnetic Resonance (NMR) spectra were obtained with the Bruker AC-200 spectrometer operating at 200.13 MHZ for ^1H and 50.1 MHZ for ^{13}C. Chemical shifts are given in parts per million (ppm) on a σ scale downfield from tetramethylsilane (TMS). The usual notations are used to describe the spectra: s=singlet, d=doublet, dd=doublet of a doublet, m=multiplet, and b=broad. ^{13}C chemical shifts are also reported using ppm scale, with the solvent peaks used as an internal standard.

Infrared spectra were recorded with a Perkin-Elmer FT-IR Spectrometer 176OX. Polymer film samples were cast from chloroform.

Glass transition temperatures (Tg), were determined using Seiko DSC220C at a heating rate of 20°/min at a temperature range of 20°C-300°C.

3.1 *Bromination of Bi/Hq PSF, [1].*

A solution of bromine (6.6 g, 41.4 mmoles) in 5 ml chloroform was added to a stirred solution of Bi/Hq PSF (5.0 g, 6.6 mmoles) in 60 ml chloroform. The mixture was stirred at room temperature for 24 hours. Excess bromine was purged from the reaction mixture to a trap half filled with water, by bubbling N_2 into the reaction mixture. The mixture was precipitated into methanol, then allowed to stand in solution for a day in order to further leach out any residual free bromine. The recovered polymer [2], (Scheme 1) was filtered, washed with water and methanol, then dried in vacuo for 2 days at 40°C. A yield of 5.13 g (82%, D.F. = 2, Tg = 200°C, [η] = 0.65) was obtained. ^1H NMR ($CDCl_3$): (Figure 1.1) 7.02-7.13 (m, aromatic H's); 7.56, 7.60 (d, 4H, aromatic H's meta-ether of biphenyl); 7.87, 7.91 (d, 8H, aromatic H's ortho-SO_2-). ^{13}C NMR ($CDCl_3$): (Figure 1.2) 116.3, 117.1, 117.6, 117.9, 118.0, 118.2, 120.7, 121.9, 123.5, 127.5, 128.6, 128.7, 129.8, 132.4, 135.7, 137.0, 137.6, 139.1, 151.7, 154.5, 155.0, 161.0, 161.5, 161.8 (aromatic C's). FT-IR; (Figure 1.3) 1044.1 cm^{-1} (-C-Br).

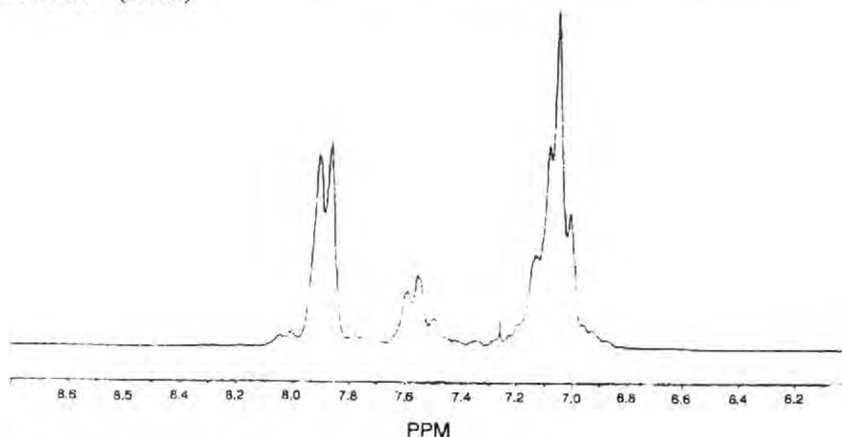


Figure 1.1 ^{1}H NMR of Brominated Bi/Hq PSF, [2].

