Preparation of Polyaryloxysilanes and Polyaryloxysiloxanes by $B(C_6F_5)_3$ Catalyzed Polyetherification of Dihydrosilanes and Bis-Phenols

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ABSTRACT: Polyaryloxysilanes and siloxanes (PAS) are an interesting and useful class of polymers with excellent flammability characteristics. The $B(C_6F_5)_3$ catalyzed dehydrocondensation of bis-phenols or their simple alkylethers with dihydrosilanes and siloxanes provides ready access to these polymers. The reaction proceeds readily even when hindered phenol or silane substrates are employed affording sterically protected PAS derivatives. The combination of steric hindrance around the silyl ether linkage, the absence of ionic impurities and the use of very low levels of the boron catalyst in these reactions produces thermally and hydrolytically robust materials, which should further enhance their utility. Phenol functional macromonomers, such as polycarbonate and PPO derivatives, are readily coupled, providing easy access to siloxane copolymers. The only severe limitation of this process for preparing PAS derivatives is that the reaction is intolerant of base functionality in either the monomers or solvents used in the reactions.

Introduction

Polyaryloxysilanes and siloxanes (PAS) are a class of polymers derived from the condensation of bis-phenols with difunctional silanes or siloxanes. These materials have long been of commercial interest due to a combination of useful properties. In addition to the property benefits expected for any silicone copolymer, such as good low temperature ductility and high temperature stability, PAS also exhibit excellent flammability characteristics either alone or when blended with other polymers.[1−21]

An issue that has plagued commercialization of these materials is the lack of a reliable synthetic process to afford robust, hydrolytically stable PAS derivatives. PAS-type polymers are commonly prepared by the reaction of bisphenols with α,ω-difunctional silanes, typically a,ω-dichloro or α,ω-diamino silanes or siloxanes. Instability of these polymers is related to the facile hydrolysis of the silyl−aryl ether linkage. Hydrolytic cleavage, which can be rapid at typical processing temperatures, leads to significant degradation in molecular weight during extrusion or molding operations. This hydrolysis/solvolysis is subject to specific acid/base and general base catalysis[22−24] so that traces of acids, bases or salts derived from the preparation of these polymers can exacerbate the problem. The presence of these components in the polymer can lead to a significant decline in molecular weight during extrusion or even during precipitative isolation due to alcoholysis of the ether linkage.

The hydrolytic instability problem can be dealt with in several ways: by incorporating substituents that sterically hinder nucleophilic attack at silicon, by minimizing or completely avoiding the presence of polar or ionic impurities that usually accompany the condensation polymerization process or by a combination of these factors.

The effect of steric hindrance on retarding attack at silicon is well-known and has been exploited in the design of silicon-based protecting groups for organic functionality.[25] In the case of silyl aryl ethers, hindrance can be incorporated at the phenol's ortho position(s) or at silicon. The relative half-lives for methanolysis of silyl aryl ethers that model the polymer linkages (Table 1) nicely demonstrate this phenomenon. In this series of model compounds, several orders of magnitude retardation in the rate of solvolysis/hydrolysis can be realized by increasing the steric bulk at both silicon and in the ortho-positions of the phenols. Indeed bis-2,6-dimethylphenoxydiphenylsilylether can be purified by recrystallization from methanol, attesting to its stability. It must be kept in mind, however, that as hindrance around the ether linkage increases, preparation of the ether becomes increasingly difficult.

The method of preparation can profoundly affect the stability of PAS materials. For example, polymers made by the condensation of bis-phenols with chlorosilanes in the presence of amines as acid scavengers do not maintain molecular weight on precipitation or extrusion unless residual amine salts are rigorously removed from the polymers. The use of silylamines in place of chlorosilanes affords more stable polymers, but the silylamines are themselves sensitive to moisture and carbon dioxide, so care must be taken to avoid these interferences if high molecular weight, stable polymers are desired. In the absence of catalyzing impurities, the silylether linkage can be quite stable.

