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Silylation in polymer chemistry

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ABSTRACT. The review is devoted to the formation and other reactions of macromolecules using silylated monomers and reagents. The methods of synthesis, reactivities, and other properties of silylated monomers of different classes are examined. Polycondensation and polyaddition processes, on the one hand, and polymerisation processes leading to the formation of macromolecules, on the other, are analysed. Reactions in the chains of polymers involving silylated monomers and reagents are also described.

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I. Introduction

The replacement of an active hydrogen atom in a wide variety of organic compounds by tris(hydrocarbyl)silyl (usually trimethylsilyl) groups makes it possible to solve effectively many synthetic problems. Silylation proved useful in peptide synthesis for the acylation of the amino-groups of α-aminoacids (the formation of an amide linkage), for the protection of carboxy- and hydroxy-groups, and also for the preparation of a wide variety of agents—acyl group donors, silylated reagents used to remove an N-protecting group, and condensing agents.[1–7] The use of silylating agents for the synthesis of esters[8] and nitriles,[9] the oxidation of alcohols in the silylated form to carbonyl compounds,[10] the synthesis of acid chlorides under neutral conditions,[11] the preparation of acyl isocyanates and isocyanates using phosgene and in a phosgene-free scheme employing CO_2,[12] and the synthesis of a wide variety of heterocycles[13] and tetra-substituted polymethylenediamines and cyclic triamines.[14] Cyclic disilazanes are used to protect amino-groups,[15] the disilyl protecting group being readily removed in an acid or alkaline medium.

Volatile liquid silylated derivatives of solid substances are convenient in analysis, for example, for the gas-chromatographic separation of a mixture of aminoacids.[16–18]

The use of silylated monomers and reagents gives rise to new possibilities also in macromolecular chemistry. Certain characteristic features of processes leading to the formation of both known and new polymers with a high molecular weight have been examined.[1,19–25] In the present review, we attempted to survey critically the available data and we supplemented them by new ones, including those concerning both polycondensation and polymerisation reactions as well as reactions in polymer chains.

II. Synthesis of silylated monomers and their properties

Synthesis of silylated Monomers

The silylation of organic compounds containing a wide variety of functional groups has been described in detail in a number of reviews.[1,2,5] Chlorotris(hydrocarbyl)silanes, usually chlorotrimethylsilane (CTMS), are common and effective silylating agents. Silylation using these compounds proceeds under mild conditions in organic solvents and with high yields. However, hydrogen chloride, capable of catalysing side reactions, is evolved in these processes, which necessitates the employment of an acceptor—a tertiary amine (B_N):

$$R-XH + Me_3SiCl \xrightarrow[-B_N\cdot HCl]{B_N} R-X-SiMe_3,$$

where X = NH†, O, etc. and B_N is a tertiary amine.

Chlorotrimethylsilane is used successfully for the preparation of silylated diamines,[26–28] diols (usually bisphenols and aromatic hydroxyacids,[29–39] bisthiophenols,[40] and bis-*o*-aminophenols.[41,42]

Dialkyl(trialkylsilyl)amines (usually Me_3SiNMe_2 and Me_3SiNEt_2) are convenient silylating agents. Silylation with their aid can be carried out without an organic solvent with evolution of the readily removable volatile dialkylamines:

$$RXH + Me_3SiNR'_2 \longrightarrow RXSiMe_3 + HNR'_2,$$

where R′ = Me or Et.

The silazanes indicated are used to silylate diamines.[43] They are especially conveneient in the treatment of aliphatic diamines in a salt form;[4] the role of the acid acceptor in such processes is assumed by the evolved dialkylamine:

$$R-NH_2\cdot HCl + Me_3SiNR'_2 \longrightarrow RNHSiMe_3 + HNR'_2\cdot HCl\downarrow.$$

Diethyl(trimethylsilyl)amine proved to be effective also in the silylation of bisaminophenols.[45–47]

Hexamethyldisilazane, evolving gaseous ammonia during the reaction, is a readily available silylating agent. However, it is not a very active donor of the trimethylsilyl group and for this reason it is

† In the case of primary aromatic amines, only one hydrogen atom is substituted by the trimethylsilyl group under the conditions indicated (see below).

particularly useful in the silylation of compounds containing an acid proton, for example, phenol and carboxylic acids:[48,49]

$$HOArOH + Me_3SiNHSiMe_3 \longrightarrow Me_3SiOArOSiMe_3 + NH_3\uparrow$$

or

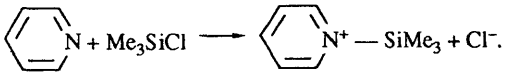
$$HOOCRCOOH + Me_3SiNHSiMe_3 \longrightarrow Me_3SiOCORCOOSiMe_3 + NH_3\uparrow.$$

O-Trimethylsilyl *N*-trimethylsilylcarbamate, in the reaction of which with alcohols gaseous side products are evolved, is an effective silylating agent of hydroxylated monomers:[50,51]

$$2ROH + Me_3SiNHCOOSiMe_3 \longrightarrow 2ROSiMe_3 + CO_2\uparrow + NH_3\uparrow.$$

N,O-Bis(trimethylsilyl)amides of carboxylic and carbonic acids [especially *N,O*-bis(trimethylsilyl)trifluoroacetamide], which are powerful donors of the trimethylsilyl group, are also promising.[2]

We may note that in many instances the silylation of monomers, particularly aromatic diamines, is carried out in solutions in inert organic solvents using a wide variety of catalysts [for example, $(NH_4)_2SO_4$,[2,43] acids, etc.[2]]. Pyridine, forming with chlorosilane a quaternary silylammonium complex (a silyl group donor), also exhibits a catalytic acitivty:[2]



Imidazole and heterocycles of similar structure are also effective agents for the transfer of the silyl group.[2]

It is essential to bear in mind that the silylation of aliphatic diamines proceeds so readily that exhaustive silylation of primary amino-groups is possible. This can lead in its turn both to the deactivation of the amino-groups and to the breakdown of stoichiometry in polycondensation (because disilylated amino-groups may be present in an indefinite amount) and to the formation of cross-linked polymers (see below).

The introduction of a second silyl group into aromatic amines (in contrast to aliphatic amines) constitutes a fairly difficult problem, which can be solved, for example,[52] using the corresponding lithium derivatives:

$$Ar-NH-SiMe_3 \xrightarrow[-C_4H_{10}]{C_4H_9Li} Ar-\underset{\displaystyle Li}{\underset{|}{N}}-SiMe_3 \xrightarrow[-LiCl]{Me_3SiCl} Ar-N(SiMe_3)_2.$$

Ethylmagnesium bromide can also be used for this purpose:[47]

$$Ar-NH_2 \xrightarrow[-2C_2H_6]{2C_2H_5MgBr} Ar-N(MgBr)_2 \xrightarrow[-MgBr_2,\ MgCl_2]{2Me_3SiCl} Ar-N(SiMe_3)_2.$$

Sodium iodide is used as the catalyst in the synthesis of silylated enolic forms of carbonyl compounds (silyl ethers of phenols—polymerisation monomers):[53]

$$CH_3-CO-R + Me_3SiCl + NaI \xrightarrow{CH_3CN} CH_2=\underset{\displaystyle O-SiMe_3}{\underset{|}{CR}}.$$

Properties of silylated monomers

The majority of silylated bisnucleophiles are liquid or comparatively low-melting substances which can be readily purified by vacuum distillation or (more rarely) recrystallisation. Silylation improves the solubility of the monomers, which significantly facilitates the choice of the solvent and polycondensation at high solution concentrations.

The silylated monomers, especially diamines, are resistant to the action of light and atmospheric oxygen.

In the condensed phase, the silylated monomers are fairly resistant also to atmospheric moisture, which may be due to their hydrophobic nature. However, in solutions in a polar organic solvent they readily split off the silyl group in the presence of traces of water (or impurities containing an active hydrogen atom). This leads to the "self-drying" and "self-purification" of the reaction system, which is important in some cases, for example in polycondensation in the vapour phase with silylated monomers of especially active biselectrophiles (acid dichlorides, bischloroformates, dianhydrides, etc.), which are capable of entering into side reactions with hydrogen-containing impurities. This is apparently one of the advantages of the silylated monomers in polycondensation ("silylated polycondensation"). On the other hand, in polymerisation silylation makes it possible to carry out processes which are difficult to achieve using the initial hydrogen-containing precursors.

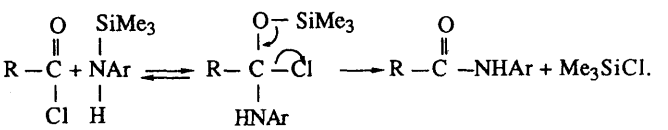
The introduction of a trimethylsilyl group into amino-groups of both aromatic and aliphatic amines lowers their electron-donating activity, which is attributed to the $(d-p)_\pi$ interaction via the Si—N bond.[54–56] An increase in the number of trimethylsilyl groups at the nitrogen atom lowers the basicity of amines still further.‡[57]

The decrease in the electron-donating activity of the silylating amino-groups together with the steric factors due to the replacement of the hydrogen atom by the bulky dimethylsilyl group lead to a decrease in the nucleophilic reactivity of aliphatic amines.[58]

On the other hand, an increase in reactivity has been noted for heterocycles, aromatic amines, and acid amides (the so called silyl activation of the nitrogen atom), at any rate in relation to acid chlorides,[1,13,59–62] which, however, requires more rigorous proof with the aid of kinetic measurements.§

The increase in the reactivity of aryl-*N*-dislylamines is attributed to a two-stage addition-elimination mechanism:[61]

Scheme 1

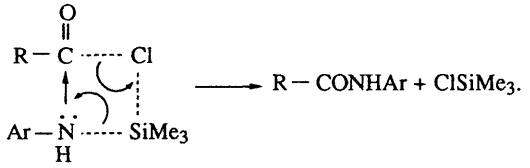


‡We may note that, in the determination of the basicity of silylamines by the titration method, special care must be excercised, because the silyl group can be transferred to the acid under the influence of protic acids, which has been indicated in particular by the results of NMR studies.[43]

§This is valid at least for monosilylated arylamines. One of the authors has established that the introduction of a second trimethylsilyl group actually entails a decrease in the activity of the amine to such an extent that it no longer reacts at an appreciable rate with benzoyl chloride on heating to 100 °C.