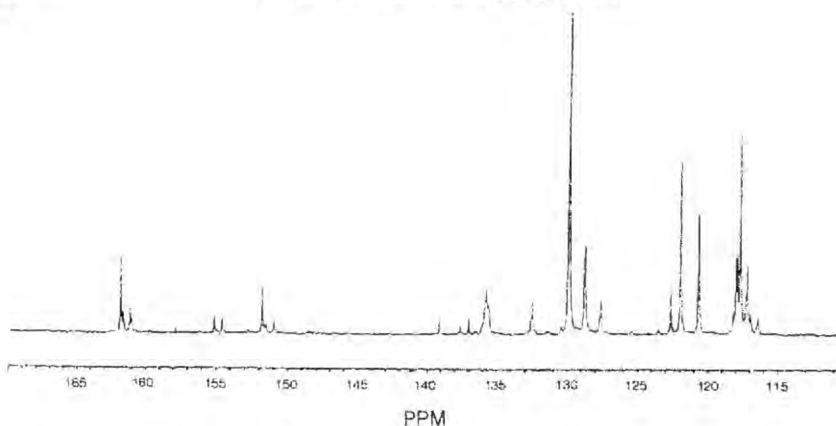


Figure 1.2 ^{13}C NMR of Brominated Bi/Hq PSF, [2].

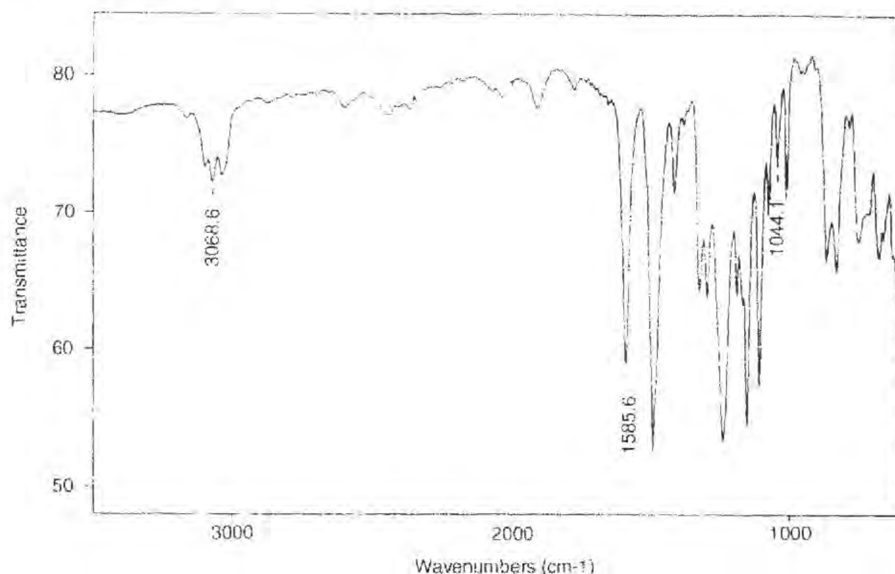
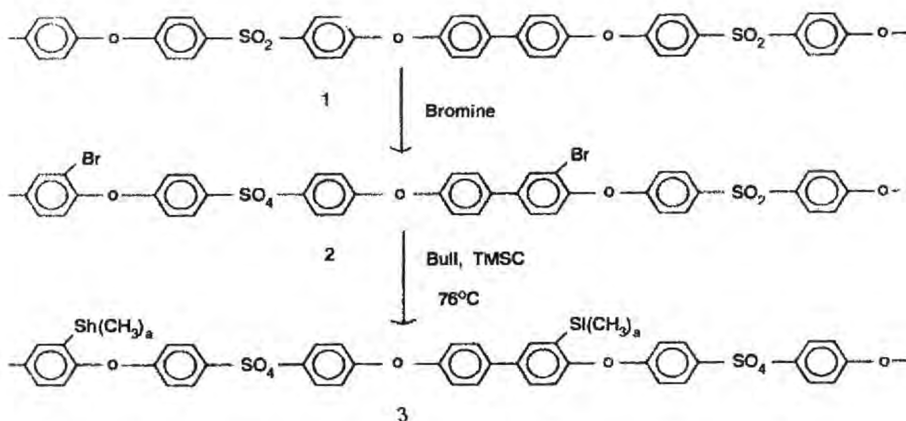


Figure 1.3 FT-1R of Brominated Bi/Hq PSF, [2].

