

Organosilane Polymer Chemistry: A Review

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Organosilane chemistry is a rapidly growing field. Over 1000 papers are published every year and the literature includes over 20,000 research papers and patents. Besides the synthetic aspects, organosilicon chemistry has become a major tool in the preparation of silylated compounds as reactive intermediates in organic synthesis and for an ever-increasing number of technical applications. This review article discusses the origin of organosilicon chemistry, the differences between carbon chemistry and silicon chemistry, and the application of silicon-carbon chemistry in the field of polymers.

KEY WORDS: Organosilane; arylsilane; organosilicon; polymers; silicon-carbon.

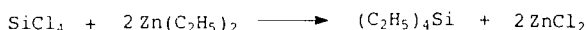
HISTORICAL BACKGROUND

Organosilicon compounds are defined as species possessing a silicon-carbon (Si-C) bond [1]. Nature does not provide a ready source of organosilicon compounds [2]; therefore they must be synthesized from elemental silicon. Although silicon is second in terrestrial abundance, it does not occur in the free state but rather is bound in a highly oxidized form with the most abundant element, oxygen, as silica or metal silicates [1]. If organosilicon compounds had utility, it was not apparent to the pioneer investigators; only curiosity could have led them to determine how to synthesize the compounds and to study their behavior [3]. The first extraction of silicon from its natural oxygen environment was accomplished by Berzelius in the early 1820s when he synthesized tetrachlorosilane by igniting sodium hexafluorosilicate and potassium in the presence of chlorine gas [4].

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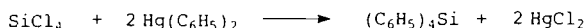
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The growth of organosilicon chemistry parallels the history of organometallic chemistry. However, while Frankland reported the use of ethyl zinc iodide and diethyl zinc as organometallic reagents in 1849 [5], it was not until 1863 that Friedel and Crafts [6, 7] synthesized the first organosilicon derivative by heating diethyl zinc with tetrachlorosilane in a sealed tube at 140–160°C (Scheme 1). Tetramethylsilane (TMS) was similarly synthesized from dimethyl zinc at 200°C [8].



Scheme 1. Synthesis of the first organosilicon derivative.

In 1873, Ladenburg reported the synthesis of the first arylsilane derivative by reacting diphenyl mercury with tetrachlorosilane (Scheme 2) [9–11].



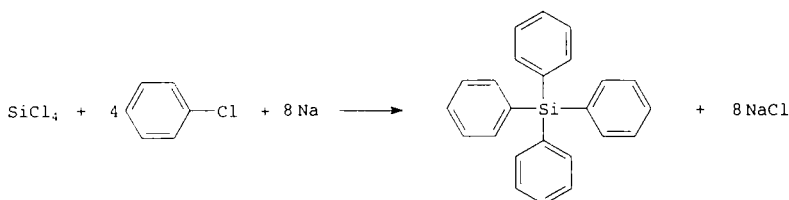
Scheme 2. Synthesis of the first arylsilane derivative.

The reaction conditions required to transfer the methyl or ethyl group from zinc to silicon were not particularly attractive, and it was not until 1884 that Pape performed an organosilicon synthesis via *in situ* generation of dipropyl zinc (Scheme 3) [12].



Scheme 3. Organosilicon synthesis via *in situ* generation of organometallic reagents.

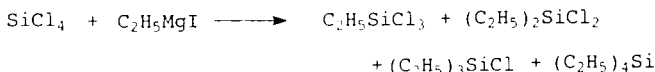
However, since the Friedel–Crafts reaction and the *in situ* synthesis were performed in sealed tubes at 150–200°C, the quantity which could be prepared was limited. In 1885, Polis used the Wurtz–Fittig reaction to prepare tetraphenylsilane for the first time (Scheme 4) [13].



Scheme 4. Organosilicon synthesis via Wurtz–Fittig reaction.

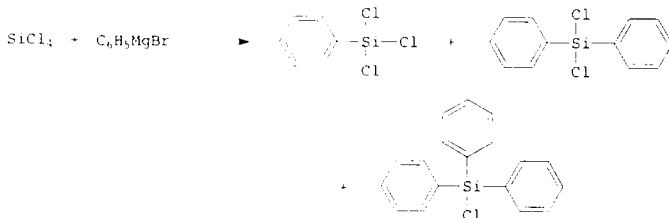
The higher reactivity of sodium alkyl eliminated the requirement of high-temperature, sealed-tube reactions. However, control of the reaction was difficult and tetrasubstituted silanes were formed.

With the invention of Grignard reagents in 1900 [14], Kipping reacted tetrachlorosilane with ethyl magnesium iodide to obtain a mixture of ethyl trichlorosilane, diethyl dichlorosilane, triethyl chlorosilane, and tetraethylsilane (Scheme 5) [15].



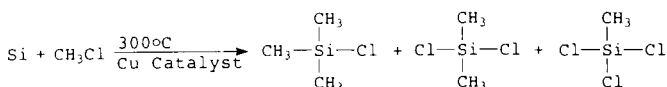
Scheme 5. Organosilicon synthesis via Grignard reaction.

During the same time, Dilthey and Eduardoff performed a similar reaction with phenyl magnesium bromide to obtain a mixture of phenyl trichlorosilane, diphenyl dichlorosilane, and triphenyl chlorosilane (Scheme 6) [16].



Scheme 6. Organosilicon synthesis via Grignard reaction.

Although formation of the Si-C bond was effected in the early 1900s, the techniques involved were energy intensive and by-product removal was very difficult. It was almost four decades after Kipping synthesized the first Si-C compound via the Grignard reaction that Rochow discovered the direct process and provided a firm footing for the future of organosilicon chemistry (Scheme 7) [17]. Industrially, the direct process, involving the reaction of methyl chloride and silicon with copper as catalyst, is the most important route for the synthesis of organosilicon compounds [18]. The



Scheme 7. Direct process for organosilicon synthesis.

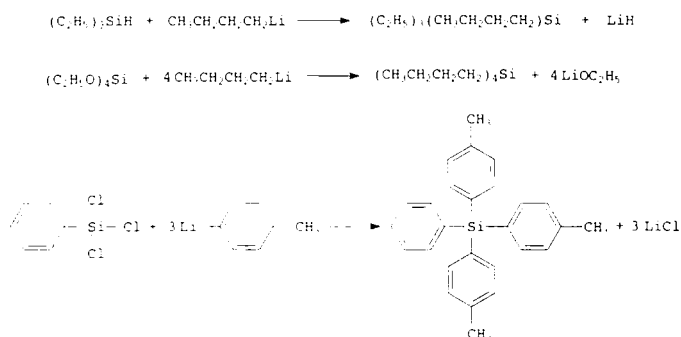
Table I. Typical Yields of Chlorosilanes from Direct Process

Compound	%	Boiling point (°C)
$(\text{CH}_3)_2\text{SiCl}_2$	75	70
$(\text{CH}_3)_3\text{SiCl}$	10	66
$(\text{CH}_3)_3\text{SiCl}$	4	58
$(\text{CH}_3)_3\text{SiHCl}_2$	6	41
SiCl_4		58
$(\text{CH}_3)_4\text{Si}$	5	26
HSiCl_3		32
Disilanes		

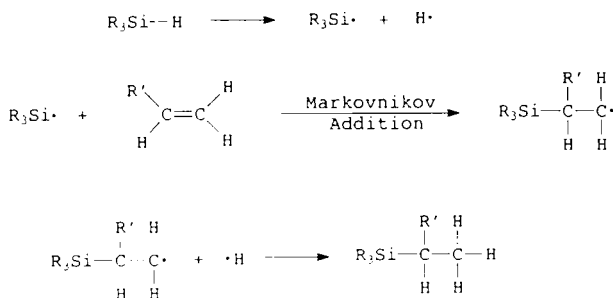
reaction is conducted on a very large scale via fluidized bed reactors and gives methyl chlorosilanes which are used as intermediates for silicone polymer manufacture. Typical yields are included in Table I.

In 1946, Gilman developed an alternative route to synthesize organosilicon compounds with organolithium reagents (Scheme 8) [19-21]. The lithium alkyls were prepared and handled much like a Grignard reagent. However, the organolithiums were more reactive than Grignard reagents toward organosilicon halides, alkoxides, and hydrides, thus making it feasible for the reactions to be performed at low temperatures in anhydrous ether.

Although synthesis of organosilicon compounds via thermal, photolytic, or free radical addition of hydrosilanes to olefins was discovered in the late



Scheme 8. Organosilicon synthesis with organolithium compounds.

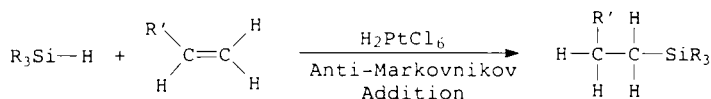


Scheme 9. Organosilicon synthesis via free radical addition of hydrosilanes (Markovnikov addition).