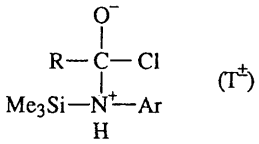
This uneconomical two-stage mechanism of the reaction occurring in the elimination stage with formation of a four-membered transition complex, is unlikely.¶ From our point of view, a single-stage concerted mechanism, similar to that proposed by Birkofer et al.,[60] is more likely. It involves the formation of a Cl–Si bond in the first stage [taking into account the increase in the reactivity of the functional groups in which the heteroatom–silicon bond is sufficiently loosened—ArNH–$SiMe_3$ and ArS–$SiMe_3$ (see below)] and further propagation of the reaction via the following transition state:

Scheme 2



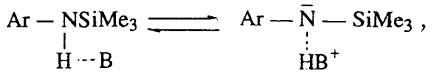
This mechanism of the reaction with acid chlorides may be supported indirectly by, for example, the lower, compared with free bases, reactivity of silylated alkylamines in relation to activated ethers.[58] In this case, the reaction apparently proceeds via the "traditional" pathway with formation of a tetrahedral zwitter-ionic intermediate or via a "reactant-like" transition state.[63,64] Under these conditions, silylation leads to a steady decrease in the nucleophilic reactivity of the amines

The formation of the silylated tetrahedral zwitter-ionic intermediate on interaction of arylsilylamines with acid chlorides, i. e.

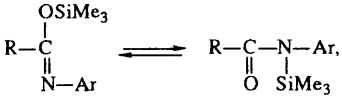


(the formation of $T^{\pm}$ is postulated in the interaction of arylamines with acylating agents[63]), which can subsequently rearrange to the neutral *O*-silylated tetrahedral intermediate see Scheme 1), is also unlikely because of steric factors.

The increase in the reactivity of the silylated primary arylamine can also be associated with the increase in the mobility of the NH proton[1] due to the effect of the electron-accepting silyl group and hence the increase in the nucleophilicity of the nitrogen atom in the presence of a proton acceptor:



¶ Bearing in mind the high oxygen affinity of silicon, in the operation of such a reaction mechanism one would expect the elimination of HCl (especially in a proton-accepting medium[1]) and the formation of a silylated amide:



which according to certain data either does not occur[62] or occurs extremely rarely.[64]

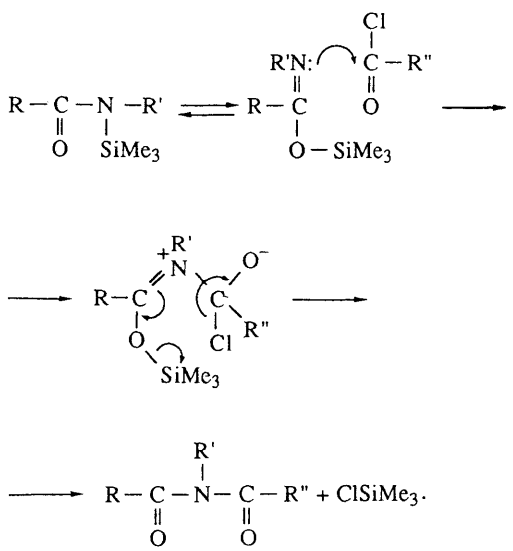
where B is the proton acceptor (solvent molecules, the amine itself, etc.).

In order to make finally sure about the "silyl activation" of aromatic amines and to give preference to one of the mechanisms examined, it is useful to compare the kinetics of the interaction of arylamines and their silylated analogues with acid chlorides and other electrophiles not containing a halogen (acid anhydrides, activated ethers, isocyanates, etc. in various media—proton-accepting and proton-inert).

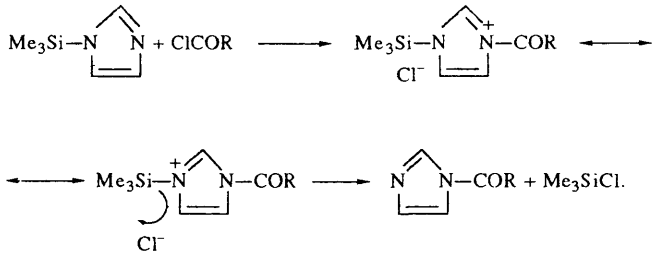
The "silyl activation" of the amide (urea) linkage has been convincingly demonstrated in a number of studies.[1,59,62] In this case there is no need for direct kinetic investigations, because the usual amides are hardly acylated by acid chlorides in the absence of tertiary amines, while silylated amides readily give rise to the corresponding acyclic imides.

The nature of the "silyl activation" of amides is in all probability somewhat different and is associated with the involvement in the reaction of the tautomeric *O*-silylated form of the amide:†

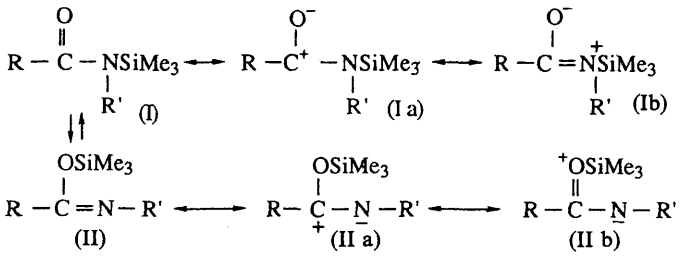
Scheme 3



† The tautomeric mechanism operates, for example, in the alkylation of heterocycles in the silylated imidol [hydroxyimide?] form.[1] It may be that a complex mechanism also underlies the "silyl activation" of the imidazole nitrogen atom and heterocycles of similar structure:[60]



It is known that silylated amides can exist in two tautomeric forms[2] (p. 63):



When R′ = alkyl, the *N*-silylated form (I) is thermodynamically preferable owing to the amide resonance [varieties (Ia) and (Ib)]. On the other hand, if R′ is capable of stabilising the negative charge on the nitrogen atom [for example in the case where R = CH_2=CH, Ph, etc.; varieties (IIa) and (IIb)], then the contribution of the *O*-silylated form (II) increases appreciably. We believe that the latter is kinetically more significant in amide acylation reactions.

The silylation of hydroxy-groups has different effects on their reactivity depending on the nature of the adjoining group. Whereas silylated alcohols readily interact with acid chlorides under mild conditions,[1,29,30] the corresponding phenols react only above 100–140 °C.[30] On the other hand, the reactivity of S-containing analogues—silylated thiophenols—approaches that of silylated amines.[40] This fact may indicate the importance of the effect of the degree of loosening of the heteroatom–silicon bond on the reactivity of the silylated nucleophile. Thus, when the nucleophilicity of the functional groups is reduced, it is possible to introduce electrophilic substituents into the molecule. For example, it is possible to obtain stable aliphatic diamines containing alkyl ester groups or hydroxyl-containing compounds with acid chloride groups, to carry out reactions with a high selectivity, etc. (see below), and, if necessary, to carry out the selective desilylation of the alcoholic and phenolic hydroxy-groups.[65]

III. Synthesis of polymers

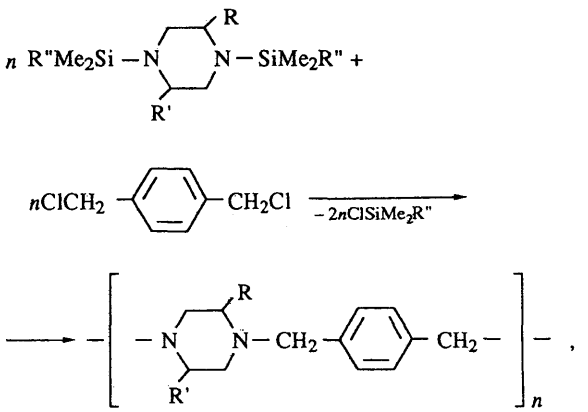
The polycondensation processes involving monomers with N–Si and O(S)–Si bonds are analysed separately below. Next to be considered are polycondensation processes *in situ* in the presence of silicon compounds, including silicon-containing condensing agents as well as polymerisation processes with participation of silylated initiators and monomers. Finally, examples of the modification of macrochains by their silylation are presented.

(a) Polycondensation

The new polycondensation methods of synthesis of polymers are based mainly on nucleophilic substitution reactions (or reactions of the type of nucleophilic substitution) with participation of silylated bisnucleophiles.