3.2 *Silylation of Brominated Bi/Hq PSF, [2].*

n-Butyllithium (8.16 mmoles, 2.5M) was added dropwise to a N_2 purged and stirred solution of dibrominated Bi/Hq PSF (3.00 g, 3.4 mmoles) in 30 ml of dry tetrahydrofuran at -78°C. A viscous pinkish solution was formed which was stirred for 30 minutes before a 15 ml solution of trimethyl-silylchloride was added. The reaction was allowed to proceed for another hour after the addition of TMSC

before the resulting solution was precipitated into isopropyl alcohol. The recovered polymer was washed several times with isopropyl alcohol, filtered and dried in vacuum. The yield was 2.90 g (98%, D.F. = 1.65, [η] = 0.64, Tg = 186°C) of silylated polymer, [3], (Scheme 1). ^{1}H NMR ($CDCl_3$): (Figure 1.4a) 0.24 (s), orthoether hydroquinone, 0.34 (s), ortho-ether biphenol, (18H, (-$Si(CH_3)_3$); 6.86-7.65 (m, 18H, aromatic H's), 7.85, 7.89 (d, 8H, aromatic H's ortho-SO_2). ^{13}C NMR ($CDCl_3$): (Figure 1.5) -0.875, 1.03, 1.25 (-$Si(CH_3)_3$), 117.3, 117.7, 117.9, 119.3, 120.4, 120.6, 121.9, 126.1, 128.7, 129.8, 131.5, 132.5, 134.4, 135.7, 137.0, 137.6, 151.8, 154.6, 160.3, 161.8 (aromatic C's). FT-IR (film from $CHCl_3$); (Figure 1.6) 2954.8, 843.2, 757.6 cm^{-1} (-$Si(CH_3)_3$).



Scheme 1 Synthesis of Brominated Bi/Hq PSF, [2], and Silylated Bi/Hq PSF, [3].

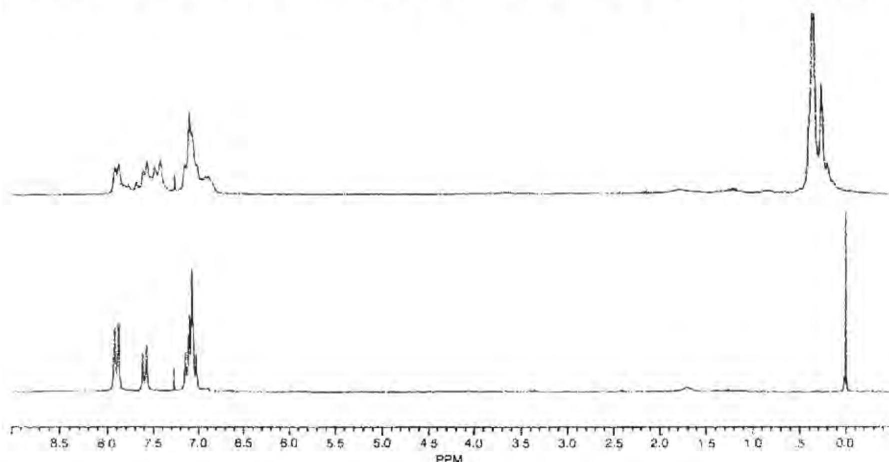


Figure 1.4a ^{1}H NMR of Ortho-Ether Silylated Bi/Hq PSF, [3].

Figure 1.4b ¹E NMR of Ortho-Sulfone Silylated Bi/Hq PSF, [4].