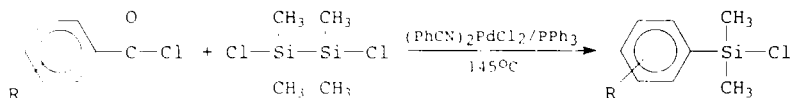
1940s (Scheme 9) [22, 23], it was not until the late 1950s that chloroplatinic acid (Speier's catalyst) [24, 25] was successfully used for hydrosilylation (Scheme 10). Since then, several transition metal catalysts including rhodium, cobalt, nickel, and iron have been developed [26, 27]. The nickel catalysts are less reactive than platinum and rhodium catalysts [28–30], and frequently phosphine–nickel complexes cause disproportionation of chlorohydrosilanes to a variety of complex by-products. Furthermore, transition metal salts other than platinum, rhodium, and nickel have been found to be effective only in special cases.

The free-radical addition of hydrosilanes to olefins follows the anti-Markovnikov rule, thereby giving the α -isomer as the major product. On the other hand, catalytic hydrosilylation gives the β -isomer as the major product. If silicon is viewed as being electropositive, catalytic hydrosilylation follows the Markovnikov addition rule.

A new synthetic scheme to arylsilane synthesis on an industrial scale was reported in 1987 (Scheme 11) [31]. The procedure relied on the reaction of chlorodimethylsilane with substituted acid chlorides and was compatible with all substituents, even those that could not be used with Grignard reagents. The rate of reaction increased as the electron-withdrawing nature of the acid chloride substituents increased.



Scheme 10. Organosilicon synthesis via free radical addition of hydrosilanes (anti-Markovnikov addition).



Scheme II. Synthesis route for arylsilanes.

In summary, the basic Si C bond formation methods have been described. The invention and use of Grignard and organolithium reagents provided the basis for modern organosilicon chemistry, and the direct process provided organochlorosilanes on an industrial scale. Hydrosilylation is an excellent complement to organometallic reagents and provided a needed degree of selectivity. Finally, the synthetic approach suggested by Rich [31] is effective industrially for arylsilane synthesis. No other generally applicable synthetic routes to organosilanes are available, and organosilane synthesis remains a challenge for the future.

SILICON-CARBON CHEMISTRY

The unifying theme underlying the early investigations of Si C chemistry was the similarities between silicon and carbon. For instance, both silicon and carbon have a *normal* covalency of four and their *normal* bonding is tetrahedral [32]. However, as research progressed, Kipping realized that the field of organosilicon chemistry did not match that of carbon and that silicon's differences far outweighed its similarities to carbon. Four major differences were apparent [33].

- Halosilanes were hydrolytically unstable, while halogenated hydrocarbons did not react with water.
- Organosilicon compounds showed no tendencies to form localized double bonds.
- Silanones ($\text{Si}=\text{O}$) and silacarboxylates ($\text{O}=\text{Si}-\text{O}$) have been reported only as reactive intermediates.
- Organosilicon compounds have a high inclination to polymerize.

For the most part, these differences can be explained by considering the following four fundamental properties of silicon:

- atomic size,
- electronegativity,
- lack of *p*-orbital involvement, and
- availability of vacant *d*-orbital.

Atomic Size

The atomic radii, relative electron densities, and electronegativity data for silicon and carbon are included in Table II.

Table II. Basic Properties of Silicon and Carbon

Property	Silicon	Carbon
Atomic radius (Å) [34]	1.176	0.772
Relative electron density [34]	8.6	13.1
Electronegativity		
Pauling [35]	1.80	2.50
Allred-Rochow [36]	1.90	2.55

The silicon atom is 1.5 times larger than the carbon atom and this increased size has several ramifications including longer bond lengths, lower energy barriers to silicon-element bond rotations, and less stable π bonds [37, 38]. The bond lengths and bond dissociation energies of silicon-element and carbon-element bonds are included in Table III.

Table III. Bond Length, Bond Dissociation Energy, and Ionic Character of Silicon-Element and Carbon-Element Bonds

Bond	Bond length (nm)	Ionic character (%)	Bond dissociation energy (kJ mol ⁻¹)
Si-H	0.148	2	339
C-H	0.109	4 ^a	420
Si-C	0.189	12	318
C-C	0.153	0	334
Si-N	0.174	30	320
C-N	0.147	6	335
Si-O	0.163	50	531
C-O	0.141	22	340
Si-F	0.160	70	807
C-F	0.139	44	452
Si-S	0.214	12	293
C-S	0.180	0	313
Si-Cl	0.205	30	471
C-Cl	0.335	6	335
Si-Br	0.221	22	403
C-Br	0.194	2	268
Si-I	0.322	12	322
C-I	0.214	0	213

^a H is more electropositive than C.

The increased bond length allows virtually free rotation of organo-silicon compounds [39]. The results are translated into essentially no rotational energy barriers and, thus, low glass transition temperatures (T_g), low viscosities, and improved impact resistance in silicone resins [40].

Electronegativity

Although silicon-element bonds are longer than carbon-element bonds, they are stronger than expected. The increase in bond strength is attributed to the lower electronegativity of silicon compared to carbon. The electronegativity values of silicon and carbon are listed in Table II. Regardless of the scale, silicon is markedly more electropositive than carbon, and the covalent bonds of silicon with other elements exhibit a pronounced ionic character. The ionic characters of several silicon-element and carbon-element bonds are included in Table III.

Further, depending on the substituent groups on the silicon or carbon, bond polarization can be enhanced or weakened. Electropositive moieties on carbon, especially hydrogen, and electronegative moieties on silicon, especially oxygen, decrease bond polarization and stabilize the bond. This is evident in poly(dimethylsiloxanes), wherein an optimal degree of cooperation exists between the hydrogen on carbon and oxygen on silicon. Other electronegative groups on silicon also stabilize the Si-C bond, e.g., trichlorosilane (Cl_3SiH) is thermally more stable than methyl silane (CH_3SiH), and chlorotriphenylsilane [$\text{ClSi}(\text{C}_6\text{H}_5)_3$] can be distilled at 378°C without decomposition [41]. On the other hand, electronegative groups on carbon directly attached to silicon decrease the Si-C bond strength. The silicon-difluoromethyl ($\text{Si}-\text{CHF}_2$) and silicon-trifluoromethyl ($\text{Si}-\text{CF}_3$) groups can be easily hydrolyzed even with cold water [42]. If an electronegative group is attached to the β -carbon atom, electron withdrawal occurs at the α -carbon atom, increasing the susceptibility of the Si-C bond to nucleophilic reagents. This " β effect" is exemplified in the hydrolytic decomposition of β -chloroethyl triethylsilanes in alkaline media [43]. Other organosilicon compounds with β electronegative substituents react in a similar way.

Lack of p -Orbital Involvement

Although stable ($2p-2p$) π -bonded compounds with carbon exist, analogous ($3p-2p$) π -bonded compounds with silicon have proven to be elusive [44-47]. At first sight, this is rather surprising, since the ($3p-2p$) π bond energy of silaethene ($\text{SiH}_2=\text{CH}_2$), determined via *ab initio* molecular orbital calculations [48], ion cyclotron resonance spectroscopy [49], and

thermochemically derived data [44-47], indicates that the bond is relatively strong. However, the bond is highly reactive owing to the strong polarizability and presence of low-lying π^* antibonding molecular orbitals. Silaethene, silabenzene, and their analogue have been generated as reactive intermediates which are stable at very low temperatures (10-50 K) or can be isolated using trapping agents [50-63].

Availability of Vacant d -Orbital

Organosilicon compounds are normally quadrivalent with silicon, forming tetrahedral sp^3 hybridized bonds. However, the vacant $3d$ orbital is considered to be responsible for a number of physical and chemical properties, and they include the following:

- (a) stabilization of reaction intermediates and transition states.
- (b) formation of additional σ bonds, and
- (c) formation of internal π bonds.

Sommer's studies on chiral silicon compounds indicate that involvement of $3d$ orbitals lowers transition-state energies for both frontal attack (resulting in retention) and backside attack (resulting in inversion) [64].

The formation of hexafluorosilicate ion (SiF_6^{2-}) is a classic example of octet expansion in silicon. X-ray crystallographic analysis [65] reveals that the six fluorine atoms are arranged octahedrally about silicon, implying a sp^3d^2 hybridization. Further, spectroscopic evidence indicates the presence of transannular interaction between nitrogen and silicon in penta-coordinated silatranes [66-71]. The formation of penta or hexavalent compounds is favored with a decrease in steric hinderance and lowering of silicon's electron density by electronegative atoms [72]. The electronegative atoms interact with silicon's d -orbital and, thus, allows it to participate in bonding [73].