Syntheses Based on Monoers with a N–Si Bond

Polyamines. One of the first heterochain polymers synthesised using silylated monomers were polyamines obtained by Klebe[26] by the reaction of *N,N′*-disilylated piperidines with *p*-xylylene dichloride in bulk at 100 °C:

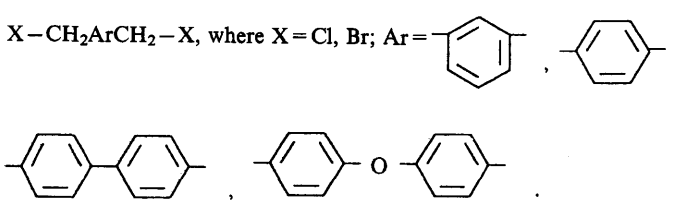


$[\eta] = 0.77 - 1.97$ dl g^{-1},

where R = R′ = H or Me or R = H and R′ = Me; R″ = Me or Ph.

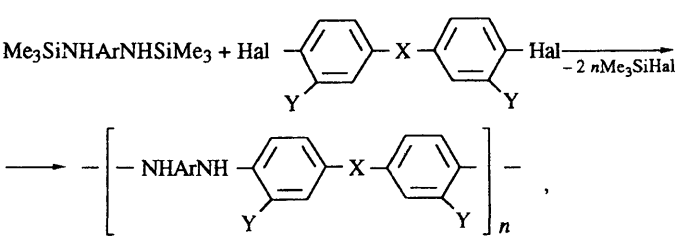
The polyamine with the highest molecular weight (M_n = 40 000—determined by osmometry), soluble in organic solvents, was obtained with R = H, R′ = Me, and R″ = Ph. It was shown that the reaction is accelerated (by a factor of 5–10) in the presence of ammonium salts and (to a lesser extent) tetramethylene sulphone (sulpholan).

Klebe[26] used in this process silylated *N,N′*-dimethylethylenediamine and alkylene halides:



Quaternisation of the polyamines synthesised with methyl iodide afforded polyelectrolytes soluble in polar solvents and water, while quaternisation with diiodopropane yielded cross-linked membranes insoluble in water.

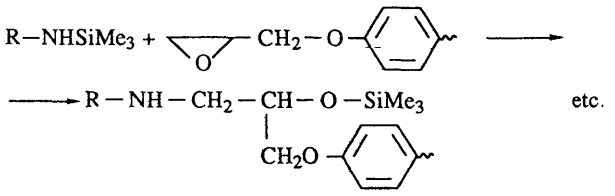
An aromatic nucleophilic substitution reaction with similar essential features has been used[66,67] to synthesise aromatic polyamines ($\eta_{init} \leqslant 0.93$ dl g^{-1}):



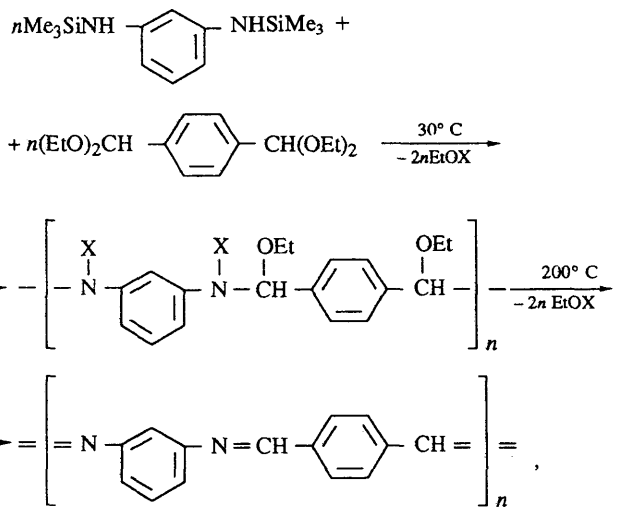
where X = NO_2 or CO, Hal = Cl or F, and Y = H or NO_2. The reaction was carried out in dimethyl sulphoxide (DMSO) at 150 °C.

The authors established that only fluorides are reactive and that the process is catalysed by CsF. Aromatic chlorides (Hal = Cl) are passive in the reactions but are appreciably activated after the introduction of a nitro-group in the *ortho*-position (Y = NO_2).

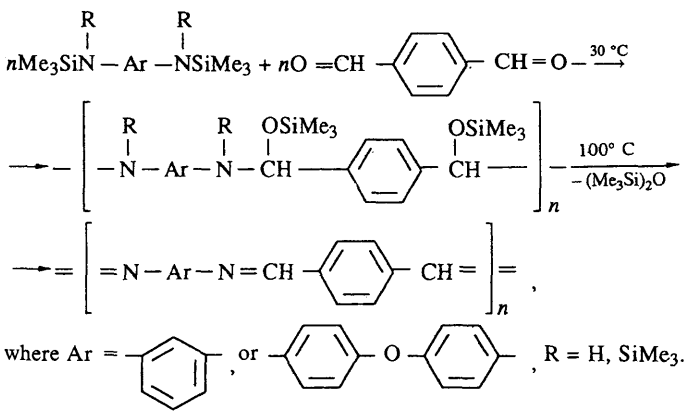
Silylamines can also be alkylated with the aid of oxiranes.[68] This process has been used to harden epoxide resins:[69,70]



Polyazomethines. Using silylated diamines as the initial monomers, high-molecular-weight polyazomethines were obtained, which made it possible to overcome difficulties associated with the insolubility and infusibility of their forms unsubstituted in the aromatic ring.[71,72] Either diacetals[71] or directly the dialdehydes[72,73] were used as the biselectrophiles:



where X = H or $SiMe_3$;

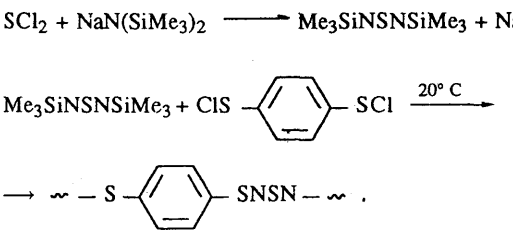


where Ar = , R = H, $SiMe_3$.

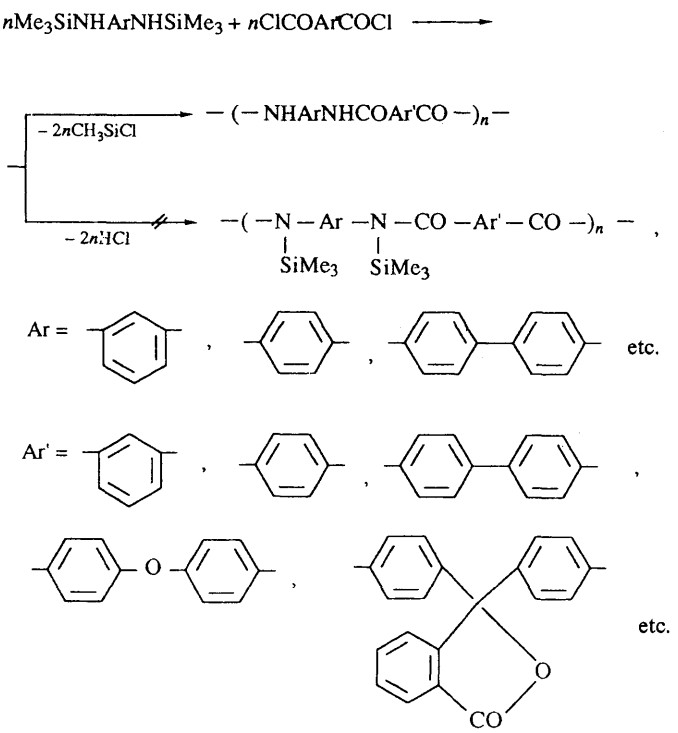
and R = H or $SiMe_3$.

The soluble film- and fibre-forming polymers formed in the first stage are converted into insoluble polyazomethines as a result of thermal β-elimination. It is of interest that in the second version fully silylated diamines were used together with *N,N'*-bistrimethylsilylated primary diamines in the reaction with the dialdehyde. As mentioned above, such fully silylated diamines should be appreciably less reactive. However, the lack of information about the molecular weights of the polyazomethines synthesised makes it impossible to decide that a particular silylated form of the diamine is preferable.

Polythiazyls. A polyconjugated electrically conducting poly-*p*-phenylenethiazyl was synthesised by a reaction similar to that for the formation of polyamines (see above).[74] Using Na-silylamide, a monomer was formed initially and was then used in polycondensation with *p*-phenylenebissulphenyl chloride in an inert solvent:



Polyamides. Since the beginning of the 1970's, silylated diamines began to be used also for the synthesis of polyamides.[75] High-molecular-weight arylamides were obtained by the polycondensation of silylated aromatic diamines with acid dichlorides in amide solvents under mild conditions:[75,76]



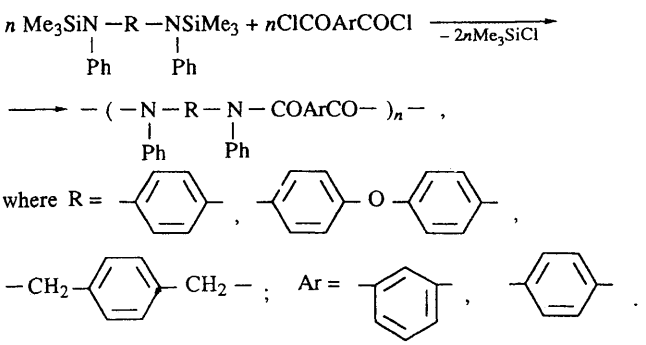
It was shown that the reaction proceeds virtually with elimination of Me_3SiCl and the formation of a "normal" polyamide. The absence of silicon from the polyamides and their solubility in organic solvents (i.e. the absence of intermolecular cross-links—see below) indicate that the alternative pathway involving the elimination of HCl and the formation of a silylated polyarylamide hardly operates.‡