Thus, a method for preparing PAS homopolymers that avoids the use of stoichiometric acid-scavengers is desirable. Further, a method that enables preparation of hindered silyl ethers is even more desirable. A potentially attractive method for doing this involves the catalytic dehydrogenative cross-coupling reaction of bis-phenols and bis-hydrosilanes.[26−31] This reaction is catalyzed by a number of transition metals including salts of Zn, Sn(II), Cu(I), Co(II) and several Pd and Rh complexes. Because the method uses only catalytic amounts metal species and affords a neutral, gaseous byproduct, hydrogen, the usual sources of PAS instability are not a factor when this method is employed. In general, however, these reactions are slow even at elevated temperatures and are therefore not well suited for polymerizations. A series of recent papers has described the successful preparation of PAS type polymers by dehydrogenative coupling of bis-phenols and dihydrosilanes catalyzed by $Pd_2(dba)_3$, Pd/C or $RhCl(PPh_3)_3$.[29−31] The polymers prepared by this process were, in general, of relatively low molecular weight (M_n 5−16K), and no examples were given for the preparation of PAS analogues having significant hindering substituents around the silicon ether linkage. We were therefore encouraged by the reports of Piers and co-workers[32] that

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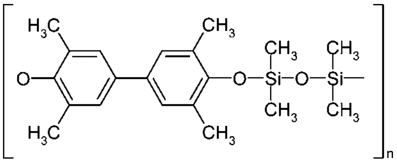
described the preparation of silylaryl ethers by $B(C_6F_5)_3$ catalyzed dehydrocoupling of hydrosilanes and phenols. Of particular interest was the fact that the reaction works well even for hindered phenols. We therefore set out to determine the suitability of this reaction for the preparation of PAS polymers, particularly those bearing hindered silylether linkages. This paper details our findings.

Experimental Section

Measurements. ^{1}H NMR spectra were recorded on a Bruker 500 MHz instrument. ^{29}Si NMR spectra were acquired on an Omega 500 spectrometer operating at 99.35 MHz. Gel permeation chromatography was carried out using a Perkin-Elmer series 200 pump and a Perkin-Elmer 235 diode array detector. Chloroform was used as the eluant at a flow rate of 1.0 mL/min through a MetaChem Technologies, 5μ linear 300 × 7.8 mm column. Molecular weights are reported relative to polystyrene standards. Differential scanning calorimetry was run on a Perkin-Elmer DSC 7 instrument.

Materials. Bis-phenols, bis-phenol ethers and dihydrosilanes were obtained from commercial sources and were used without purification. Tris-pentafluorophenylboron was obtained from Boulder Scientific Company.

Preparation of Polymers. A representative procedure for the preparation of PAS polymers is illustrated by the preparation of the polymer, **1**, derived from 2,6,2′,6′-tetramethyl-4,4′-biphenol and 1,1,3,3-tetramethyldisiloxane.

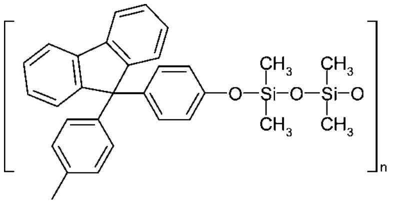


1

To a stirred mixture of 24.2 g (0.1 mol) of tetramethylbiphenol and 55 mg (0.0001 mol) of tris-pentafluorophenyl boron in 60 mL of CH_2Cl_2 was added over 50 min a solution of tetramethyldisiloxane in 40 mL of CH_2Cl_2. Gas evolved vigorously with each drop of silane added, and the mixture became viscous near the end of the addition. The polymer was isolated as a gummy mass by precipitation into isopropyl alcohol. The molecular weight of the polymer was determined by gel permeation chromatography to be $M_w = 108K/M_n = 52K$, $M_w/M_n = 2.08$. ^{1}H NMR ($CDCl_3$): δ 7.20 (s, 4, ArH), 2.2 (s, 12, Ar-CH_3) and 0.18 ppm (s, 12, Si-CH_3). The T_g of **1** is 54 °C by DSC.

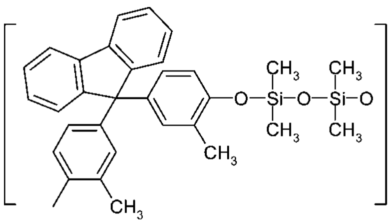
Pertinent data for other PAS derivatives prepared by this method are presented in Table 2.

Polymer 2:^{1}H NMR ($CDCl_3$): δ 7.8−7.15 (m, 8, fluorenyl-H), 7.05 and 6.65 (AB-doublets, 8, phenol C−H) and 0.10 ppm (s, 12, $SiCH_3$).



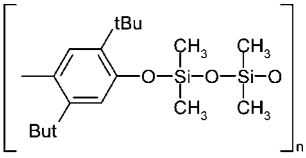
2

Polymer 3:^{1}H NMR ($CDCl_3$): δ 7.8−7.2 (m, 8, fluorenyl-H), 6.9−6.6 (m, 6, phenol-CH), 2.0 (s, 6, Ar-CH_3) and 0.15 ppm (s, 12, $SiCH_3$).



3

Polymer 4:^{1}H NMR ($CDCl_3$): δ 6.80 (s, 2, ArH), 1.25 (s, 18, *t*-Bu) and 0.24 ppm (s, 12, $SiCH_3$).