Although d -orbital involvement in coordination expansion by σ bond formation is accepted, there is controversy over proposals of ($p-d$) π bonding [34, 64, 74-76]. The controversy arises from the fact that, contrary to σ electrons, π electrons do not lie between the nuclei but are directed away from the internuclear axis. Therefore, ($p-d$) π bond strength depends on the nature of the group providing the p -electrons and the bond overlap integral [77].

The quantum chemical calculations of Nagy and Reilly [78] indicate that the ($p-d$) π bonding between the unoccupied d -orbital of silicon and the phenyl ring in trimethylphenylsilane is 11%, and the dipole moments of the bonds are significantly higher than those for *t*-butylbenzene.

In an attempt to explain the two contradicting forces of electron donation via inductive effects and electron withdrawal via (*p d*) π bonding, several investigations including acid–base strength analysis [79, 80], spectroscopic studies [81, 82], dipole moment determinations [83, 84], and kinetic studies [85] have been reported.

The acid strength comparison of *p*-trimethylsilyl benzoic acid and *p*-*t*-butyl benzoic acid to explain the existence of (*p d*) π bonding in the silicon-based acid has been highly controversial. For instance, Chatt and Williams [79, 80] reported that *p*-trimethylsilyl benzoic acid was a stronger acid than *p*-*t*-butyl benzoic acid, and attributed the increased acidity to electron withdrawal by the trimethylsilyl moiety via (*p d*) π bonding. This report was in direct conflict with studies by Roberts *et al.* [83, 86] and Benkeser and Krysiak [87], who reported the acidity of *p*-trimethylsilyl benzoic acid to be similar to or weaker than that of benzoic acid. Later, Zuckerman *et al.* [88] reported that the acid dissociation constants were dependent upon the solvent and solvation effects, and not upon (*p d*) π bonding.

Conclusive evidence for (*p d*) π bonding was observed in electron spin resonance (ESR) studies by Bedford *et al.* [89]. ESR studies of trimethylsilyl benzene and *t*-butyl benzene indicated that the trimethylsilyl group was electron withdrawing and the *t*-butyl group was electron donating. Supporting this tenet, Curtis and Allred [90, 91] suggested the presence of (*p d*) π bonding in 4-trimethylsilyl biphenyl and 4,4'-bis(trimethylsilyl) biphenyl. In yet another study, Cowell *et al.* [92] reported that the bis(2,2'-biphenyl) methane radical anion was paramagnetic, while delocalization of the two unpaired electrons into the 3*d* orbital of silicon made the bis(2,2'-biphenyl) silane radical anion diamagnetic. Finally, Bock *et al.* [93] indicated that *p*-xylene, on reduction, formed the 1,2-dihydro species, since the electron-donating tendencies of methyl group lowered the stability of the 1,4-radical anion. However, reduction of 1,4-bis(trimethylsilyl) benzene gave exclusively the 1,4-dihydro species since the 1,4-diradical anion was stabilized via electron delocalization into the 3*d* orbital.

The study of electronic environment of an atom and the substituent effects can be studied by nuclear magnetic resonance (NMR) spectroscopy, and this technique is a powerful tool in investigating (*p d*) π bonding. Vignollet and Marie [94] reported that the interaction between the trimethylsilyl group and benzene in trimethylsilylbenzene occurred purely via inductive effects, whereas the electron-withdrawing effect of phenyl substituents was due mainly to (*p-d*) π bonding. However, if electron-donating groups were attached to the phenyl ring, then (*p d*) π bonding effects were diminished [94–96].

Freeburger and Spialter [97] studied the correlation between the C-H coupling constant (J) and the respective Hammett σ values for the methyl group of the substituted trimethylphenylsilanes. The data suggest that silicon is a more efficient transmitter of electronic effects in comparison to its carbon, oxygen, or nitrogen analogues, and attributed this distinguishing feature to ($p-d$) π back-bonding.

^1H NMR chemical shifts of 2-silyl furans [98] confirm an electron-withdrawing effect when silicon atom is directly bonded to the furyl ring. However, when the silyl group is separated by resonance-defeating methylene units, inductive effects dominate. Similar results have been reported for silyl thiophenes, silyl pyridines, silyl pyrroles [99], and main-chain arylsilanes [39].

Bowden and Braude [100] reported a bathochromic shift in the ultraviolet (UV) spectrum of p -trimethylsilyl benzene relative to p - t -butylbenzene, and attributed this effect to ($p-d$) π bonding electron delocalization. Gilman *et al.* [101] wrote that the absorption maximum and molar absorptivity of phenyl- and methyl-substituted disilanes increased with increased phenyl ring substitution and optimum conjugation across the silicon-silicon bonds. A comparative UV analysis of polyphenylated silanes and siloxanes with polyphenylated paraffins and paracyclophanes was performed by Brown and Prescott [81], who found that in such cases silicon always behaves as an electron-withdrawing group, and they attributed this behavior to the presence of ($p-d$) π bonding. The electron-withdrawing power increased when the silane group was replaced with siloxy group.

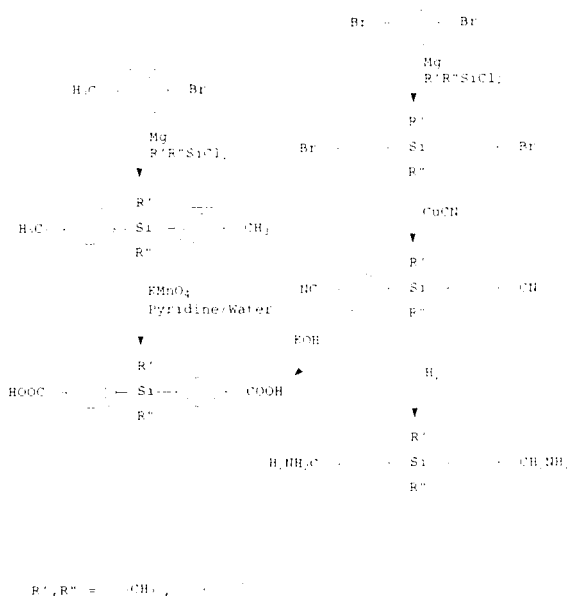
Gas-phase electron diffraction studies performed by Dakkouri and Typke [102] confirm that the Si-C bond length in cyclopropylsilane is shorter than that in vinyl silane. The shortening of the bond length was attributed to the delocalization of electrons in the cyclopropyl ring as a result of enhanced interaction of silicon's d -orbital.

ORGANOSILICON POLYMER CHEMISTRY

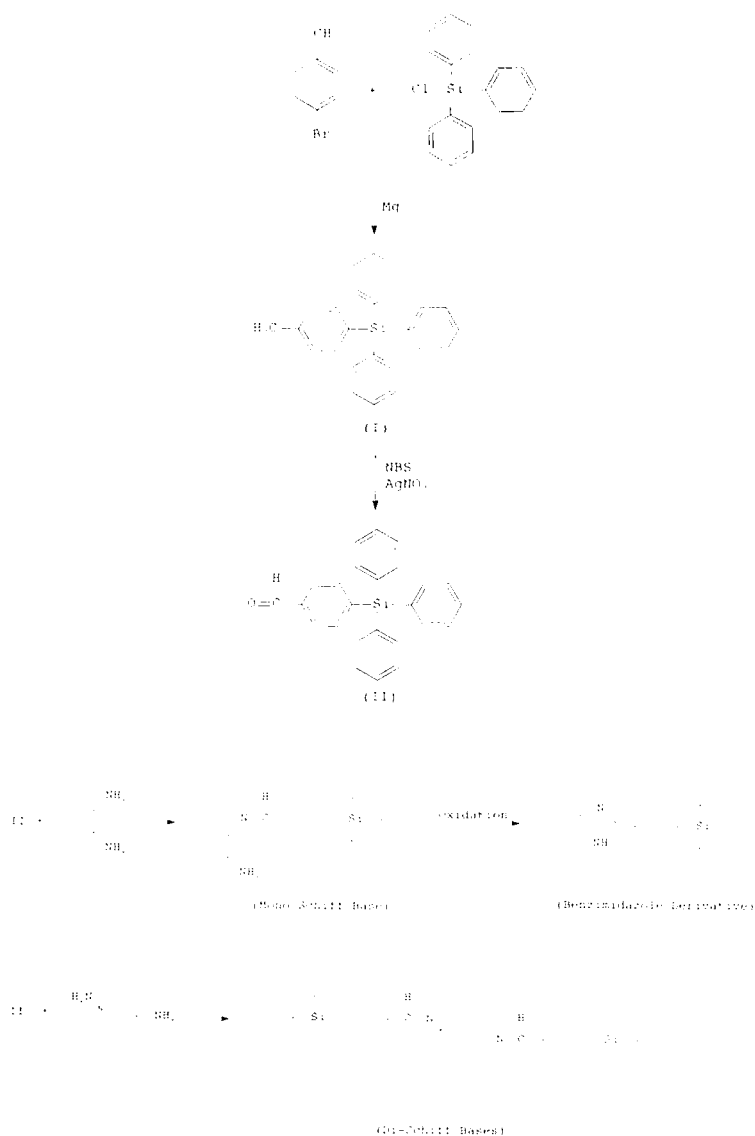
Organosilicon polymers can be subdivided into four major categories based on the silicon-element linkage, which includes polysilanes (Si-Si linkage), polysiloxanes (Si-O linkage), polysilazanes (Si-N linkage), and polysilalkylenes and polysilyarylenes (Si-C linkage) [103]. Of these, the polysiloxanes or silicone polymers have been widely studied and have the greatest commercial importance [104-109]. The polysilanes [104, 110], polysilazanes [111, 112], and polysilalkylenes and polysilyarylenes are finding applications in specialized fields. Since this research has focused on compounds with a Si-C bond, the ensuing discussion is restricted to the growth and development of silalkylene and silarylene polymers.