Bearing in mind the increased solubility of the silylated monomers in the solvent used, it is possible to carry out the polycondensation in more concentrated solutions.[75] An advantage of this polyamide formation scheme is that it leads to the formation of polyamides with higher molecular weights ($\eta_{log} \leqslant 7.4$ dl g^{-1}) than in the case where free diamines are used ($\eta_{log} \leqslant 3.0$ dl g^{-1}).[76]

It is believed[76] that this is associated with the higher reactivity of the silylated diamine and hence with the higher rate of polycondensation, characterised by the time variation of the viscosity of the polyamides. However, these data are insufficient to draw unambiguous inferences about the rate of the process and it is essential to carry out direct kinetic studies, particularly since analysis of the numerous results of the investigation of the low-temperature polyamide formation does not provide grounds for such a conclusion. The formation of polyarylamides with higher molecular weights may be due to the following factors: (1) the greater purity and resistance to oxidation of the silylated aromatic diamines; (2) the absence of salt formation (protonation of the amino-group by HCl); (3) "self-purification" of the reaction system (see above). In the absence (more precisely on sharp reduction) of the contribution of side reactions, the rate of increase in the viscosity of the polyamides rises.[78]

The possibility of carrying out the process in inert solvents ($CHCl_3$, CH_3CN, $PhNO_2$), which do not exhibit a proton-accepting activity (this is essential in the formation of polyamides using free aromatic diamines), should be included among the advantages of the "silyl polyamide formation".

The "silyl polyamide formation" reaction has also been used to obtain high-molecular-weight ($\eta_{log} \leqslant 2.21$ dl g^{-1}) *N*-phenylated polyamides[27,79] from relatively unreactive bisphenylenediamines:[80]



‡It is known that chlorosilane is split off in an inert medium, while in the presence of a proton acceptor (triethylamine) the elimination of HCl and the formation of a silylated amide is actually observed.[1] In weak bases (forming, however, strong hydrogen bonds[77]), this pathway is nevertheless probably possible (see below). Apparently the silylated arylamides formed do not interact with terminal acid chloride groups and are readily desilylated by traces of moisture or HCl, which is not bound to the amide solvent quite so strongly as to triethylamine.

The reaction was carried out in sulpholan at elevated temperature (80–200 °C depending on R).

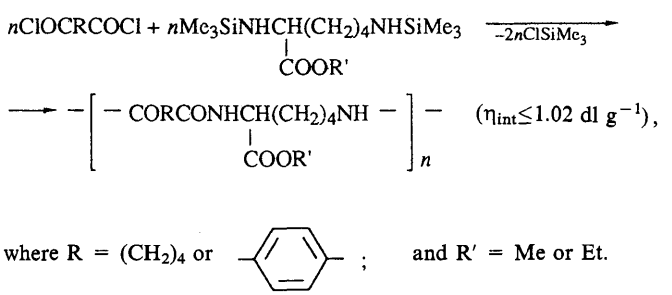
We may note that the ability of the system to undergo "self-purification" and the use of an acid solvent are especially important in the synthesis of *N*-phenylated arylamides, because the reaction proceeds under fairly severe conditions and *N,N*-diaryl-substituted polyamides, which belong to the category of "activated amides",[81] can interact destructively with a wide variety of impurities, especially basic ones.

Silylation has been successfully used for the synthesis of polyamides from other relatively unreactive monomers—the weakly electrophilic perfluroisophthaloyl chloride[82] and the sterically hindered perfluoro-*m*-phenylenediamine.[83] This clearly indicates the silyl activation of aromatic amino-groups, although we repeat that direct kinetic measurements are essential for final conclusions.

The formation of high-molecular-weight polyamides with participation of weakly basic highly sterically hindered silylated secondary aromatic diamines, where direct lateral attack[84] on the carbonyl carbon atom with formation of a tetrahedral intermediate (Scheme 1) is unlikely, may serve as evidence in support of an alternative mechanism (see Scheme 2).

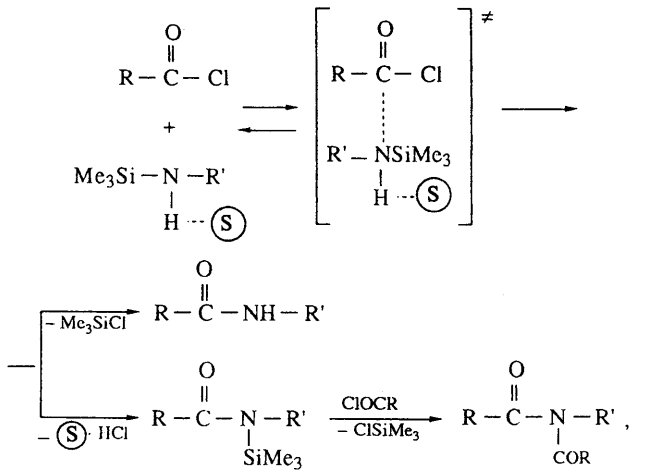
In order to obtain fine arylamide film coatings, the relatively high volatility of silylated aromatic diamines in their reaction with acid dichlorides involving deposition from the gas phase has been used successfully.[85] The advantage of the silylated diamines over the free bases consists in this case also in the ease of removal of the neutral, volatile chlorotrimethylsilane.

High-molecular-weight polyamides with functional group substituents have been obtained by the reaction of acid dichlorides with alkyl esters of N^{α},N^{ε}-bis(trimethylsilyl)lysine in an organic solvent:[44]



It is essential to note that this reaction is accompanied by the formation of a cross-linked polymer (particularly vigorous in the case of an aliphatic acid dichloride), which may be due to the partial formation of a trimethylsilylated amide in a solvent capable of forming strong hydrogen bonds [dimethylacetamide (DMA),

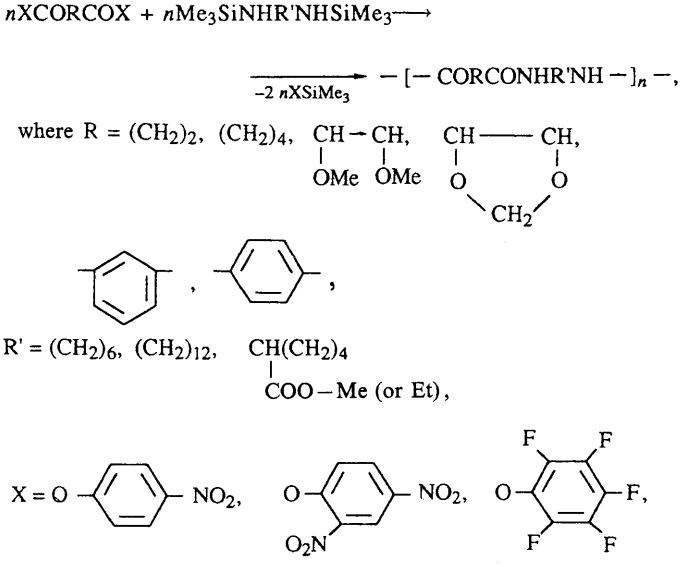
hexamethylphosphoramide (HMPA)] (see above) and its subsequent interaction with the acid chloride group:

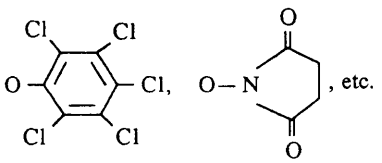


where (S) = solvent molecule.

The proposed mechanism of the formation of intermolecular bonds is supported by the synthesis of a cross-linked polyamide also in the case of an aromatic acid dichloride, which, in contrast to aliphatic acid dichlorides[86] with a "normal" amide linkage, does not react under the conditions investigated. The reaction using an aromatic acid dichloride at a reduced temperature (−10 − 0 °C) leads to the formation of a soluble polyamide.

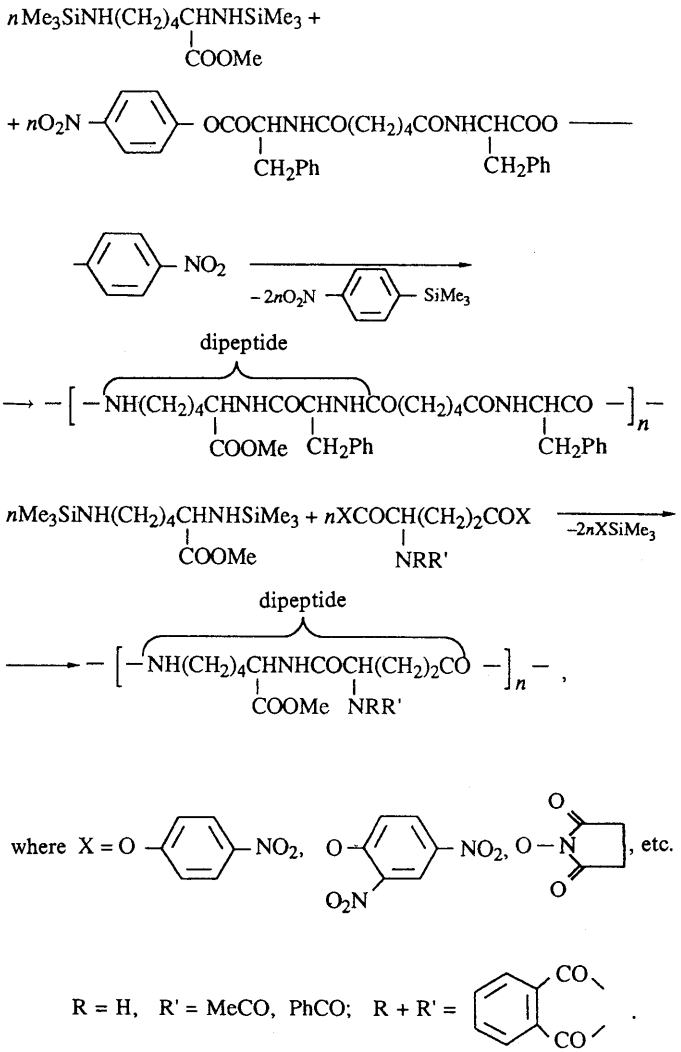
Yet another piece of evidence is the synthesis of soluble polyamides from an aliphatic acid dichloride and an alkyl ester of N^{α},N^{ε}-bis(trimethylsilyl)lysine in solvents with a weak proton-accepting capacity (acetonitrile, dichloroethane). Apart from acid dichlorides, a wide variety of activated dicarboxylic acid diesters react vigorously with trimethylsilyated aliphatic diamines. Such interaction under mild conditions in a wide variety of organic solvents, including inert ones, leads to the formation of high-molecular-weight (of the order of 40 000 − 60 000) polyamides:[44,87−90]