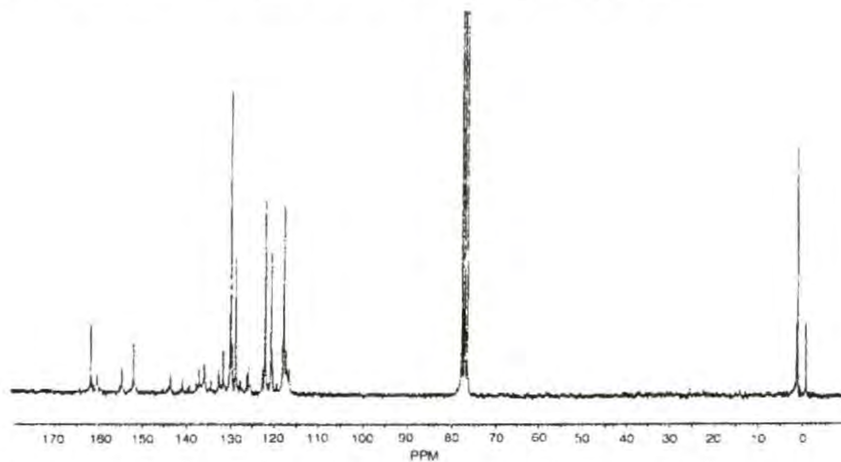


Figure 1.5 ¹³C NMR of Ortho-Ether Silylated Bi/Hq PSF. [3].

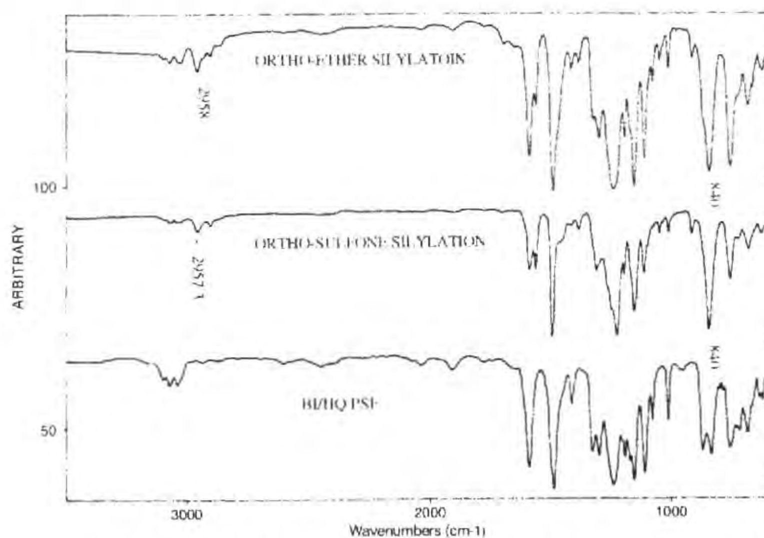
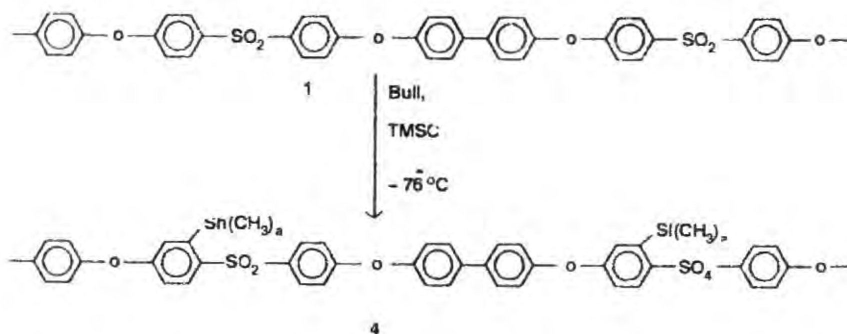


Figure 1.6 FT-1R of Ortho-Ether Silylated Bi/Hq PSF. [3]. and Ortho-Sulfone Silylated Bi/Hq PSF, [4].

3.3 *Silylation of Bi/Hq PSF, [1]*

n-Butyllithium (10 mmoles, 2.5M) was added dropwise to a N_2 purged and stirred solution of Bi/Hq PSF (3.0g, 3.99 mmoles (in 75 ml of THF at -78°C. The solution was stirred for 30 minutes before 10 ml of TMSC was added. The reaction was allowed to continue for another hour before precipitating into isopropyl alcohol. The recovered silylated polymer [4], (Scheme 2) was washed several times with isopropyl alcohol, filtered, and dried in vacuo to yield 3.20 g (89%, D.F. = 2.3, [η] = 0.61, Tg = 176°C). ^{1}H NMR ($CDCl_3$): (Figure 1.4b) 0.35 (s, 18H, (-Si(CH_3) ($_3$) ortho-sulfone); 6.85-7.58 (20H, aromatic H's) 7.85, 7.89 (d, 6H, aromatic H's ortho-SO_2). ^{13}C NMR ($CDCl_3$): (Figure 1.7) 1.03, 1.25 (-Si(CH_3($_3$), 116.4, 116.8, 117.7, 117.9, 120.4, 120.6, 121.8, 125.6, 126.1, 128.5, 129.5, 129.8, 131.5, 132.5, 135.7, 136.7, 137.0, 140.8, 143.4, 151.8, 154.6, 154.8, 160.1, 160.2, 161.8 (aromatic C's). FT-IR: (Figure 1.6) 2954.8, 843.2, 757.4 cm^{-1} (-Si(CH_3)$_3$).