The first silicon-containing polymer was synthesized by Speck in 1953 [113]. Organosilicon dicarboxylic acids and dibenzylamines were prepared via the synthetic routes of Scheme 12. Polyamides were synthesized by heating dicarboxylic acids with organosilicon diamines or 1,6-hexamethylene diamine under reduced pressure. The thermal stability and mechanical properties of the silicon-containing polyamides were similar to those of their carbon analogues. X-ray diffraction patterns indicated that the silicon-based polyamides were amorphous and highly unoriented. The ethylene glycol polyesters of bis(*p*-carboxy phenyl) dimethylsilane and bis(*p*-carboxy phenyl) diphenylsilane possessed mechanical and thermal properties similar to those of their carbon analogues, except that they were amorphous and softened at lower temperatures.

In the early 1960s, the need for heat-resistant polymers intensified. Marvel *et al.* reported that Schiff bases [114, 115] and benzimidazole derivatives [116–118] were suitable building blocks for thermally stable polymers. However, these polymers were insoluble in most organic solvents and processibility was difficult. In an effort to improve processibility, Kovacs *et al.* [119] synthesized model silicon-containing Schiff bases and benzimidazole derivatives by reaction of *p*-triphenylsilyl benzaldehyde with



Scheme 12. Synthesis of the first organosilane monomers.



Scheme 13. Synthesis of silicon-containing Schiff bases and benzimidazole derivatives.

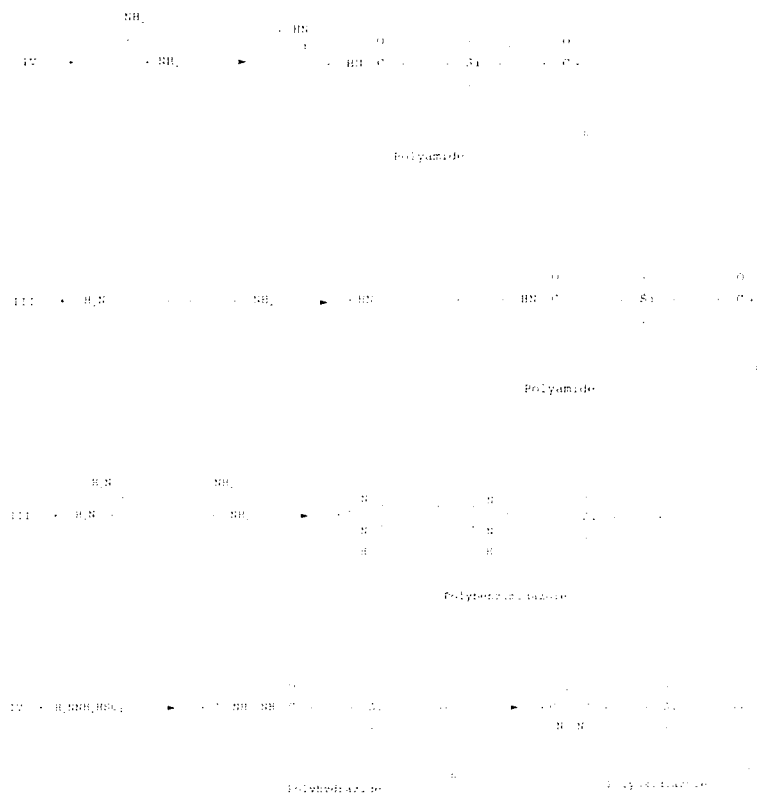
phenylene diamines (Scheme 13). Thermogravimetric analysis (TGA) data indicated that the relative order of heat resistance of these compounds was similar to that of their carbon analogues. However, the silicon-containing Schiff bases and benzimidazole derivatives were soluble in organic solvents.

With the data obtained from the model compound studies, Kovacs *et al.* [120-122] synthesized novel silicon-containing amides, benzimidazoles, hydrazides, and oxidiazole polymers (Scheme 14) and studied their oxidative-thermal stability and solubility characteristics. The polymers were soluble in organic solvents, and films cast from solution firmly adhered to glass and metal surfaces. Even after being heated in air for 100 h at 300°C and then for 3.5 h at 450°C, the films possessed excellent flexibility and adhesion on aluminum. Infrared analysis of the residues indicated that the polymer structures were essentially unchanged.

As a part of a continuing research program to improve processing characteristics of high-temperature polymers, Johnston and Jewell [123]



Scheme 14. Synthesis of silicon-containing amide, benzimidazole, hydrazide, and oxidiazole polymers.



Scheme 14 (Continued)

reported the synthesis and characterization of two series of aromatic polyimides via reaction of novel silicon-containing dianhydrides with aromatic diamines (Fig. 1). They compared their properties with those of 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride-based polyimides. The organosilane polyimides were soluble in chlorinated hydrocarbons. Thermal analysis by torsional braid and thermomechanical techniques indicated that the T_g was lowered by 7–48 °C when silyl groups were incorporated into the polymer backbone. Dynamic thermogravimetric (DTG) studies showed that the degradation of silicon-containing polyimides began at significantly lower temperatures than for conventional aromatic polyimides.

Ghatge and Jadhav [124] synthesized polyimides via the diisocyanate dianhydride route (Scheme 15). The organosilane diisocyanates were

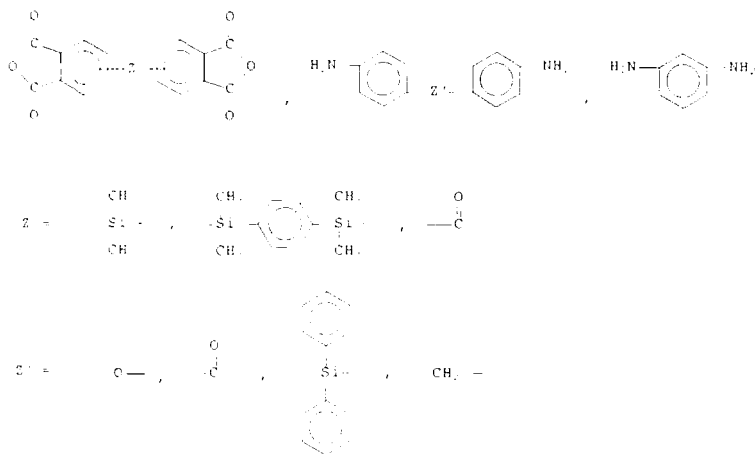
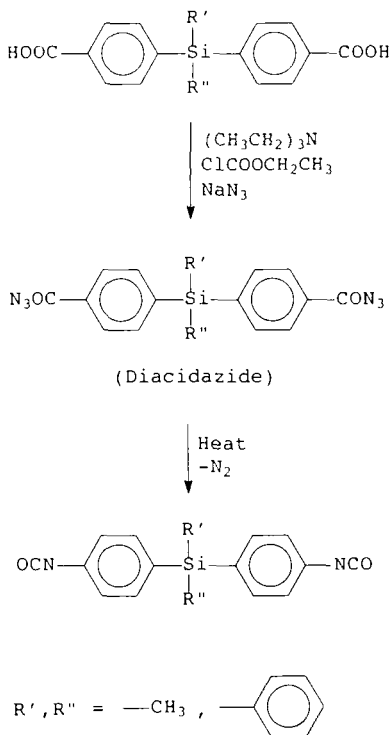
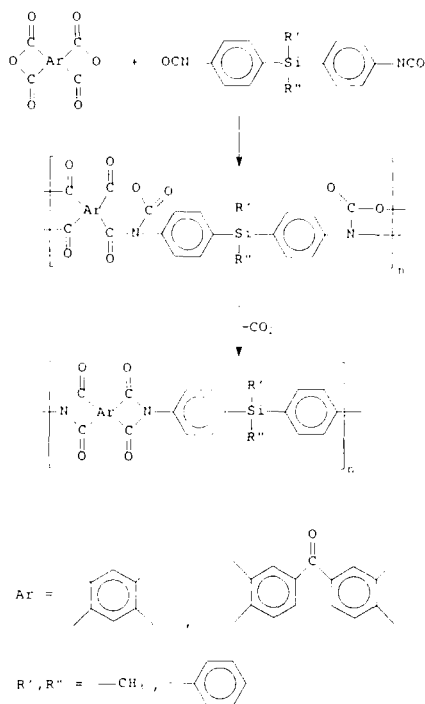


Fig. 1. Silicon-containing dianhydrides and aromatic diamines used in polyimide synthesis.