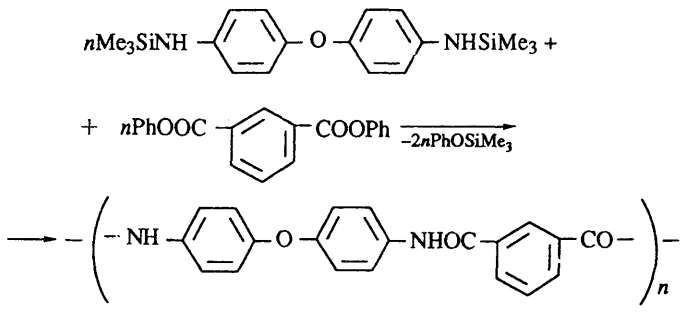


In this case, the role of the desilylating agent at different stages of the reaction can be fulfilled by the evolved acid hydroxylated compound HX[58,91] — a vigorous acceptor of the trimethylsilyl group,[2] which leads to the synthesis of the "normal" polyamide. This factor appreciably facilitates the synthesis of linear polyamides based on silylated aliphatic diamines.

"Activated silylated" polycondensation has been used successfully to obtain polyamides with functional-group substituents from lysine[44] and can be useful for the introduction into the macrochain of fragments carrying additional functional groups, for example dipeptide units capable of undergoing enzymic cleavage:[92,93]

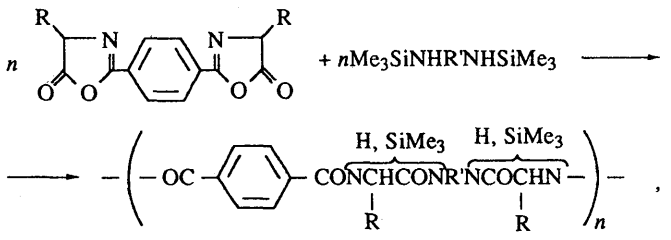


We may note that under more severe conditions (100 °C) the non-activated diphenyl isophthalate enters into the reaction with the silylated diamine (even a comparatively unreactive aromatic diamine):[94]



(η_{log} = 0.43 dl g^{-1} in DMA).

High-molecular-weight ($\eta_{init} \leqslant 0.68$ dl g^{-1}) film-forming polyamides have also been synthesised by the reaction of silylated diamines with bisazlactones in DMA (in a number of instances in the presence of 5% of LiCl) at 70–100 °C:[95]



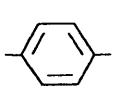
where R = Me, $(CH_2)_2Me$, $CH(Me)_2$, $(CH_2)_3Me$, $CH_2CH(Me)_2$, CH(Me)Et, $(CH_2)_2SMe$, CH_2Ph;

R' = $(CH_2)_6$, $CH(CH_2)_4$ (COOMe (or Et)).

This polyadditive scheme, leading to silylated polymers (cf. the synthesis of polyurethanes described below) has been used to obtain dipeptide-containing polyamides from L-lysine. Such polymers are promising as biodegradable temporary implants capable of undergoing bioerosion.[96]

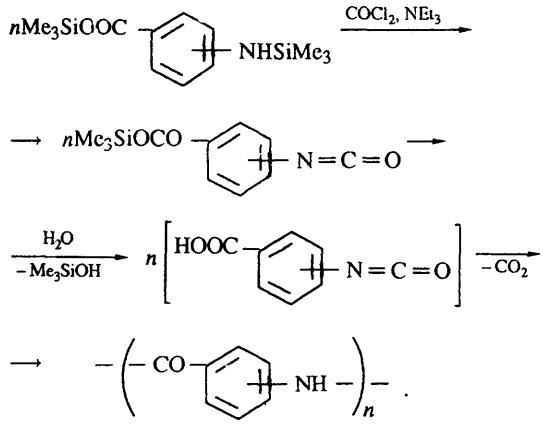
A novel method of synthesis of polyamides (with yields up to 94%) has been proposed by Kozyukov et al.[97] It consists in the high-temeprature AB-polycondensation in solution in *N,O*-disilylated aminoacids (glycine, *p*-aminobenzoic acid):

$$n\text{Me}_3\text{SiNHRCOOSiMe}_3 \xrightarrow[\text{DMF}]{150\ ^\circ\text{C}} -(-\text{NHRCO}-)_{\bar{n}} + n(\text{Me}_3\text{Si})_2\text{O},$$

where R = CH_2, .

The process takes place in a polar medium and is catalysed by Lewis acids. This factor is apparently in fact responsible for the possibility of obtaining and purifying by vacuum distillation at fairly high temperatures disilylated aminoacids without appreciable self-condensation.

An alternative method, proposed by the same authors, involves the preliminary treatment of the *N,O*-disilylated monomer with phosgene:[98]



An essentially similar process has been used also in AA–BB-polycondensation to obtain a high-molecular-weight polyamide-6,6 without the intermediate formation of a salt AX;[99] under these conditions, one of the monomers can be used in the non-silylated form:

$$n\text{YHN}(CH_2)_6\text{NHY} + n\text{Y'OCO}(CH_2)_4\text{COOY'} \xrightarrow{220\text{–}250\ ^\circ\text{C, in bulk}}$$

$$\longrightarrow -(-\text{NH}(CH_2)_6-\text{NHCO}-(CH_2)_4-\text{CO}-)_n-,$$

where (a) Y = H and Y' = $SiMe_3$, (b) Y = $SiMe_3$ and Y' = H, and (c) Y = Y' = $SiMe_3$.

Polyurethanes. The processes leading to the formation of polyurethanes using silylated diamines are in many respects similar to those involved in "silylated polyamide formation".

Film-forming ($\eta_{int} \leqslant 0.48$ dl g^{-1}) linear polyurethanes have been obtained by the polycondensation of a silylated diamine with bischloroformates in dimethylacetamide (DMA) under mild conditions (0–20 °C):[100]

$$n\text{Me}_3\text{SiNH}(CH_2)_6\text{NHSiMe}_3 + n\text{ClCOOAlkOCOCl} \xrightarrow{-2\ \text{Me}_3\text{SiCl}}$$

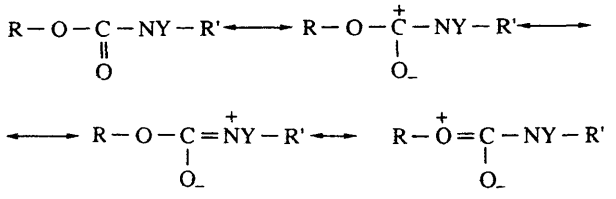
$$\longrightarrow -(-\text{NH}(CH_2)_6\text{NHCOOAlkOCO}-)_n -$$

Alk = $(CH_2)_3$, $(CH_2)_2CH(Me)$, etc.

The reaction of silylated diamines and bischloroformates, which occurs effectively in solution under mild conditions, leads to interesting possibilities in the synthesis of one of the most important classes of heterochain polymers. Since the neutral chlorotrimethylsilane and not HCl is evolved under these conditions, there is no need to use an acid acceptor (a tertiary amine), which interacts vigorously with chloroformates, such reaction involving the termination of the growing polymer chain. A side reaction of this kind is known[101] to limit significantly the application of the chloroformate method in the synthesis of polyurethanes in solution.

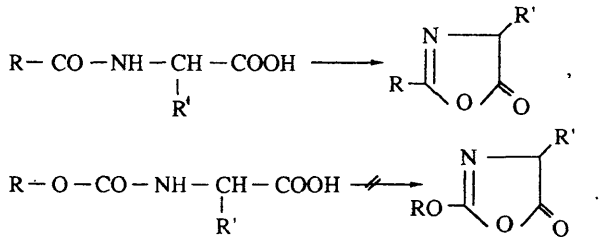
It is essential to note that in the interaction of silylated diamines with bischloroformates, in contrast to their reaction with aliphatic acid dichlorides, the formation of a cross-linked polymer was not observed even in a proton-accepting medium. This finding can

support the tautomeric mechanism of the acylation of a silylated amide examined above (see Scheme 3). Urethanes (and apparently also their silylated forms) showed a smaller tendency to undergo tautomeric transformations—they do not enter into reactions with participation of the tautomeric form of the NH–CO linkage. This may be associated with the greater loss of "resonance energy" because the carbonyl group in urethanes is conjugated with both nitrogen atoms and with the oxygen atom:

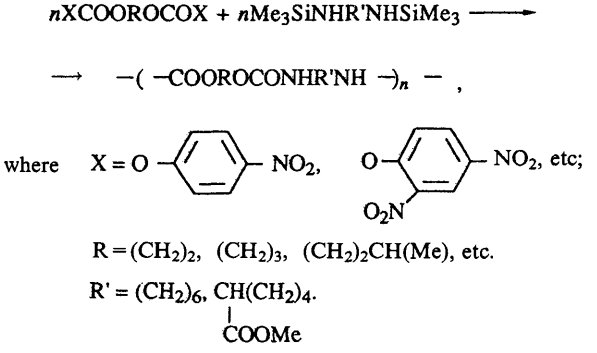


(Y = H, $SiMe_3$).

