Preparation of Aromatic Silanes as High Thermal Stability Coupling Agents

Youlin Pan^{1a}, Barry Arkles^{1b} and James Kendenburg^{1c}

¹Research and Development, Gelest Inc., 11 East Steel Rd, Morrisville,
 PA 19067, USA

^aypan@gelest.com; ^b executiveoffice@gelest.com; ^cjkendenburg@gelest.com

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Abstract. Four different synthetic methods for preparation of aromatic silanes have been developed and the hydrosilylation route has been proved to be one as the most commercially significant. A series of specialty aryl silanes have been synthesized for the potential applications of high performance and high temperature as silane coupling agents. The thermal stabilities of the bridged aromatic silanes have been examined using thermal gravimetric analysis(TGA) and compared against the gamma-substituted alkylsilanes and phenyltrimethoxysilane. These materials have greater thermal stability than the gamma-substituted, but marginally lower than phenyltrimethoxysilane.

Introduction

Organofunctional silanes are a class of fascinating compounds, they not only enable new and sophisticated materials to be developed, but also are served as the technologically advancing-materials themselves. These include widely used coupling agent, adhesion promoter, surface modifier, crosslinker and moisture scavenger in many high technology industries such as automotive, aerospace, DNA microarray and microelectronics^{1,2,3,4}.

Organofunctional silanes integrate the functionality of organic groups and the reactive inorganic silicates in the same molecule, act as molecular linkers between inorganic substrates and organic polymers, and bond those two dissimilar materials across boundaries.

A general structure of the silane coupling agents is

Where (RO) is a hydrolysable group such as methoxy, ethoxy or acetoxy, and X are the organofunctional groups of acetoxy, amino, mercapto, glycidoxy and methacryloxy etc. The commercial silane coupling agent has organic functionality separated from the silicon atom by three carbon atoms. Others common class of silanes separated by two or one carbon atom. They are commonly called as gamma-, beta- and alpha-substituted silane, while beta-substituted silane is generally not be used as coupling agent due to low thermal stability. The order of the thermal stability of those three kinds is depicted in the following chart:

Relative Thermal Stability of Silanes

The gamma-substituted silanes have the highest thermal stability and can withstand short-term process condition of 350 °C and long-term continuous exposure of 160 °C^{5,6}. However, this is not sufficient for some applications in the aerospace industry since they demand the composite materials to offer lightweight, high strength, extreme temperature and stiff weather resistant. Also because of their intractability and unreactivity, these types of materials often either cause poor bonding with the organic polymers or a loss of bond strength over times, strong adhesion of these two dissimilar materials in extreme high temperature environment are highly required^{7,2}.

Experimental Section

Synthesis of Aromatic Silanes

1. Ethyl- 4-(triethoxysilyl)benzoate

A 500 mL, 3-neck flask equipped with a magnetic stirrer, a pot thermometer and a water cooled condenser was charged with 1.1 g of Rh(acac)(cod) and 50 ml of DMF. A mixture of 55.2 g (0.2 mol) of 4-Iodoacetophenone, 50.0 g(0.3 mol) of (EtO)₃SiH, 50.6 g(0.5 mol) of Et₃N and 150 ml of DMF was added at a pot temperature of 80 °C over 1 h. After heating at 80 °C, the pot mixture was cooled to room temperature, 200 ml of dry ether was then added. The mixture was filtered and the salts were washed with 750 ml of heptanes two times. The filtrates was combined and subjected to high vacuum distillation: 43.7 g(yield:69.9%) of pale yellow liquid were obtained; bp: 119-121 °C/0.3 mmHg; IR and NMR are consistent with the target structure. Density of the product at 20 °C: 1.029.

2. 4-(Triethoxysilyl)acetophenone

This compound can prepared in the same manner by using 4-Iodoacetophenone yield 56.1% as pale yellow liquid; bp: 119-121 °C/0.3 mmHg; IR and NMR are consistent with the target structure. Density of the product at 20 °C: 1.017.