Scheme 2 Synthesis of Silylated Bi/Hq PSF, [4]

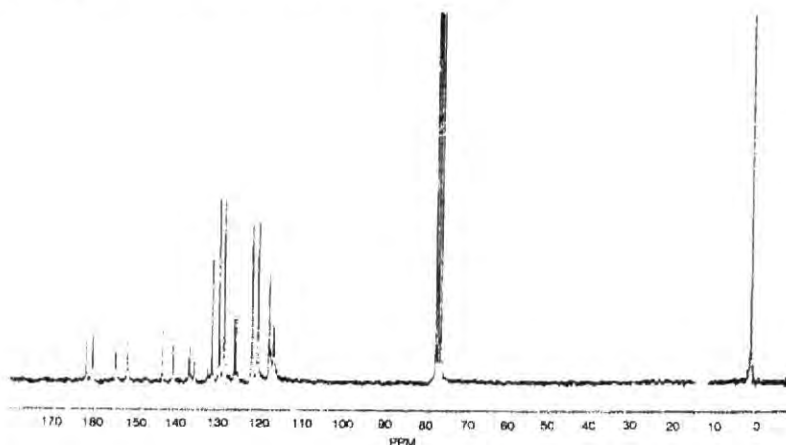
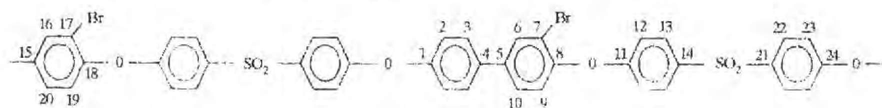


Figure 1.7 ^{13}C NMR of Ortho-Sulfone Silylated Bi/Hq PSF, [4]

Table 1. Comparison of Calculated and Experimental ^{13}C NMR Chemical Shifts of Brominated Bi/Hq PSF, [2].



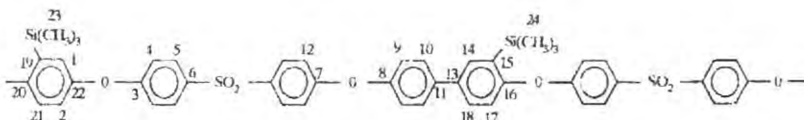
C	Calculated	Expt.	C	Calculated	Expt.
1	156.6	155.0	13	127.1	127.8
2	119.5	118.0	14	138.8	139.1
3	127.7	128.6	15	154.5	151.7
4	136.2	135.7	16	122.6	123.5
5	138.4	137.0	17	113.9	117.1
6	131.0	132.4	18	155.6	154.5
7	114.1	116.3	19	121.5	120.7
8	159.9	161.0	20	118.3	118.2
9	121.9	121.9	21	138.8	137.6
10	126.7	127.5	22	127.1	128.7
11	164.4	161.8	23	120.2	117.6
12	120.2	117.9	24	164.4	161.5

4. Results and Discussion

The structures of the brominated and silylated polysulfones were assigned on the basis of chemical shifts in ^{1}H NMR, ^{13}C NMR and infrared spectra. Degree of functionalization (DF) was determined by integration of the ^{1}H NMR using the integral of the aromatic protons ortho to the sulfone as internal standards. ^{13}C NMR chemicals shifts were assigned for each polymer in a manner consistent with the calculated values using addivity rules (40) (Table 1 - Table 3). The presence of functional groups, like bromine (-Br) and silyl (-Si(CH_3) ($_3$) were confirmed by FT-IR.