For example, in contrast to *N*-acyl-α-aminoacids, *N*-alkoxycarbonyl-α-aminoacids do not cyclise to the corresponding azlactones:[102]



High-molecular-weight polyurethanes ($\eta_{init} \leqslant 0.7$ dl g^{-1}) are formed readily on polycondensation of silylated diamines with activated diol biscarbonates—promising monomers for the synthesis of linear polyurethanes under polycondensation conditions in solution:[103]

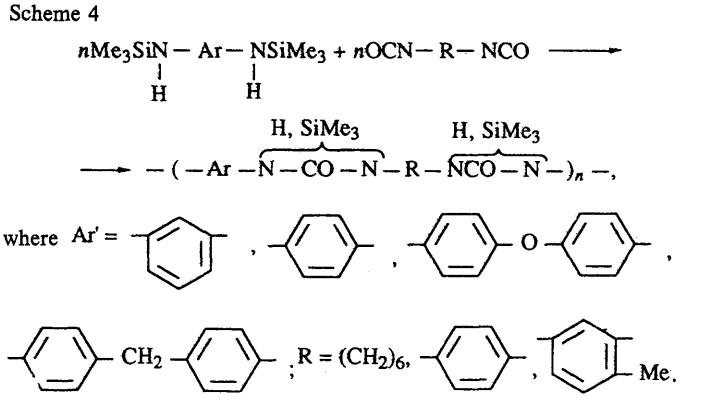


The polyurethane formation reactions using silylated diamines are convenient for the synthesis of polyurethanes with functional-group substituents, for example those based on L-lysine.[104]

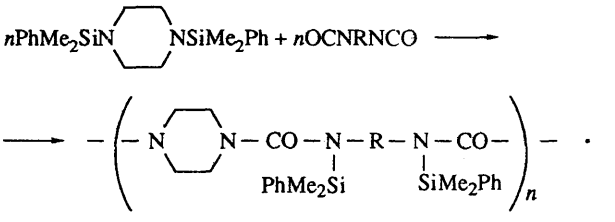
Polyureas. One of the first representatives of heterochain polymers, synthesised using silylated diamines, were polyureas together with polyamines.

Klebe[105] achieved the synthesis of polyureas by the reaction of diisocyanates with silylated aromatic amines in tetrahydrofuran (THF), benzene, toluene, or their mixture:

Scheme 4

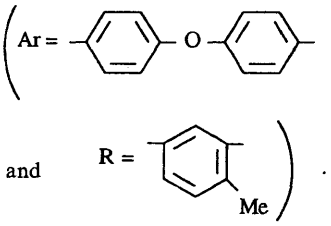


When a silylated secondary diamine—*N,N'*-bis(dimethylphenylsilyl)piperazine—is used in the above reaction, a fully silylated polyurea is formed:



It is remarkable that the silylated secondary amine, containing no NH proton, reacts vigorously with the diisocyanate via a polyadditive mechanism with evolution of heat. In contrast to silylated primary diamines, a polyurea with a fixed N–Si bond is formed under these conditions.

Polyureas in which 50% of the NH protons have been substituted by the silyl groups exhibit an increased solubility in organic solvents. The fully silylated piperazine-based polymer is soluble in benzene and toluene, which may be associated, apart from the absence of intermolecular hydrogen bonds, with the presence of the bulky phenyl substituents in the silyl group. The silylated polyureas are also characterised by lower melting points, which (in contrast to non-silylated analogues) are lower than the decomposition temperatures. This greatly facilitates the formation of articles from them. Strong films have been obtained via Scheme 4 from silylated polyurea ($\overline{M}_W$ 120 000, light scattering)



Under the influence of atmospheric moisture, slow desilylation takes place in such films, which is significantly reflected in their properties (Table 1). Polyureas are rapidly desilylated when methanol is added to the final solution.

The reaction of diisocyanates with silylated diamines in DMA has been used successfully to obtain polyureas with functional-group substituents from natural carboxylic diaminoacids:[106]

$$n\mathrm{OCNRNCO} + n\mathrm{Me_3SiNHR'NHSiMe_3} \longrightarrow$$

$$\longrightarrow -(-\mathrm{COHNRNHCONHR'NH}-)_n-,$$

where R,R' = $\mathrm{CH(CH_2)_3}$ (COOEt), $\mathrm{CH(CH_2)_4}$ (COOEt), $\mathrm{CHCH_2}$ (COOEt), $\mathrm{SS-CH_2CH}$ (COOEt).

The difference from the scheme proposed by Klebe[105] consists in the fact that a diamine desilylated ina preliminary step participated in the reaction. The diamine was desilylated by introducing an equimolar amount of methanol.

Table 1. Properties of films of silylated urea and of its hydrolysed analogue.

Properties	Initial polyurea	Film after 30% surface hydrolysis
Tensile strength, kg cm^{-2}	560	450
Elongation at rupture, %	30	150

*The film was maintained for several weeks at room temperature in air. The hexamethyldisiloxane formed on hydrolysis and remaining in this film played the role of a plasticiser.

One of the authors of this review established that the reactions between aliphatic monomers proceed vigorously with evolution of heat also without preliminary desilylation. Thus the reaction of hexamethylene diisocyanate with *N,N'*-bis(trimethylsilyl)hexamethylenediamine in DMA results in the formation of a viscous solution of a 50% silylated polyrea:

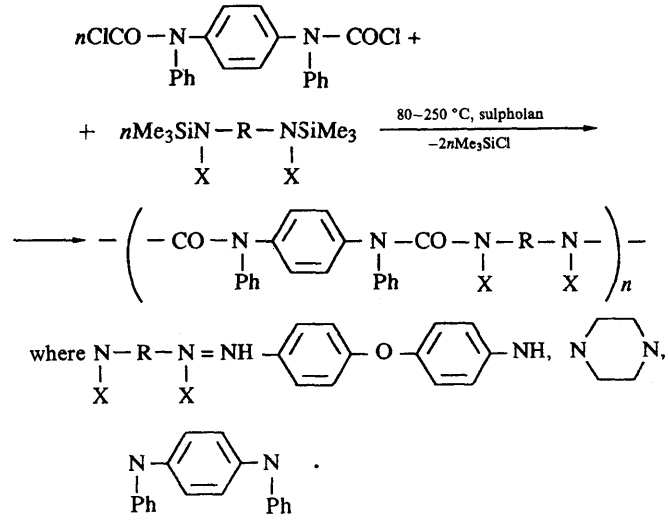
$$(n/2)\mathrm{OCN(CH_2)_6NCO} + (n/2)\mathrm{Me_3SiNH(CH_2)_6NHSiMe_3} \longrightarrow$$

$$\longrightarrow -\left[-(\mathrm{CH_2})_6-\overbrace{\mathrm{N-CO-N}}^{\mathrm{H,\ Me_3Si}}-\right]_n \xrightarrow{\mathrm{MeOH}}$$

$$\longrightarrow -\left[-(\mathrm{CH_2})_6\mathrm{NHCONH}-\right]_n- .$$

After the addition of methanol to the reaction solution, a polyrea in the H-form is rapidly precipitated. It contains in all probability intermolecular cross-links, because it is insoluble in trifluoroacetic and sulphuric acids [a polyurea having a similar structure, obtained in a different way (see below), does not dissolve in DMA but is soluble in the acids indicated]. We may note that a tendency towards the rapid exchange of the trimethylsilyl group leads to interesting possibilities for the use of silylated polyreas as polymeric reagents—effective donors of the silyl group and especially convenient for the separation of the reaction products.

Polyureas have been synthesised by the reaction of *N*-phenylbiscarbamoyl chloride [*N,N'*-bis(chloroformyl)-*p*-dianilinobenzene] with silylated diamines, including secondary diamines:[28]



The viscosity of polyureas ($\eta_{\log} \leqslant 0.35$ dl g^{-1}), obtained in accordance with this scheme, is higher than that of the analogous specimens obtained by the reaction of *p*-dianilinobenzene with the corresponding diisocyanate ($\eta_{\log} \leqslant 0.18$ dl g^{-1});[107] best results were achieved using a piperazine derivative as the amine component.