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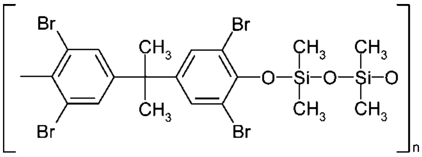
Polymer 5:^{1}H NMR ($CDCl_3$): δ 7.25 (s, 4, ArH), 1.53 (s, 6, $C(CH_3)_2$) and 0.25 ppm (s, 12, $SiCH_3$).



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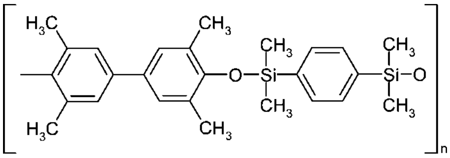
Polymer 6:^{1}H NMR ($CDCl_3$): δ 7.68 (s, 4, ArH), 7.15 (s, 4, ArH), 2.15 (s, 12, $ArCH_3$) and 0.53 ppm (s, 12, $SiCH_3$).



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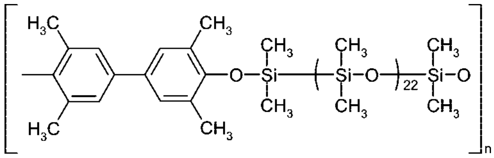
Polymer 7:^{1}H NMR ($CDCl_3$): δ 7.20 (s, 4, ArH), 2.25 (s, 12, Ar-CH_3) and 0.12 ppm (s, 144, $SiCH_3$).



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Coupling of Phenol Capped Macromonomers with Dihydrosilanes. *PAS−BPA−PC Copolymer* **8** *(2 Step Method).* A phenol capped oligocarbonate was prepared by interfacial phosgenation of BPA as follows: A 500 mL indented flask fitted with a condenser and nitrogen inlet, overhead stirrer, base delivery tube and phosgene delivery tube was charged with BPA, 22.8 g (0.1 mol); methylene chloride, 110 mL; water, 90 mL; and triethylamine, 140 μL (0.001 mol). Phosgene, 7.66 g (0.077 mol), was introduced at approximately 0.6 mL/min into the well-stirred two phase mixture while the pH was maintained at about 10.5 by metered addition of 30% aqueous sodium hydroxide. When phosgene addition was complete, the mixture was stirred an additional 15 min until all the phosgene was consumed. The mixture was transferred to a separatory funnel, and the aqueous phase was discarded. The organic phase was washed with 10% HCl (2×) and water (3×), and the oligomer was isolated by precipitation into about five volumes of

Table 1. Relative Half-Life for Methanolysis of Representative Silyl Aryl Ethers at 25 °C

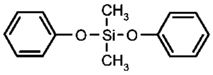
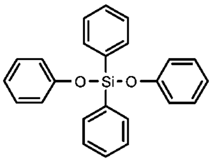
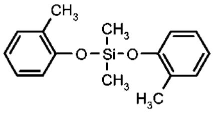
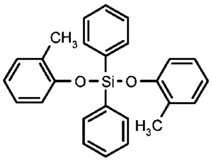
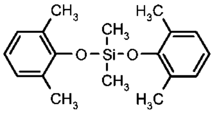
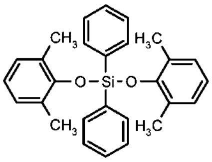
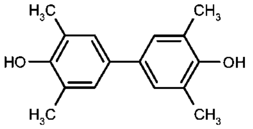
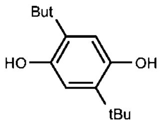
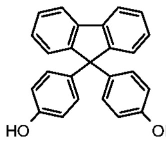
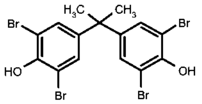
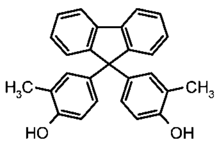
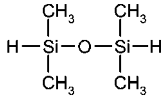
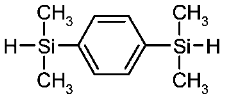
Compound	$t_{1/2}$ (hours)	Compound	$t_{1/2}$ (hours)
	1		27
	4.5		96
	96		1050