3. 4-Aminophenyltrimethoxysilane

A 12L, 4-neck flask equipped with a mechanical stirrer, a pot thermometer, and additional funnel and a condenser was charged with 102.2 g (4.2 mol) of Mg and 500 ml of THF. 10 ml of 1,2-dibromoethane was dropped into the pot to initiate the reaction, 1265.0 g(4.0 mol) of bis(trimethylsilylamino)phenyl bromide in 4L of THF was then slowly added at a pot temperature

of 40 to 60 °C over 5h. After heated at 60 °C for another 5 h, the Grignard solution was cooled to room temperature and pushed out into a 2X4L bottle under the protection of N₂. 1826.6 g (12.0 mol) of Si(OCH₃)₄ were charged into above reactor, followed by addition of the fresh made Grignard solution through additional funnel at a pot temperature of 30 to 40 °C. After heated at 40 °C for 2h, 5 fold excess of MeOH was added into the pot. The mixture was heated at 40 °C for another 6h, cooled to room temperature, filtered to give a clean solution. The filtrates was then subjected to high vacuum distillation: 373.4 g(yield: 46.6%) of pale yellow liquid were obtained; bp: 114-6 °C/0.5 mmHg; IR and NMR are consistent with the target structure. It becomes solids when cooled to room temperature; mp: 60-2 °C.

4. Tolytrimethoxysilane

A 12L, 4-neck flask equipped with a mechanical stirrer, a pot thermometer, an additional funnel and a condenser was charged with 97.2 g (4.0 mol) of Mg and 500 ml of THF. 10 ml of 1,2-dibromoethane was dropped into the pot to initiate the reaction, 684.1 g(4.0 mol) of 4-bromotoluene in 4L of THF was then slowly added at a pot temperature of 30 to 40 °C over 6h. After heated at 40 °C for another 3 h, the Grignard solution was cooled to room temperature and pushed out into another flask under the protection of N₂. 1826.6 g(12.0 mol) of Si(OCH₃)₄ were charged into above reactor, followed by addition of the fresh made Grignard solution through additional funnel at a pot temperature of 30 to 40 °C. The mixture was heated at 80 °C for 6h to remove ca 3.0L of THF and addition of 3.0 L of heptanes. The mixture was then cooled to room temperature, filtered to give a clean solution. The filtrates was then subjected to high vacuum distillation: 540.4g(yield: 67.0%) of pale yellow liquid were obtained, bp: 75-8 °C/8 mmHg; IR and NMR are consistent with the target structure. Density of the product at 20 °C: 1.033.

5. Biphenyltrimethoxysilane

A 5L, 4-neck flask equipped with a mechanical stirrer, a pot thermometer, an additional funnel and a condenser was charged with 466.2 g(2.0 mol) of biphenyl bromide in 2L of THF. After cooled to -78 °C, 1200 mL of n-BuLi (1.7 M in hexane, 2.0 mol) was added slowly while vigorously stirring. After stirring for 30 min. at -78° C, the mixture was slowly warmed up to room temperature and continued to stir for 4 hours at room temperature. 913.3 (6.0 mol) of Si(OCH₃)₄ were charged into another reactor, followed by addition of the fresh made Lithium reagent through additional funnel at a pot temperature of 10 to 20 °C. The mixture was stirred at 80 °C for 6h to remove ca 1.5L of THF and addition of 1.5 L of heptanes. The mixture was filtered and the salt was washed with 500 ml of dry heptanes two times. The filtrates was combined and subjected to high vacuum distillation: 312.9g(yield: 57.0%) of pale yellow liquid were obtained, bp: 133-5 °C/0.3 mmHg; IR and NMR are consistent with the target structure. Density of the product at 20 °C: 1.026.

6. 1-Naphthyltrimethoxysilane

This compound can prepared in the same manner as Biphenyltrimethoxysilane by using biphenyl bromide: yield 49.3% as pale yellow liquid; bp: 152 °C/2 mmHg; IR and NMR are consistent with the target structure. It becomes solids when cooled to room temperature; mp: 33-5 °C.

7. Styrylethyltrimethoxysilane

A 12L, 4-neck flask equipped with a mechanical stirrer, a pot thermometer, dual additional funnels and a condenser was charged with 4g of phenothiazine and 500 g (ca 0.6 liters) of Heptane. After heat to 90 °C, 4 g of 10 wt% CPA/THF catalyst solution was added into the pot, 2055.2g(12mol) of DVB and 1918.3 g(14 mol) of TCS were added through the separated funnels at

a rate to maintain reaction temperature between 70-80 °C, do not let either the DVB or TCS addition get ahead of the other. The pot mixture was heated at 80 °C for 2 h after addition was completed. The volatiles was removed till pot temperature of 80 °C with 1 mmHg, the pot remain was esterified at 80 to 120 °C to convert chlorosilane to alkoxy silane, then subjected to WIFE distillation to give 100.3 g(yield: 27.7%) of pale yellow liquid, bp: 98 °C/0.1 mmHg; IR and NMR are consistent with the target structure. Density of the product at 20 °C: 1.023.