High-molecular-weight polyureas are formed in the reaction of silylated diamines with phosgene:[108]

$$n\mathrm{COCl_2} + n\mathrm{Me_3SiNH-R-NHSiMe_3} \xrightarrow[-2n\mathrm{Me_3SiCl}]{}$$

$$\longrightarrow -(-\mathrm{CONH-R-NH}-)_n- .$$

Diphosgene and triphosgene, which are experimentally more convenient, are also used in this reaction instead of phosgene. The employment of other sources of the CO group—crystalline activated carbonates—likewise proved fruitful:[108]

$$n\mathrm{XCOX} + n\mathrm{Me_3SiNH-R-NHSiMe_3} \xrightarrow[-2n\mathrm{XSiMe_3}]{}$$

$$\longrightarrow -(-\mathrm{CONHRNH}-)_n-,$$

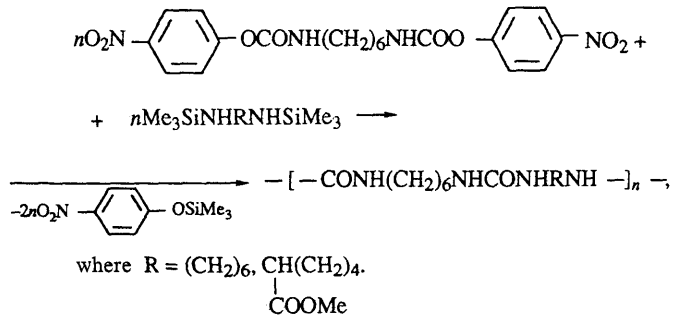
where X = O–C$_6$H$_4$–NO$_2$, O–C$_6$H$_3$(O$_2$N)–NO$_2$, R = $(\mathrm{CH_2})_6$, $\mathrm{CH(CH_2)_4}$ (COOEt) etc.

The interaction of activated carbonates and silylated diamines takes place at room temperature in DMA. However, in many instances the temperature is raised to 90–100 °C and LiCl is added in order to homogenise the solution and complete the reaction

(under heterogeneous conditions, the polyurea chain propagation stops). Polyureas with $\eta_{int} \leqslant 0.95$ dl g^{-1}, soluble in organic solvents and possessing film- and fibre-forming properties, have been synthesised under such conditions.

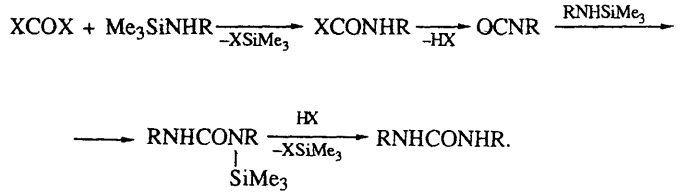
This scheme is particularly convenient in the synthesis of L-lysine-based polyureas with functional-group substituents.[104,108] A polymer with a microstructure in which symmetrical "head-to-head" and "tail-to-tail" triads predominate (with a microheterogeneity coefficient[109] $K_m = 0.6$) are formed in accordance with this scheme, while a polyurea with a normal statistical distribution of triads (with a slight predominance of the "head-to-tail" triads having $K_m = 1.1$) formed[110] in accordance with the isocyanate scheme presented above.[106]

The polycondensation of silylated diamines by reaction with an activated carbamate also leads to the synthesis of high-molecular-weight polyureas;[111]

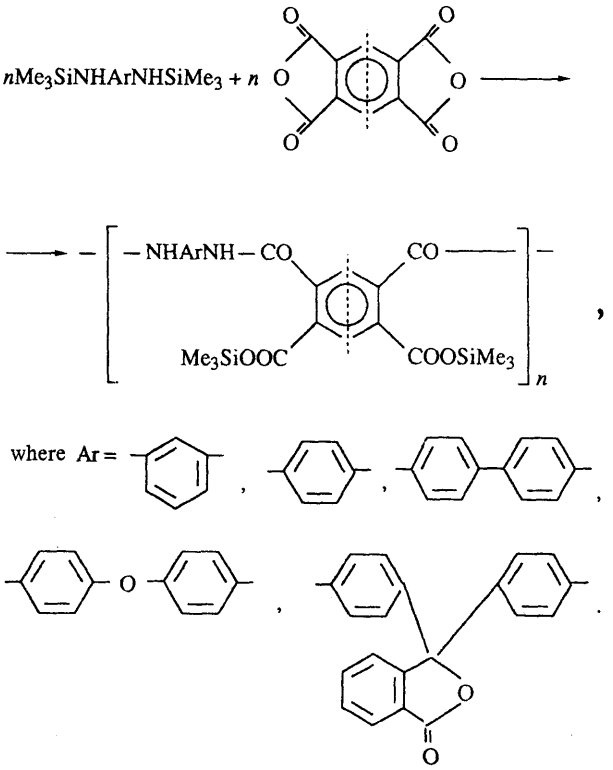


This scheme is also effective in the synthesis of L-lysine-based polyureas with functional-group substituents.

In contrast to polyamide and polyurethane formation processes, the synthesis of polyureas using phosgene and its derivatives proceeds via the intermediate formation of an isocyanate;[108]

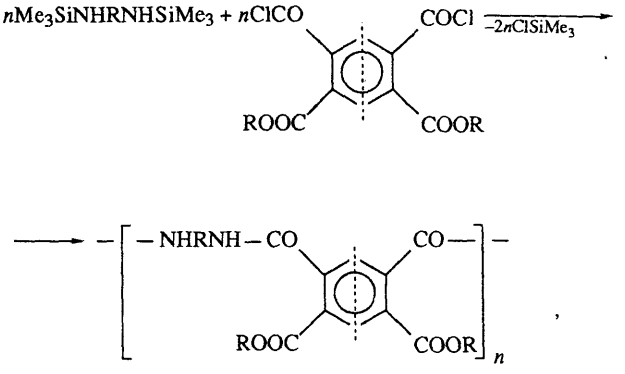


Polycycloimides. *The two-stage method.* The possibility of synthesising polymides via silylated diamines was first examined by Klebe.[1,112] In the polycondensation of cyclic anhydrides with trimethylsilylated aromatic diamines, trimethylsilyl esters of polyamidoacids (Si-PAA) are formed under mild conditions. The Si-PAA differ from the free PAA by their stability in inorganic solvents. For example, the viscosity of Si−PAA does not change during 120 days at room temperature in DMA,[113] which may also be a consequence of the "self-purification" of the system (see above):[1,94,112−117]



An interesting feature of these processes is that the $COOSiMe_3$ group "departs" in the reaction and a Si-PAA is formed.

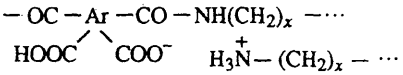
Precursors of the polyimides can be synthesised via an alternative scheme involving a reaction similar to that described above (see "Polyimides") between silylated diamines and tetracarboxylic acid diester dichlorides:



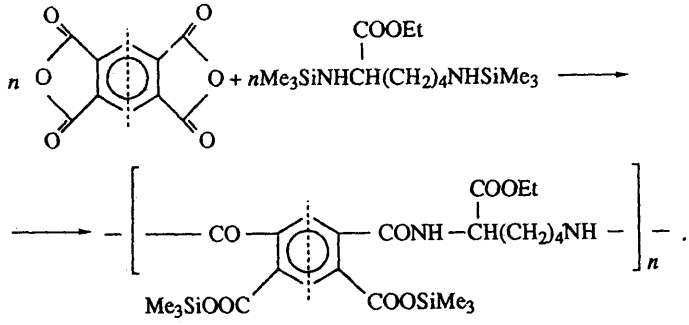
where R = Me, Et, etc.

An advantage of the formation of polyamides from silylated aliphatic diamines using cyclic acid dianhydrides is the formation of high-molecular-weight Si-PAA ($\eta_{log} \leqslant 1.0$ dl g^{-1}). When the corresponding free polymethylenediamines are employed, low-molecular-weight PAA are also obtained ($\eta_{log} \leqslant 0.2$ dl g^{-1}), which

is due to the strong inhibition of the process as a result of the formation of stable salts by highly basic aliphatic amines with the carboxyl side groups of the PAA, the salts precipitating:§[118]



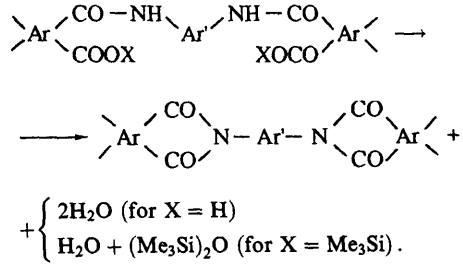
The interaction of silylated diamines with dianhydrides has been used for the synthesis of L-lysine-based polyamides with functional-group substituents:[115,116]



We may note that silylated forms of PAA are stable in the reaction solutions. During isolation by precipitation using an excess of a precipitant, they are readily desilylated (apparently by traces of moisture). Si-PAA can be maintained in an intact form only when the solvent (DMSO) is removed by lyophilising the solutions.

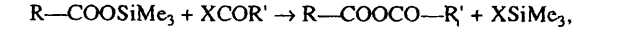
The thermal cyclisation of Si-PAA proceeds extremely effectively (according to certain data, it is faster than the cyclisation of free PAA) with formation of the target polyimides having a high molecular weight and basic properties identical with those of the polyimides obtained by the traditional method.[117]

It is significant that hexamethyldisiloxane and an amount of water smaller by a factor of 2 than in the conversion of PAA into the imide form are produced in the thermal cyclisation of Si-PAA:



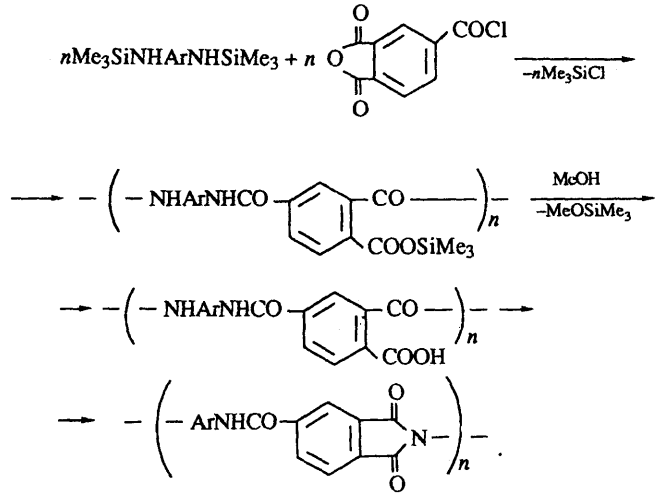
Water is formed in the case of Si-PAA on condensation of two molecules of trimethylsilanol, in all probability in the gas phase, which protects the PAA from hydrolysis (degradation).