Table 2. Preparation and Properties of Polyaryloxysilanes and Polyaryloxysiloxanes

bis-phenol[a]	dihydrosilane[a]	polymer	mol % catalyst	M_w (K)	M_w/M_n	T_g (°C)
tmbp	tmds	**1**	5	28.3	2.89	
tmbp	tmds	**1**	4	53.3	3.01	54
tmbp	tmds	**1**	0.5	105		54
tmbp	tmds	**1**	0.1	108	2.08	54
bpf	tmds	**2**	0.1	34.6	2.18	91.7
dmbpf	tmds	**3**	0.1	33.7	2.00	97.7
dtbhq	tmds	**4**	4	43.9	>3	nd
tbbpa	tmds	**5**	0.5	13.7	2.55	nd
tmbp	btmsb	**6**	0.04	26.0	1.95	43.9 (T_m 112)
tmpb	$M^HD_{22}M^H$	**7**	0.1	101	2.23	oil

[a] Legend:

tmbp		dtbhq	
bpf		tbbpa	
dmbpf		tmds	
btmsb			

methanol in a blender. A molecular weight of 2385 was determined for this oligomer by integration of the ^{1}H NMR signal for the phenol (4.7 ppm) vs the BPA methyls (1.6 ppm).

The oligomer prepared as described, 9.54 g (4.0 mmol) was dissolved in 20 mL of dry methylene chloride and $B(C_6F_5)_3$, 2.0 mg (0.004 mol), was added. To this solution was added 1,1,3,3-tetramethyldisiloxane, 0.47 g (3.48 mmol). When addition was complete and gas evolution was no longer discernible, the mixture was stirred an additional 30 min and the polymer was isolated by precipitation into methanol The precipitated polymer had M_w =

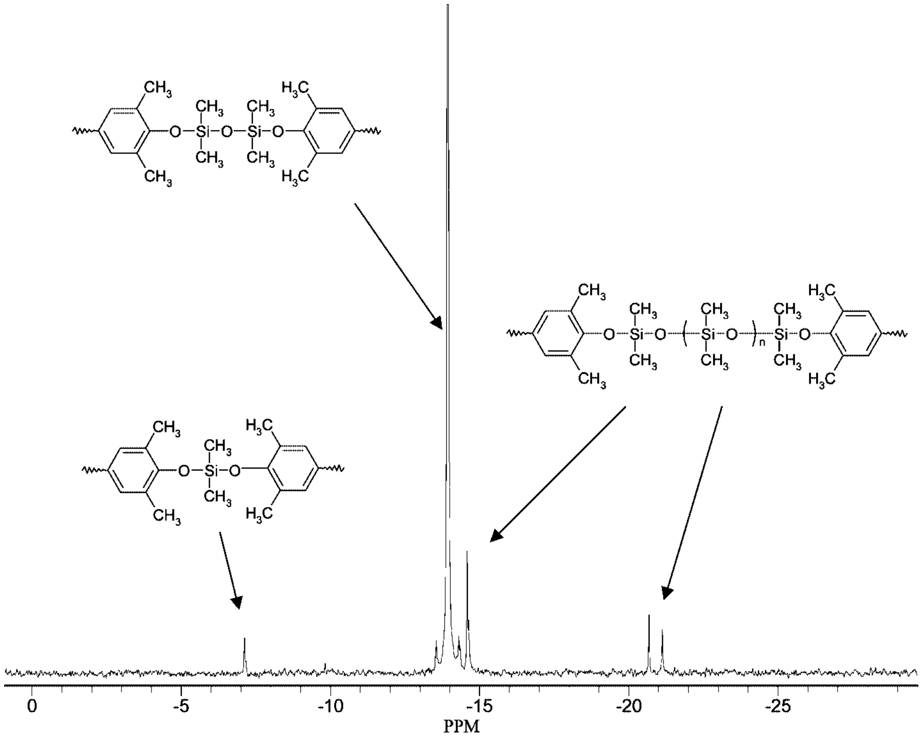
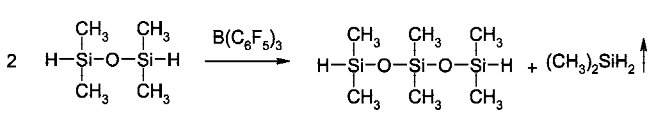


Figure 1. ^{29}Si NMR of the polyaryloxysiloxane **1** from TMDS and TMBP.

Scheme 1. Disproportionation of $M^HD_nM^H$ in the Presence of $B(C_6F_5)_3$



42.8K; $M_n = 10.0$K. ^{1}H NMR (CDCl$_3$): δ 7.3−7.2 (AB doublet, 8, ArH), 1.6 (s, 6, BPA-CH$_3$'s) and 0.2 ppm (s, 1, SiCH$_3$). ^{29}Si NMR (CDCl$_3$): δ −12.34 Ar−O−Si−-OAr. ^{13}C NMR (CDCl$_3$): δ 152.09, 148.98, 148.24, 143.35, 127.89, 120.30, 42.53, 30.89 and −0.52 ppm. DSC shows $T_g = 127$ °C.