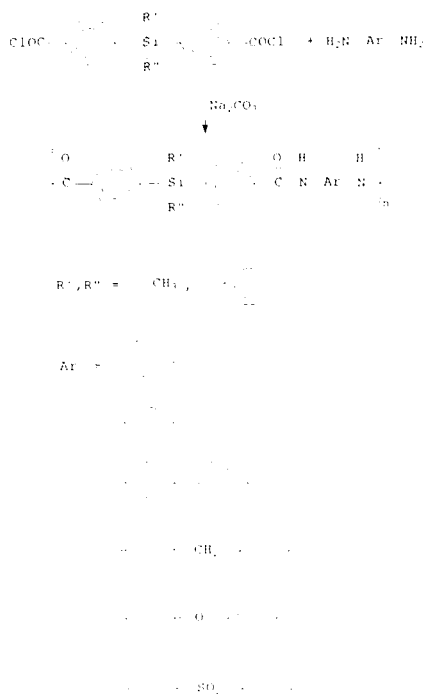
Scheme 15. Synthesis of organosilicon diisocyanates.



Scheme 16. Synthesis of organosilicon polyimides from dianhydrides and organosilicon diisocyanates.

prepared from the corresponding dicarboxylic acids via the Wienstock-Curtis modified rearrangement [125] of the diacid azide intermediate (Scheme 16) [126]. Silicon-containing polyimides were synthesized by the reaction of pyromellitic dianhydride or 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride and organosilane diisocyanates via a seven-membered ring intermediate [127]. The TGA, DTG, and differential thermal analysis (DTA) data demonstrated that polymer degradation begins at 350–420°C, with maximum degradation at 470°C; temperatures which were lower than reported for conventional polyimides synthesized with carbon analogues [128, 129].

Jadhav *et al.* [130] reported the synthesis of organosilane aramids via low-temperature, interfacial polycondensation (Scheme 17). DTA studies showed that the majority of the polymers had T_g values between 245 and 270°C, and TGA and DTG analysis established that the onset degradation temperature ranged from 380 to 400°C [130, 131]. The T_g increased and the thermal stability improved with increasing aromatic content. Most of

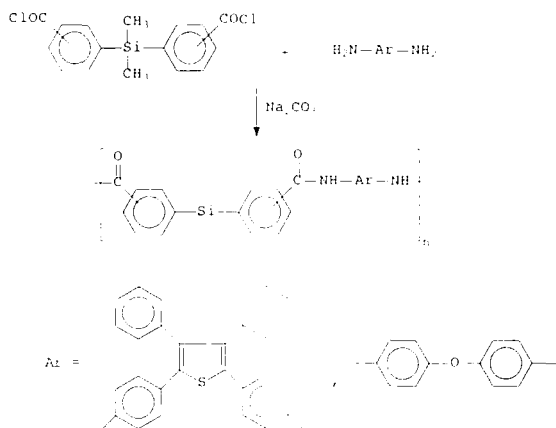


Scheme 17. Synthesis of organosilicon amides.

the aramids were soluble in polar solvents such as *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and 1-methyl-2-pyrrolidinone (NMP) [130]. Solution-cast films were tough, giving a tensile strength of 820–895 kg cm⁻² and elongation at break of 20–25% [132]. The insulation resistance, volume resistivity, breakdown voltage, dielectric constant, and dissipation factor of the films confirmed good electrical insulating properties of the aramids [132].

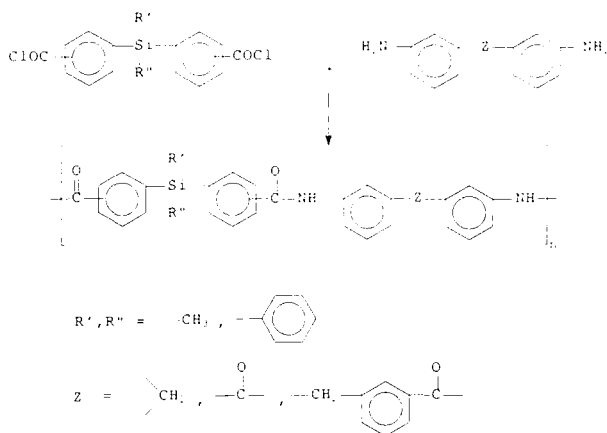
Marvel *et al.* [133] later reported the synthesis of high molecular weight aramids containing silicon and pendent phenyl groups via a low-temperature, interfacial polycondensation technique (Scheme 18). All polymers were completely soluble in DMAc, NMP, and DMF. TGA data confirmed no weight loss below 325°C in both air and nitrogen atmospheres.

Johnston *et al.* [134, 135] reported the synthesis and characterization of aromatic polyamides with benzophenone and compounds with dimethylsilyl, diphenylsilyl, phenylmethylsilyl, diarylsulfide groups, or three phenyl

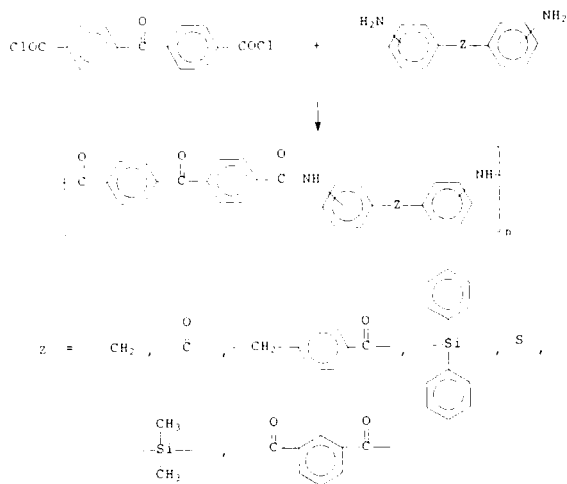


Scheme 18. Synthesis of silicon-containing aramides.

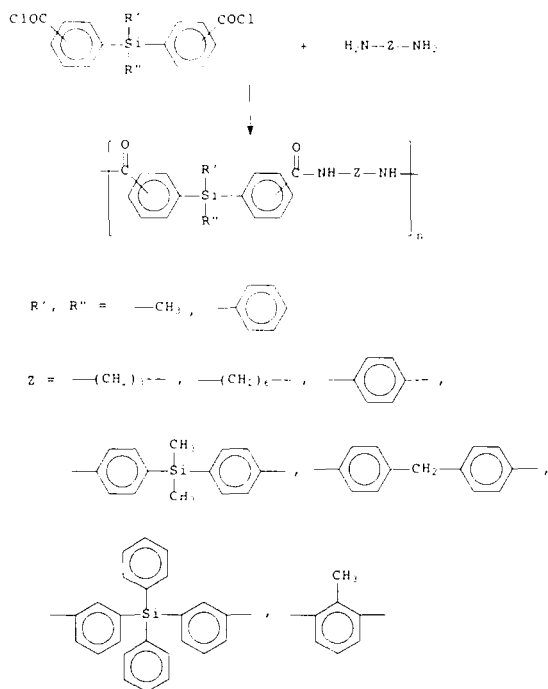
groups separated by a methylene or carbonyl group in the polymer backbone (Schemes 19 and 20). In contrast to some of their carbon and sulfur analogues, the silicon-containing polymers possessed lower T_g values and were soluble in most organic solvents such as DMAc, *m*-cresol, and *p*-cresol. However, dynamic TGA studies indicated that the thermal stability of the silicon-containing polymers was slightly inferior to that of their carbon and sulfur analogues.



Scheme 19. Synthesis of silicon-containing polyamides.