The two-step process of bromination/lithiation of the polysulfone is an efficient procedure for introducing trimethylsilyl substituents unto arylene ether groups. The bromination proceeded well in the presence of elemental bromine without the use of

Table 2. Comparison of Calculated and Experimental ^{13}C NMR Chemical Shifts of Ortho-Ether Silylated Bi/H1 PSF, [3].

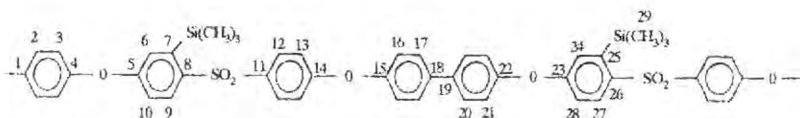


C	Calculated	Expt.	C	Calculated	Expt.
1	123.7	121.9	14	132.1	134.4
2	118.2	117.7	15	132.9	132.5
3	164.4	161.8	16	161.0	160.3
4	120.2	120.4	17	118.4	119.3
5	127.1	129.8	18	126.1	126.1
6	138.8	137.6	19	132.7	131.5
7	164.4	161.8	20	156.7	154.6
8	156.6	154.6	21	118.2	117.3
9	119.5	117.9	22	151.2	151.8
10	127.7	128.7	23		−0.88
11	136.2	137.0	24		1.03
12	120.2	120.6			
13	135.1	135.7			

a catalyst at room temperature. An evolution of white clouds of hydrogen bromide was observed within half an hour of addition of bromine to the reactant. The brominated polysulfone showed a slight decrease in viscosity, and was still soluble in halogenated hydrocarbon solvents, NMP, DMF, DMSO and THF. A small increase in glass transition temperature of the brominated polysulfone compared to the unmodified polymer was also observed.

The reactive position for aromatic bromination was always ortho to the aryl ether linkage in biphenol and hydroquinone portion of the repeat unit. This was expected due to the activating effect of the oxygen atom towards electrophilic substitution. Although previous studies showed that a maximum of two bromine atoms can be substituted per repeat unit (9, 18) without polymer degradation, we were able to introduce three bromine atoms to Bi/Hq PSF without further degradation as shown by the viscosity measurements.

Table 3. Comparison of Calculated and Experimental ^{13}C NMR Chemical Shifts of Ortho-Sulfone Silylated Bi/Hq PSF, [4].



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C	Calculated	Expt.	C	Calculated	Expt.
1	152.3	151.8	16	119.5	117.9
2	119.3	116.4	17	127.7	129.5
3	119.3	116.8	18	136.2	136.7
4	152.3	151.8	19	136.2	135.7
5	163.3	160.1	20	127.7	128.5
6	124.6	125.6	21	119.5	117.7
7	140.5	140.8	22	156.6	154.6
8	143.2	143.4	23	163.3	160.2
9	126.0	131.5	24	124.6	126.1
10	119.1	120.4	25	140.5	140.8
11	138.8	137.0	26	143.2'	143.4
12	127.1	129.8	27	126.0	132.5
13	120.2	121.8	28	119.1	120.6
14	164.4	161.8	29		1.03
15	156.6	154.8			

A low temperature lithiation of the brominated polysulfone was carried out with relative ease. Formation of a pinkish to reddish highly viscous gel was observed shortly after the addition to BuLi. The lithiated intermediates were not isolated, but were immediately quenched with TMSC. Hydrolysis of the resulting silylated products were avoided by precipitation into isopropanol. The silylated polymers showed no significant change in intrinsic viscosities.

The silylated polymers showed significant decreases in glass transition tempertures; both the ortho-ether and ortho-sulfone silylated derivatives exhibited the same degree of reduction of glass transition temperatures. A competitive

metal-hydrogen exchange was observed in the silylated products of the Bi/Hq (C-25= 1.25 ppm) due to the acidic protons of the biphenyl moiety.

The one-step lithiation/silylation process of polysuflone gave a silylated product with substitution preferentially ortho to the sulfone moiety of the diphenylsulfone group. This metal-hydrogen exchange was due to the increased acidity of the ortho-sulfone hydrogens compared to the other protons in the molecule. A small degree of competition was observed with acidic protons in the meta-ether position of the biphenyl group of Bi/Hq PSF.