PAS−BPA−PC (1 Step Method). A 500 mL indented flask fitted with a condenser and nitrogen inlet, overhead stirrer and addition funnel was charged with BPA, 22.8 g (0.1 mol); methylene chloride, 100 mL; and $B(C_6F_5)_3$, 3.0 mg (0.006 mmol). 1,1,3,3-Tetramethyldisiloxane, 1.34 g (0.01 mol), in 10 mL of methylene chloride was added dropwise over about 20 min. The addition funnel was replaced with a base inlet tube and a phosgene inlet tube, and water, 80 mL, and triethylamine, 130 μL, 0.094 g (0.93 mmol), were added. An excess of phosgene, 10.9 g (0.11 mol), was introduced at a rate of approximately 0.6 g/min while the pH was maintained at about 10.5 by metered addition of 50% aqueous NaOH. When phosgene addition was complete, the mixture was stirred until no more phosgene was detected. The mixture was then transferred to a separatory funnel, the aqueous phase was discarded and the organic phase was washed with 10% HCl (2×) and water (3×) followed by precipitation into about 5 volumes of methanol. The polymer 8 prepared in this fashion had $M_w = 41.9$K, $M_n = 20.3$K, $M_w/M_n = 2.06$. ^{1}H NMR δ (CDCl$_3$): δ 7.3−7.2 (AB-doublets, 8, ArH), 1.66 (s, 6, C(CH$_3$)$_2$ and 0.2 ppm (t, 0.91, SiCH$_3$). Integration of the BPA methyl signals versus the silicon methyls indicates approximately 87% incorporation of the disiloxane in the polymer. DSC analysis indicates the T_g of this polymer is 115.4 °C.

PAS-poly-2,6-dimethylphenylene)oxide. Amine-free poly-2,6-dimethylphenylene oxide was obtained by the base catalyzed coupling of 4-bromo-2,6-dimethylphenol according to the method of Percec and Shaffer.[33] The DP of the polymer was estimated from the integration of the ^{1}H NMR signal for the phenol end group (4.25 ppm) vs the arylene methyls (2.1 ppm) to be 91 ($M_n \sim 11$K). The oligo-2,6-dimethylphenyleneoxide, 1.00 g (0.09 mmol), was dissolved in 30 mL of toluene. The solution was dried by azeotropic distillation (~15 mL removed). To the cooled solution was added 0.23 mL of a 1 mg/mL solution of $B(C_6F_5)_3$ in dry toluene, 0.23 mg (4.5×10^{-4} mmol). To this solution was added 1,1,3,3-tetramethyldisiloxane, 0.006 g (0.045 mmol). The mixture was stirred at room temperature for 60 min, at which point gas evolution was minimal. It was then heated for 3 h at 80 °C. The cooled solution was poured slowly into a blender containing 150 mL of methanol. The white powder was isolated by filtration. ^{1}H NMR (CDCl$_3$): δ 6.45 (s, 2, ArH), 2.15 (s, 6, ArCH$_3$) and 0.08 (s, 0.04, SiCH$_3$). Integration of the BPA methyl signals versus the silicon methyls indicated that about 66% of the siloxane was incorporated.