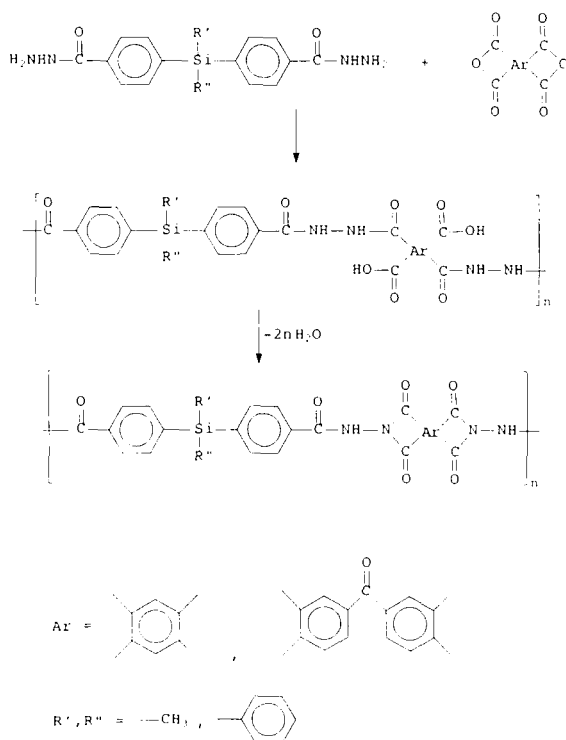
Scheme 20. Synthesis of silicon-containing polyamides.



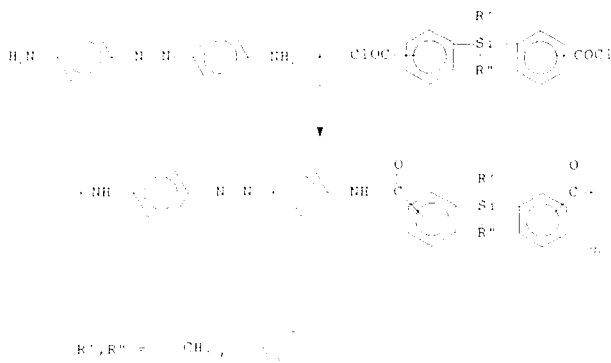
Scheme 21. Synthesis of silicon-containing polyamides.

Massey and Thames [136] reported the synthesis of dimethylsilyl-, diphenylsilyl-, and methylphenylsilyl-based polyamides (Scheme 21). All polymers were soluble in polar aprotic solvents such as DMF, DMAc, DMSO, and NMP. The TGA studies indicated that the polymers possessed a good thermooxidative stability. Differential scanning calorimetry (DSC) data showed that the methylphenyl-based polyamides gave lower T_g values than the dimethylsilyl- and diphenylsilyl-based polymers.

Jadhav [137] reported the synthesis of four new poly(amide imide)s via low-temperature, solution polycondensation of aromatic dianhydrides and organosilane dihydrazides (Scheme 22). The polymerization proceeded via soluble polyhydrazide intermediates which, on thermal cyclization, gave poly(amide imide). The solubility of the intermediate polyhydrazide in DMF, DMAc, DMSO, and NMP was attributed to interchain hydrogen bonding of the amido group. Indeed, TGA data showed that the silicon-containing poly(amide imide) polymers possessed an excellent thermal



Scheme 22. Synthesis of organosilane poly(amide imide)s.



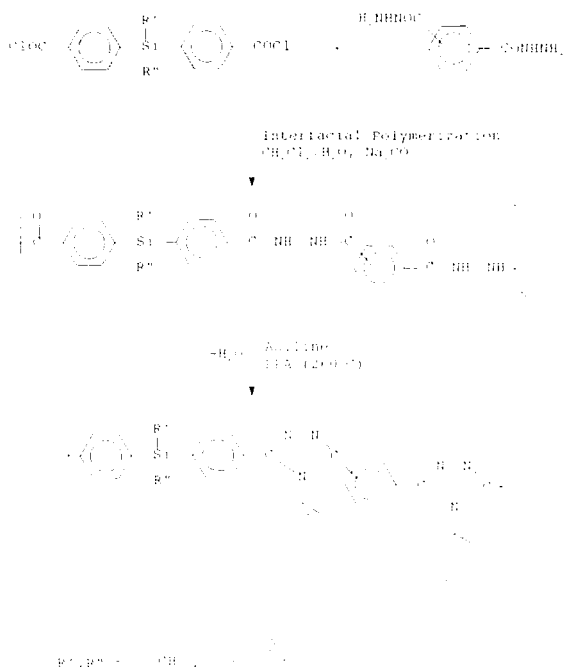
Scheme 23. Synthesis of silicon-containing azopolyamides.

stability, which increased as a function of aromatic content, yet DTA data gave no T_g or melt endotherm (T_m).

Ghatge *et al.* [138] next reported the low-temperature, interfacial polymerization of silicon-containing azopolyamides by reaction of 4,4'-diaminoazobenzene with organosilicon acid dichlorides in a methylene chloride water system (Scheme 23). The polymers were soluble in polar solvents such as DMF, DMAc, DMSO, and NMP. X-ray diffractograms of the azopolyamides presented no intense peaks, suggesting that the polymers were amorphous, while DTA studies showed no T_g or T_m values. TGA and DTG studies indicated that the polymers were stable up to 350–400 C, with maximum degradation occurring between 470 and 520 C. The thermal stability of the para-substituted polymers was superior to that of the meta-substituted polymers, and in each series, the thermal stability improved with a higher aromatic content.

Ghatge *et al.* [139] synthesized unique silicon-containing 1,2,4-triazoles by reaction of polyhydrazide precursors and aniline in polyphosphoric acid at 260 C (Scheme 24). The silicon-containing triazoles were soluble in formic and sulfuric acids. DTA studies revealed no T_g or T_m , while TGA studies indicated that the thermal stability of these polymers ranged between 350 and 400 C, with maximum degradation occurring between 530 and 570 C. The thermal stability improved with increasing aromatic character in the polymer backbone.

Vernekar *et al.* [140, 141] recently reported a low-temperature, solution condensation polymerization (Scheme 25) of polyamides and copolyamides of silicon and sulfone ether functionality. Solubility in tetrahydrofuran (THF), pyridine, nitrobenzene, DMF, DMAc, DMSO, and NMP was achieved. X-ray diffraction analysis confirmed that the

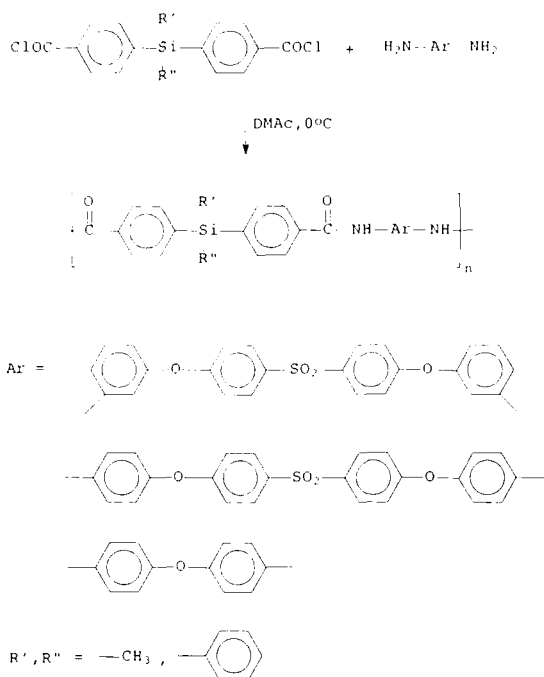


Scheme 24. Synthesis of organosilicon poly-1,2,4-triazoles.

polymers were semicrystalline, while the DTA data showed T_g values for a number of polymers. Polymer crystallinity and T_g increased with higher aromatic content and para substitution. TGA data indicated polymer stability between 400 and 450 °C, with maximum thermal degradation between 470 and 500 °C.

Yökelson *et al.* [142] modified commercially available polysulfone engineering resins with trimethylsilylchloride. Scanning electron microscopy studies demonstrated that trimethylsilyl-grafted polysulfone resins were more resistant to plasma exposure than the unmodified polymer, and the etch rate decreased from 4200 to 400 and 70 Å min at 4.3 and 11.8%, by weight, silicon incorporation, respectively. X-ray photoelectron spectroscopy data revealed that plasma exposure transformed the organic silane into a protective inorganic silicate which possibly retarded the surface etching.