8. Chloromethylphenylethyltrimethoxysilane

A 12L, 4-neck flask equipped with a mechanical stirrer, a pot thermometer, dual additional funnels and a condenser was charged with 2g of BHT and 500 g (ca 0.65 liters) of Heptane. After heat to 90 °C, 4 g of 10 wt% CPA/THF catalyst solution was added into the pot, 3804 g(25 mol) of VBC and 3702 g(27.5 mol) of TCS were added at a volume ratio of ~1.1:1 through the separated funnels at a rate to maintain reaction temperature between 95-100 °C, do not let either the VBC or TCS addition get ahead of the other. The pot mixture was heated at 100 °C for 4 to 6h after addition was completed. The volatiles was removed till pot temperature of 80 oC with 1 mmHg, the pot remain was treated with esterified at 80 to 120 °C to convert chlorosilane to alkoxy silane, then subjected to high vacuum distillation to give 5041 g(yield: 73.2%) of pale yellow liquid, bp: 115 °C/1.5 mmHg; IR and NMR are consistent with the target structure. Density of the product at 20 °C: 1.092.

Results and Discussion

It has been showed that extremely high thermal stability can obtained through aromatic silane coupling agents. The specific substitution on benzene ring also plays a significant role in their thermal stability, while electron withdrawing substitution reduces thermal stability, electropositive groups enhance thermal stability⁶.

Continue our systematically studies on the organofunctional silanes^{8,9,10,11}, we have developed four different approaches for preparation of aromatic silanes and synthesized a series of specialty aryl silanes:

Route One: Silylation of Functional Halogenated Aromatics¹²

Silylation of aryl iodides by triethoxysilane in the presence of ruthenium catalyst affords compound **1** and **2**.

Route Two: Grignard Intermediates¹³

Compound **3** is obtained by preparation of a Grignard reagent from N,N-bis(trimethylsilyl)-p-bromomaniline and Mg in THF, reacting with tetramethoxysilane and deprotecting with methanol.

Compound **4** are conveniently synthesized through Grignard route from the corresponding aryl bromides, Mg turnings, tetramethoxysilane in THF.

Route Three: Lithium Reagents¹⁴

Although compounds **5** and **6** can also be prepared from the corresponding aryl bromides, Mg turnings, tetramethoxysilane in THF, organolithium reagents offer the advantages of shorter reaction times and higher yield.

Route Four: Hydrosilylation^{15,16,17,18}

Hydrosilylation of the corresponding vinyl monomers with CPA as catalyst yields the precursors of compound **7** and **8**. The precursors are then converted into the compound **7** and **8** by alkoxylation.

Out of above four routes, the hydrosilylation route has been proved to be one as the most commercially significant. It not only just produced the desired product in high yield and most economic, but also compound **8** can also be serviced as starting materials for other functional aromatic silanes.

The thermal stabilities of some aromatic silanes have been examined using thermal gravimetric analysis(TGA)¹⁹ and compared against the gamma-substituted functional alkylsilanes and phenyltrimethoxysilane. Their thermal stability data can be summered in the following table:

Thermal Stability of Silanes

$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	360 °C
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	390 °C
$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	395 °C
$\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{Si}(\text{OCH}_3)_3$	530 °C
$\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{Si}(\text{OCH}_3)_3$	485 °C
$\text{HOOC}-\text{C}_6\text{H}_4-\text{Si}(\text{OCH}_3)_3$	510 °C
$\text{ClCH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	495 °C
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	435 °C
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	460 °C

From this study²⁰ we learnt that the bridged aromatic silanes have greater thermal stability than the gamma-substituted functional alkylsilanes, but marginally lower than phenyltrimethoxysilane.

Summary

1. Four different synthetic methods for aromatic silanes have been developed and the hydrosilylation route has been proved to be one as the most commercially significant.

2. A series of specialty aryl silanes have been synthesized for the potential applications of high performance and high temperature as silane coupling agents. The thermal stabilities of the aromatic silanes have been examined using thermal gravimetric analysis(TGA) and compared against the gamma-substituted alkylsilanes and phenyltrimethoxysilane.

3. These materials have greater thermal stability than the gamma-substituted, but marginally lower than phenyltrimethoxysilane.

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