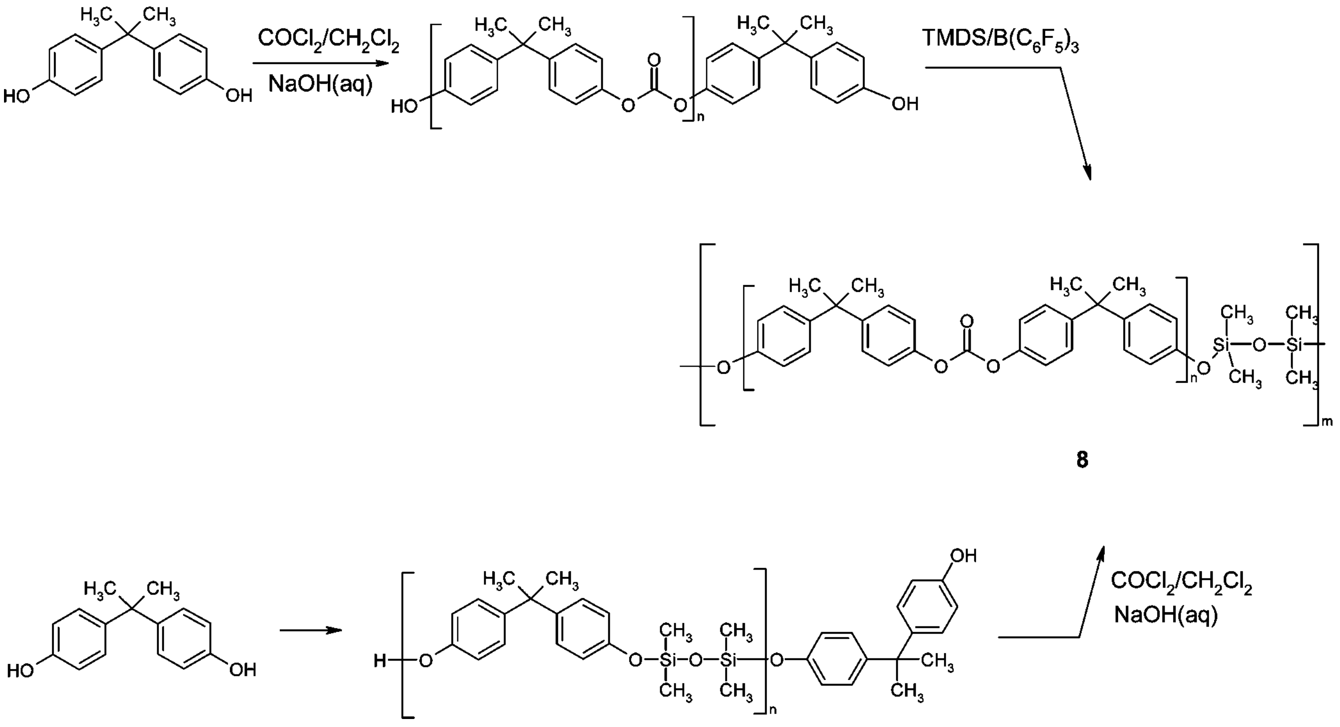
Condensation of Diphenylsilane with Hydroquinone Dimethyl Ether. A solution of diphenylsilane, 1.84 g (0.01mol), in 5 mL of dry methylene chloride was added slowly at room temperature to a solution of 1,4-dimethoxybenzene, 1.38 g (0.01 mol), plus $B(C_6F_5)_3$, 5 mg (0.01 mmol), in 10 mL of methylene chloride. Gas evolution did not commence until about 10% of the silane had been added, at which point vigorous evolution of methane occurred.

CAUTION: In some cases, particularly when the organohydrosilane is added to the bis-phenol, the reaction may not start after addition of the first few drops of silane. The reaction may start suddenly after a significant amount of organohydrosilane is added with very high exotherm and rapid gas evolution. In that situation it is important to run experiments on a small scale and in a large enough flask so significant volume is available for expansion of the reaction mixture. It may be preferable to add the bis-phenol to a mixture of the hydridosilane plus catalyst.

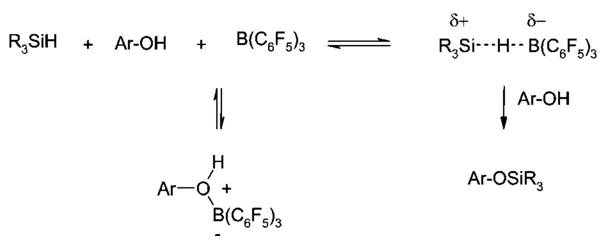
A sample of the viscous reaction mixture was analyzed by GPC prior to completion of the gas evolution which indicated $M_w = 15.1$K; $M_w/M_n = 3.16$. The mixture solidified on cooling and could not be redissolved.

Condensation of 1,4-Bis-dimethylsilylbenzene with Hydroquinone Dimethyl Ether. 1,4-Bis-dimethylsilylbenzene, 4.85 g (25 mmol), in toluene (10 mL) was added over about 30 min to a solution of hydroquinone dimethyl ether, 3.454 g (25 mmol), and $B(C_6F_5)_3$, 0.005 g (0.01 mmol), in toluene (15 mL). After a slight induction period, a rapid, exothermic gas evolution commenced.

Scheme 2. Preparation of Polycarbonate−Siloxane Copolymers 8



Scheme 3. Mechanism of $B(C_6F_5)_3$ Mediated Phenyl Silyl Ether Formation



When addition of the silane was complete and the reaction mixture had cooled, solids separated from the solution. Methanol was added to the mixture, and the solids were collected by filtration. The yield of white powdery solid after drying at 100 °C in a vacuum oven was 5.78 g (77%). GPC analysis of the soluble fraction indicated $M_w = 2.3K$; $M_w/M_n = 1.52$. Analysis of the solid by DSC indicated it to be reversibly crystallizable from the melt, $T_c \sim 128$ °C, $T_m \sim 155.7$ °C.