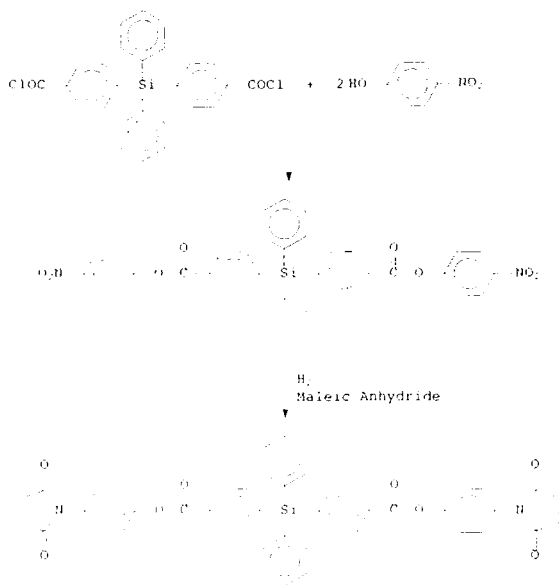
Varma *et al.* [143] reported the synthesis of diphenylsilane-based bismaleimide resins (Scheme 26) possessing an excellent thermal stability and a char yield of 51–55% at 800 °C, which is better than for any state-of-the-art bismaleimide resin. They later modified the bismaleimide resins with



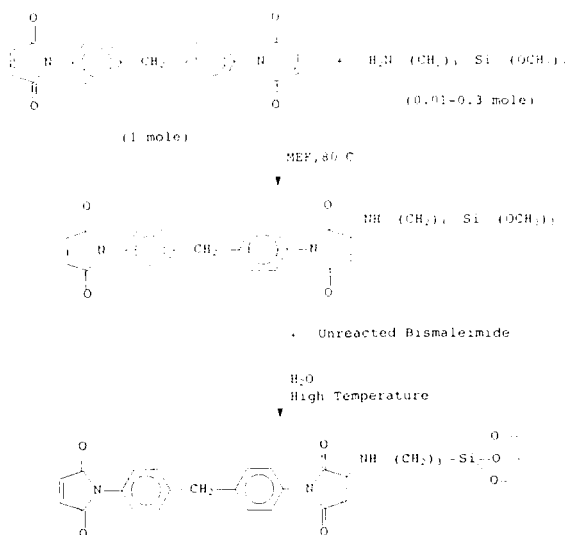
Scheme 25. Synthesis of organosilicon polyamides containing sulfone units.

γ -aminopropyl trimethoxysilanes (Scheme 27) [144, 145]. DSC data showed that T_m values of the modified bismaleimides decreased with increasing silane incorporation, and finally, the endothermic transitions disappeared. Similarly the onset, peak, and final curing temperatures decreased with increasing silane content in the polymers. The TGA data revealed that the thermal stability of these polymers was slightly lower; however, the char yield at 800°C was in the range of 45–50%. Finally, Varma *et al.* [146] reported improved thermal stability in trimethoxy-silane-modified ethyl methacrylate and butyl methacrylate and their copolymers (Scheme 28).

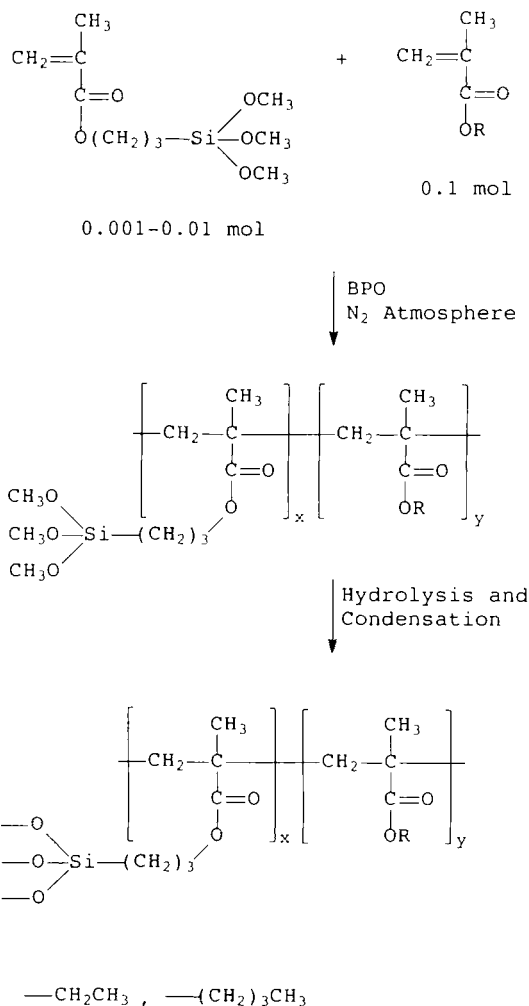
Yi *et al.* [147] reported the synthesis of semiconducting organosilane polymers of thiophene and terthiophene units (Scheme 29). The electrical conductivity of the organosilane terthiophenes (10^{-4} – 10^{-6} S/cm) was better than that of the thiophene polymers (10^{-7} S/cm) and was attributed to the higher thiophene content in the former. However, TGA data indicated that the organosilane thiophene polymers of higher silicon



Scheme 26. Synthesis of silicon-containing bismaleimides.



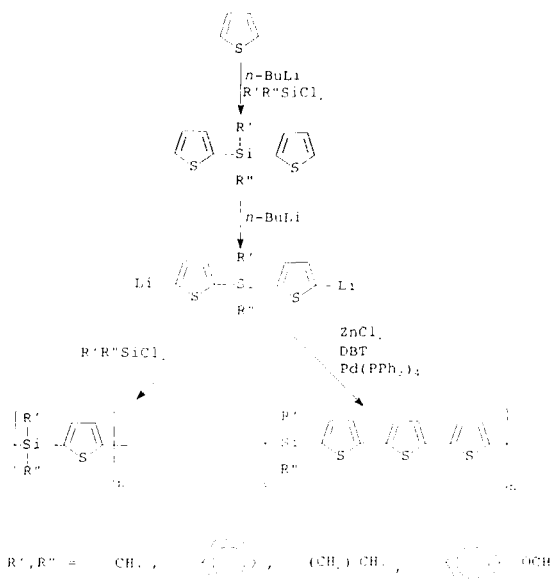
Scheme 27. Synthesis of trimethoxysilane-substituted maleimide resins.



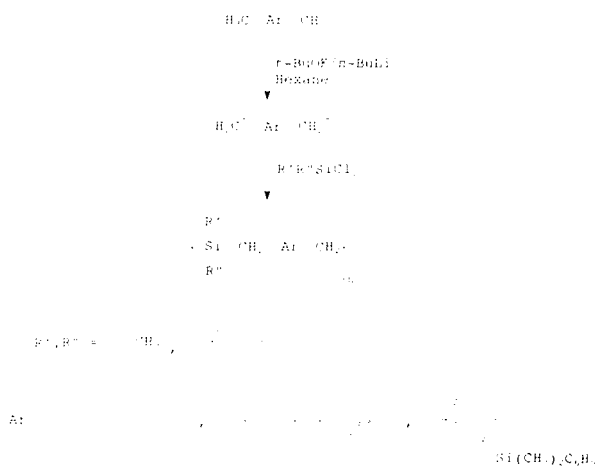
Scheme 28. Synthesis of trimethoxysilane-modified alkyl methacrylates.

content were thermally more stable (420–470°C) than the terthiophene polymers (250–280°C) and retained 40–50% weight at 800°C.

Loftus *et al.* [148, 149] focused their research on the synthesis of silicon-containing polymers via carbanion chemistry (Scheme 30). DSC studies indicated that the silicon-containing polymers possessed low T_g values and some of the polymers exhibited liquid crystalline behavior. TGA studies revealed that the polymers were thermally stable and the decomposition temperatures ranged from 375 to 540°C.



Scheme 29. Synthesis of organosilicon polymers containing thiophene and terthiophene units.

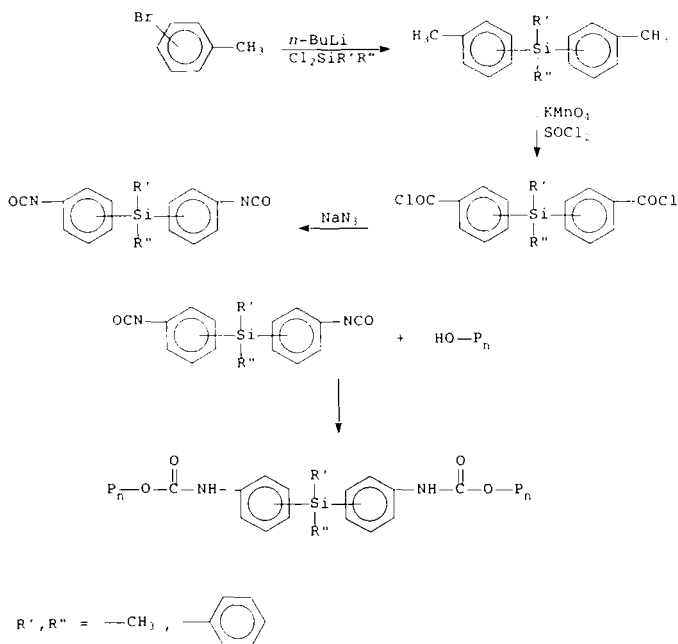


Scheme 30. Synthesis of silicon-containing polymers via carbanion chemistry.