The change in glass transition temperatures and viscosities of the silylated polymers formed by the metal-hydrogen exchange followed the same pattern as the silylated polymer obtained by halogen-metal exchange.

In the initial studies done on the resist characterization of the silylated polymers, we were able to establish the conditions needed for the dissolution and spin coating of the polymers from 5% and 10% solution of 1,2-dichloroethane onto silicon wafers. Film thicknesses can easily be altered by varying the spin rate and solution concentrations. Optically clear coatings which exhibit good tear resistance were formed after drying the plates at 100°C for 45 minutes. Initial flood exposures to soft x-rays at 3×10^6 Rad, of the silylated polymers spun in 3-inch silicon wafers at 10 Kv gave no indication of degradation or crosslinking at 8 mJ/cm^2. Either these materials are very stable to radiation or a higher exposure dose is needed. Future x-ray exposures are now planned; exposures of 500 mJ/cm^2 or more are quite feasible using the synchrotron.

Although our final goal is to make available polymeric resists which are subject to dry development processes such as reactive ion or plasma etching, the unavailability of these tools at the moment has led us to examine solvent development of the exposed polymers. We anticipated that radiation-induced cleavage would introduce phenolic end-groups and thus enhance the solubility of the exposed polymers in alkaline media. Indeed, tetramethylammonium hydroxide diluted with isoamyl acetate appeared to induce selective etching of the exposed regions. Post-exposure processing conditions, such as temperatures and times needed for soft baking and/or hard baking of exposed polymers, sequence of solvent development, i.e. rinsing, soaking or spraying, also remain to be established. Future work in the development area awaits the arrival of a stronger exposure tool. Utilization of condensation polymers in the production of microdevises has been limited to polyimides employed as dielectric planarizing layers and fiberglass mother boards. Development of submicron lithography requires materials which combine ultrasensitivity to X-ray radiation with high thermal stability and low dielectric potentials. Condensation polymers exhibit physical properties more consistent with these requirements than addition polymers. Increased use of condensation polymers will hinge on the ability to make the selective modifications to tailor the properties to the specific application. The work described in this reasearch is the first step toward that goal.

5. Conclusion

By choosing the appropriate reaction conditions, silylations of Bi/Hq PSF can be effected at both positions ortho to ether linkages and ortho to sulfone linkages within the polysulfone molecule. It is possible to introduce one trimethylsilyl group per aromatic ring without crosslinking or degrading the polymer. This concentration of silyl groups should be adequate for a barrier resin, which leaves a SiO_2 layer upon exposure to reactive ion etching with an oxygen plasma.

Modification of the positions ortho to ether structures can be achieved by a two-step process involving electrophilic bromination followed by lithiation and quenching with trimethylchlorosilane. Soluble polysulfones with degrees of functionality as high as three can be produced and metalated quantitatively. Upon quenching with TMSC, highly soluble modified polysulfones are formed a minimum of chain scission.

Modification of the positions ortho to sulfone units can be achieved regiospecifically by direct lithiation on the polymers. The neighboring sulfone group stabilizes the lithium counterion when the anionic charge is the ortho position so hydrogen abstraction occurs readily. Our results indicate that hydrogens meta to biphenylene oxide linkages were labile enough to undergo exchange with BuLi. The competition between the two sites of metalation can be controlled by the polysulfone to butyl lithium mole ratios. Stoichiometric ratios lead to ortho metalation; the meta metalation occurs when large excesses of butyl lithium are employed. Quenching of the lithiated intermediates with the electrophile, TMSC leads to soluble silylated derivatives. Significant lowering of glass transition temperature was observed in the silylated polysulfones.

If molar excesses of butyl lithium relative to brominated polysulfones are employed, both halogen metal exchange and abstraction of hydrogen atoms ortho to sulfone linkages occur. Using this technique every aromatic ring in the poly (arylene ether sulfone) can be silylated. Films can be cast from the poly silylated resins; their etch resistance remains to be tested.

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