Results and Discussion

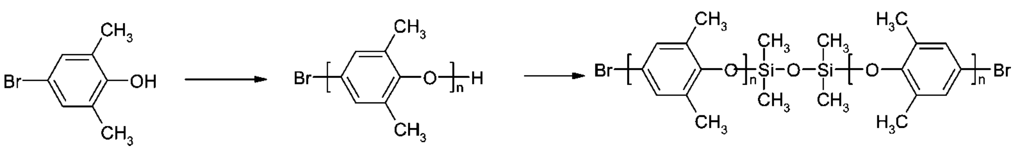
Bis-phenols react rapidly and efficiently with dihydrosilanes at ambient temperature either neat or in dry solvents in the presence of catalytic amounts (0.1 −0.025 mol%) of $B(C_6F_5)_3$ to afford high molecular weight polyaryloxysilanes or polyaryloxysiloxanes. The reaction is so rapid at ambient temperature that care must be taken to avoid loss of volatile components by entrainment with the escaping dihydrogen. The reaction can be controlled by adjusting the rate of addition of the silane to the bis-phenol or vice-versa. Table 2 lists results of the reactions of various bis-phenols with α,ω-dihydrosiloxanes.

Examination of Table 2 reveals several features of the polymerization process. Polymers obtained from reactions employing relatively high catalyst loadings (2−5 mol %) produce lower molecular weight polymers than those obtained with low catalyst loadings (0.5−0.1 mol %). The polymers produced using high catalyst loadings, moreover, were unstable to precipitation into alcoholic solvents and suffered substantial molecular weight degradation during this process. It was found that catalyst levels could be reduced by more than 2 orders of magnitude with no significant diminution in rate of the reaction. As the catalyst levels decreased, polymer stability to degradation during a precipitation increased to the point where it was no longer a problem. If desired, residual catalyst can be quenched by addition of small amounts of base prior to precipitation or simply by adding a slight excess of hydrosilane followed by heating. The latter process takes advantage of the thermally induced cleavage of a pentafluorophenyl ring from the borane catalyst by silicon hydrides to produce an inactive diarylboron hydride species.[32]

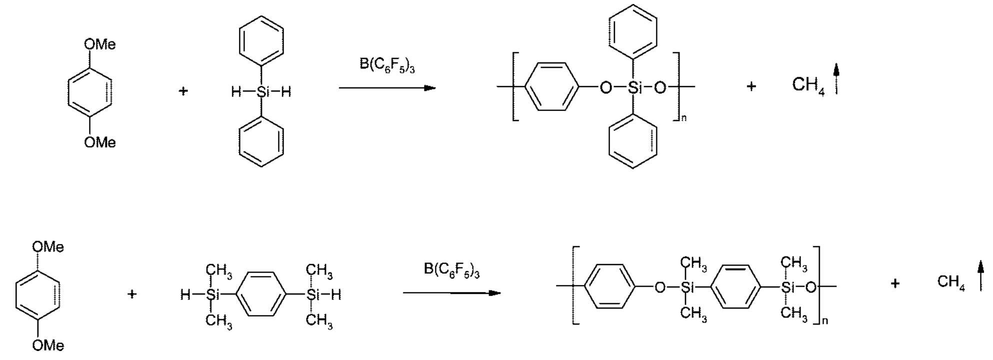
These polymerizations, which are generally completed in less than an hour, afford high molecular weight, stable polymers. The reactions are exothermic, and time to completion is dictated mainly by the rate at which addition is carried out. As can be seen from the range of bis-phenols studied, the reaction works well with hindered bis-phenols. Even the extremely hindered 2,2′,6,6′-tetrabromo-BPA affords a polymer, **5**, with respectable molecular weight in this reaction.

The ^1H and ^{29}Si NMR spectra of these polymers indicate that, for the most part, the polymers obtained by this process are derived from simple replacement of silicon hydride by a phenoxy group. Close examination of the ^{29}Si spectra, however, reveals that low levels of higher siloxanes are produced as well (Figure 1). Undoubtedly, some of the higher siloxanes result from the $B(C_6F_5)_3$ catalyzed hydrolysis of the hydrosilanes by traces of water in the reagents or solvents followed by catalyst mediated silanol−hydrosilane coupling.[34] When care is taken to minimize levels of water in the system, the formation of higher siloxanes is diminished, but it is never completely eliminated. The source of the higher siloxanes in these dry reactions is likely the result of a competitive siloxane redistribution reaction.[35,36] In the absence of phenols TMDS undergoes a $B(C_6F_5)_3$ catalyzed disproportionation leading to $M^HD_3M^H$ plus dimethylsilane[36] (Scheme 1). The formation of dimethylsilane and its coupling products with phenols continues as long as M^H species remain. Fortunately, this process is not competitive with phenol silylation, so that as long as a stoichiometric balance of

Scheme 4. Preparation of Amine Free PPO



Scheme 5. Coupling of 1,4-Dimethoxybenzene with Hydridosilanes



phenolic and M^H groups is maintained, silyl-phenyl ether formation is the dominant process.