Thames and Patel [150, 151] were the first to report the utilization of organosilicon compounds as curing agents for epoxy-based powder coatings. The silicon-containing powder coatings possessed excellent flexibility, impact resistance, adhesion, and hardness; improved solvent, electrical, and corrosion resistance; and enhanced gloss and gloss retention on weathering; and they cured more rapidly than their carbon counterparts. Similar results were found with epoxy polyester powder coatings with pendent organosilicon compounds as curing agents [152, 153].

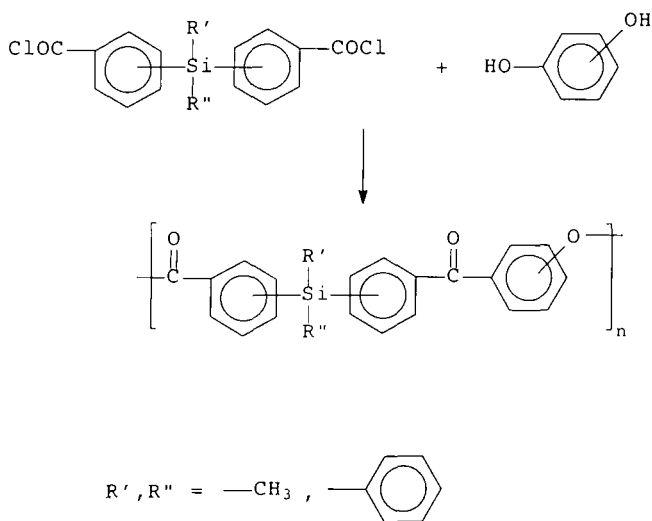
Later, Thames and Malone [154-156] reported the synthesis of silicon-containing diisocyanates and their polyurethanes (Scheme 31). All polymers were soluble in DMF, DMSO, and THF. The silicon-containing isocyanates were more reactive and the thermal stability and weather resistance of the polyurethanes were better than those of their carbon analogues. Further, no loss in hardness, impact resistance, toughness, or adhesion was observed for the silicon-based coatings.

Thames and Malone [157, 158] reported the synthesis of arylsilane polyesters and their carbon analogues via condensation polymerization of



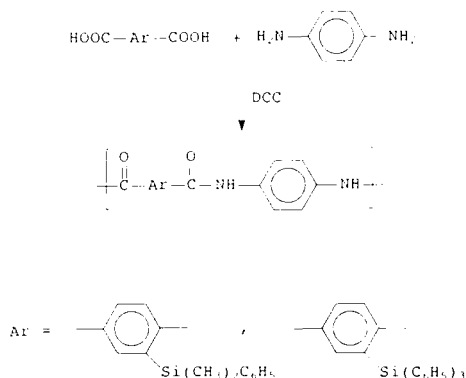
P_n = Hydroxyl Containing Acrylic Copolymer

Scheme 31. Synthesis of arylsilane diisocyanates and their polyurethanes.

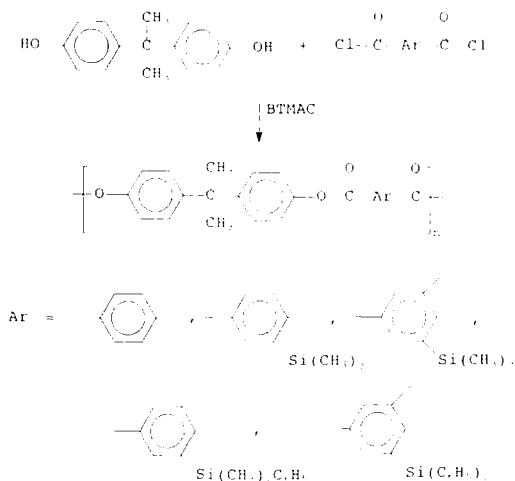


Scheme 32. Synthesis of arylsilane polyarylates.

silyl ether and various diols with silicon and carbon-based diacid chlorides (Scheme 32). The silicon-containing polymers exhibited better solubility in DMF, DMSO, NMP, THF, and chloroform (CHCl_3) than analogous carbon compounds. Solution-cast films were hard and gave excellent adhesion. TGA studies indicated that the thermal stability of the silicon-containing polyesters up to 400°C was slightly better than that of their carbon analogues.



Scheme 33. Synthesis of pendant arylsilane amids.

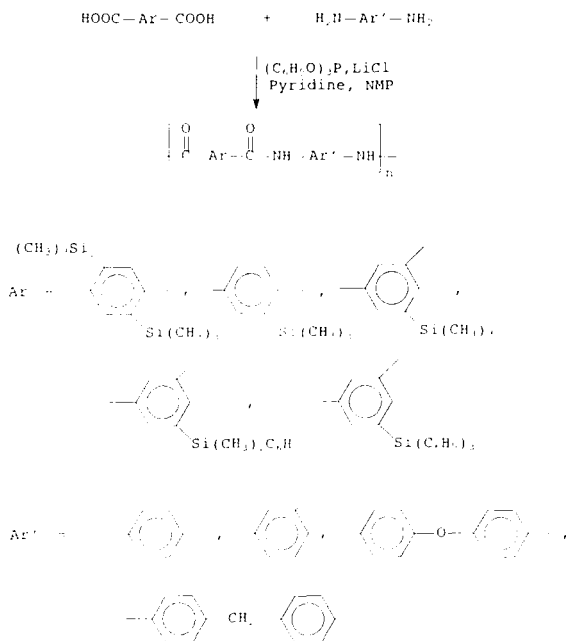


Scheme 34. Synthesis of polyarylates containing pendant silyl groups.

Thames *et al.* [159] were the first to report the synthesis of pendant arylsilane aramids via low-temperature, solution polycondensation of silicon-containing dicarboxylic acids with 1,4-phenylene diamine (Scheme 33). The arylsilane aramids were incorporated into high-performance epoxy amine coatings as molecular reinforcements. The silane-modified coatings manifested excellent tensile strength, hardness, adhesion, and impact resistance.

Choi *et al.* reported the synthesis of aromatic polyesters and polyamides with pendant silyl groups [160, 161]. The pendant organo-silane polyarylates were synthesized via room-temperature, phase transfer-catalyzed polymerization (Scheme 34) [160]. The polymers were readily soluble in common organic solvents such as chlorinated hydrocarbons, THF, and pyridine. It was possible to obtain transparent, flexible, and tough films with a good thermal stability from the polymer solutions. The tensile strength of films cast from a CHCl_3 solution was 6.0–6.7 kg mm^{-2} . TGA data confirmed a 10% weight loss between 437 and 495 °C, and the residual weight at 800 °C varied between 27 and 40%.

The silicon-containing polyamides were synthesized by direct polycondensation (Scheme 35) [161] and were soluble in polar aprotic solvents such as NMP, DMSO, and DMF. DSC studies showed T_g values (240–320 °C) for only the meta-substituted polymers. TGA showed all polymers to be highly stable, with 10% weight loss occurring between 358 and 500 °C, giving a residual weight at 700 °C between 46 and 67% under a nitrogen atmosphere.



Scheme 35. Synthesis of aromatic polyamides containing pendant silyl groups.

Stern *et al.* [162] recently studied the gas permeability and selectivity of silicon-containing polyimides to hydrogen (H_2), oxygen (O_2), nitrogen (N_2), carbon dioxide (CO_2), and methane (CH_4). The gas permeability of the silicon-containing polymers was substantially higher than that of the carbon analogues, possibly because the large silicon atoms in the backbone chain increase the polymer free volume. Their permselectivity to CO_2/CH_4 , O_2/N_2 , H_2/CH_4 , and N_2/CH_4 was slightly lower than or similar to that of the carbon counterpart.

Lu *et al.* [163] later reported the gas permeability and selectivity of silicon-containing polyimides with pendant alkyl groups to H_2 , O_2 , and N_2 , suggesting that the pendant alkyl chains increased the permeability of the small gas penetrants such as H_2 but lowered the permeability of large gas penetrants such as O_2 and N_2 . Thus, the selectivity between H_2/O_2 and H_2/N_2 increased.

Recently, Lu *et al.* [164] reported the synthesis of silicon-containing polypyrrolone polymers and copolymers for gas separation application. The silicon-containing polypyrrolones were more permeable to H_2 , O_2 , and N_2 , but the permselectivity was lower than their carbon counterpart.

However, in comparison to the silicon-containing polyimides, the polypyrrolones possessed better permeability and permselectivity.

The past four decades have seen tremendous interest, vitalization, and growth in organosilicon polymer chemistry. Silicon-containing polymers have earned a prominent place in space exploration, high-performance applications, and even cosmetics [165]. The impetus for this rapid growth lies in the fundamental change in attitude from attempting to force silicon chemistry into the existing framework of carbon chemistry to realizing and utilizing the unique characteristics that silicon provides to organic compounds. It is precisely this search for uniqueness in organosilicon chemistry that is the underlying theme of this research endeavor.

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