The facility with which this silylation polymerization proceeds makes it well suited to couple phenol capped macromonomers to produce siloxane copolymers. An example of this process is illustrated by the preparation of the polycarbonate−polysiloxane copolymer **8**. Two process variants could be used to prepare **8** as depicted in Scheme 2. In the first, a phenol-capped polycarbonate ($M_n \sim 2385$), prepared by partial phosgenation of BPA. This oligomer was isolated by precipitation and analyzed by ^{1}H NMR to determine the value of M_n. The dried oligomer was then allowed to react with a stoichiometric equivalent of TMDS in the presence of $B(C_6F_5)_3$. A high molecular weight copolymer was obtained ($M_w = 42750$; $M_n = 10023$) that exhibited a T_g of 127 °C (T_g of BPAPC = 150 °C). The ^{29}Si NMR spectrum of this polymer consisted of a single signal at −12.35 ppm indicative of the arylsilyl ether linkage in the backbone. A similar copolymer was prepared in a one-pot reaction by first silylating an excess of BPA with TMDS/$B(C_6F_5)_3$ followed by coupling of the oligomers with phosgene (Scheme 2). ^{1}H NMR analysis of this polymer indicated 87% siloxane incorporation. The high molecular weight polymer ($M_w = 41937$, $M_w/M_n = 2.06$) had a T_g of 115 °C.

Attempted coupling of commercial poly-2,6-dimethylphenylene oxide (PPO) by this process serves to illustrate one of the limitations of the $B(C_6F_5)_3$ coupling methodology. Commercial PPO contains amine residues, usually at the phenol termini.[37] These are derived from the Cu-amine catalysts used to prepare the commercial polymer. Commercial PPO did not react with TMDS/$B(C_6F_5)_3$ even in the presence of relatively high catalyst loadings (2−5%). Evidently, the amine functionality in the commercial polymer inhibited the reaction, presumably by tying up the borate catalyst. Piers and co-workers[32] have reported this type of inhibition, and its origin is illustrated in Scheme 3. According to this postulate, the borane catalyst coordinates reversibly at all basic sites in the reaction mixture and only the free catalyst interacts with the Si−H functionality to activate the silane toward nucleophilic attack.

In the case of commercial PPO, the amine functionality ties up the catalyst so effectively that no “free” borane is available to catalyze silylation. This process limitation can be significant in dealing with any monomer or polymer system that contains basic sites, such as amines and ethers. At the low catalyst loadings required for this reaction, even small amounts of basic contaminants can completely shut down the polymerization process. The PPO silylation problem was overcome by synthesizing amine-free PPO by the phase transfer catalyzed polymerization of 4-bromo-2,6-xylenol[33] (Scheme 4). The amine free PPO was readily coupled by the TMDS/$B(C_6F_5)_3$ system.

An additional variant of this process worth mentioning is the use of dialkylethers of bis-phenols in place of bis-phenols in the condensation with dihydrosilanes. In this case a hydrocarbon is liberated as the reaction byproduct instead of hydrogen gas.[38] This variant can be of value in cases where the bis-phenol has limited solubility in the reaction solvent. For example, while hydroquinone is only sparingly soluble in typical reaction solvents, toluene or dichloromethane, its dimethyl ether dissolves readily affording high molecular weight polymer on reaction with either diphenylsilane or 1,4-bis-dimethylsilylbenzene in the presence of $B(C_6F_5)_3$ (Scheme 5). The latter polymer exhibits reversible crystallization from the melt ($T_c \sim 128$ °C, $T_m \sim 155.7$ °C).

Conclusions

In summary, we have shown that the $B(C_6F_5)_3$ catalyzed reaction of bis-phenols with dihydrosilanes and dihydrosiloxanes provides easy access to an interesting and useful class of polymers. The fact that even hindered phenols and silanes react readily means that sterically protected PAS derivatives are accessible from this reaction. These derivatives should exhibit good thermal and hydrolytic stability, which should greatly enhance their utility. The method uses readily available bisphenols and dihydrosilanes and employs very low levels of the boron catalyst. The only severe limitation of this reaction for the preparation of PAS derivatives is that it is not tolerant of basic functionality in the monomers or solvents from which they are prepared.

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