Si-PAA also undergo readily chemical cyclisation in the presence of a pyridine–acetic anhydride (or acetyl chloride) mixture with intermediate formation of a mixed anhydride. This process can apparently be achieved in the absence of the organic base, because it is known that the silyl esters of carboxylic acids form anhydrides fairly readily on treatment with the acyl group donors indicated above:[1]

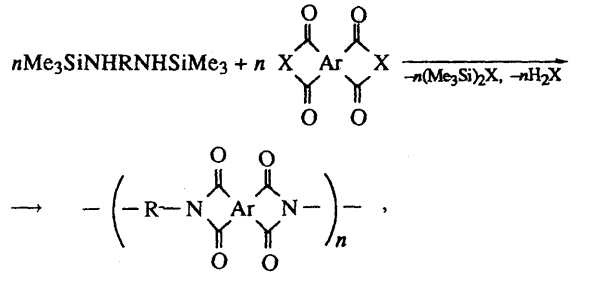


where X = Cl or MeCOO.

The advantages of the "silylated polyamide formation reaction" using cyclic dihydrides were taken into account in the synthesis of copolyimides (aliphatic and aromatic diamines were used as the comonomers), the microstructure of the chains of which was regulated (by means of degradative and exchange processes) in the stages involving the formation of Si-PAA and their cyclisation.[114] We may note that high-molecular-weight copolyimides were obtained both from the Si-alkylenediamine/Si-arylenediamine pair despite the possible exchange of the silyl group in the latter case and the appearance in the system of free aliphatic amino-groups. The combination in the first stage of the acid chloride and anhydride "silylated polyamide formation reactions" made it possible to synthesise high-molecular-weight polyamidoimides based on 4-chloroformylphthalic anhydride:[117]



The single-stage method. Using Si-diamines of different nature and cyclic dianhyrides (including dithioanhydrides[119]), high-molecular-weight polyimides were obtained in a single stage in solution at elevated temperatures:[114,119,120]



where X = O or S. It was established that there is no appreciable difference between the reactivities of diamines and their silylated analogues both in the single-stage polyimide formation reactions and in the reactions involving the aminolysis of polyimides.[120]

§The polymeric salt based on the dianhydride of oxydi(3,4-dicarboxybenzene) and dodecamethylenediamine is insoluble in polar solvents even after prolonged heating at 100 °C.

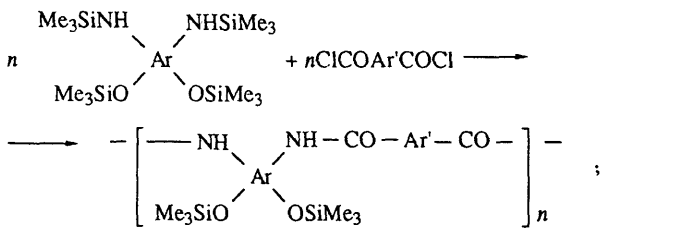
Acyclic linear polyimides. The "trimethylsilyl activation" of the amide nitrogen, which was discussed above, has been used successfully to acylate acid amides i.e. to synthesise acyclic analogues of polyimides:[62]

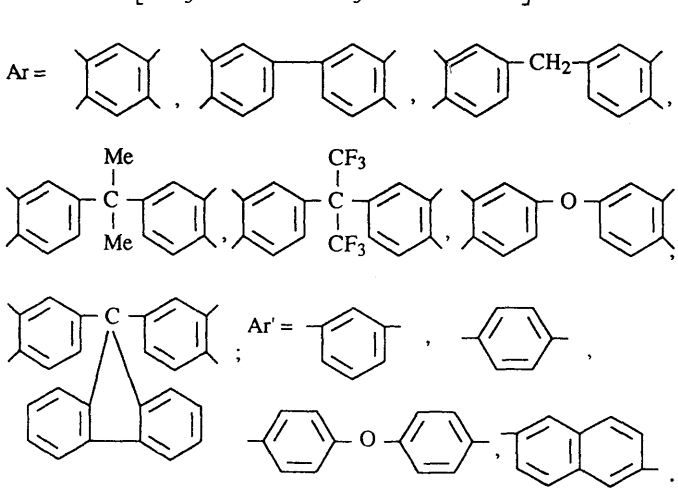
$$n(Me_3Si)_2NH + {}^{n}/_{2}\,ClCORCOCl \rightarrow {}^{n}/_{2}\,Me_3SiNHCORCONHSiMe_3 \rightarrow$$
$$\xrightarrow{{}^{n}/_{2}\,ClCORCOCl} -(-COR - CONHCO - R - CONH)_{n/2} - .$$

A characteristic feature of this reaction is that the primary amine behaves as a bifunctional reactant. Disilylated primary monoamines $(SiMe_3)_2NR'$ can apparently be used also under analogous conditions.

Like polyanhydrides,[121–123] the polyimides examined are of potential interest as rapidly degradable polymers for medical-biological purposes, especially since both R and R′ can carry different functional groups.

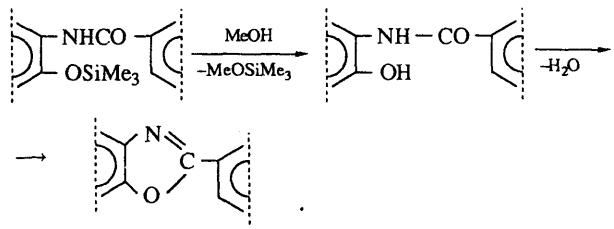
Polybenzazoles. The use of silylated monomers also for the synthesis of polybenzoxazoles by a two-stage method proved fruitful:[24,25,42,94,124–129]



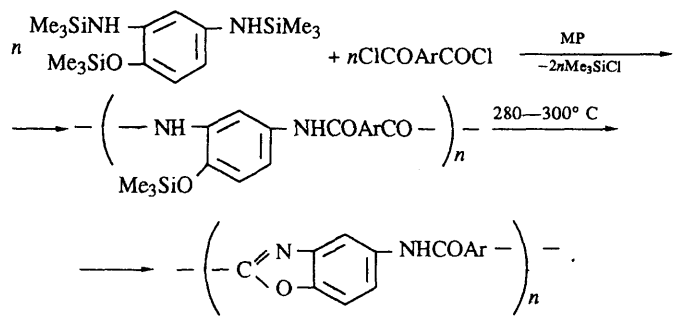


Higher-molecular-weight poly-*o*-hydroxyphenylamides ($\eta_{log} \leqslant 0.64$ dl g^{-1}) can be obtained from silylated bis-*o*-aminophenols[41] than from the free bases ($\eta_{log} \leqslant 0.33$ dl g^{-1}).[42] Here one can assume that the reaction proceeds with participation of the silylated amino-groups, because the silylated hydroxy-groups do not interact with acid chlorides under the conditions of low-temperature polycondensation (see below).

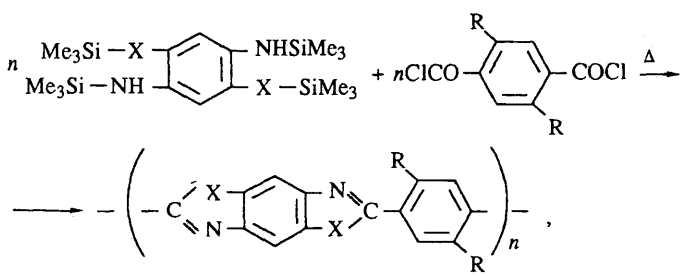
In order to facilitate the second reaction stage (cyclisation to the target benzoaxole), the hydroxy group is desilylated by treating the polymers with methanol:



Imai and co-workers[1] synthesised film-forming polyimido-benzoxazoles ($\eta_{log} \leqslant 1.49$ dl g^{-1}) in *N*-methylpyrrolidinone (MP) in accordance with the following scheme:

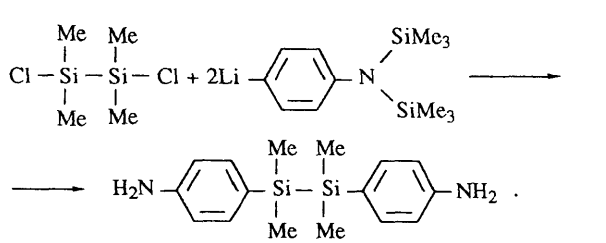


Kricheldorf and co-workers[24,25,128] obtained rod-like poly-benzoxazoles and polybenzothiazoles with the aid of "silyated polycondensation":



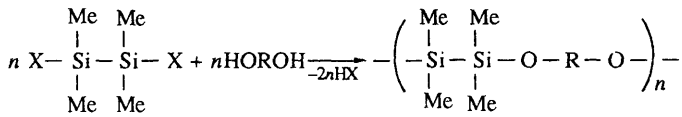
where X = O or S. According to the authors, the minimal contribution of side reactions is an advantage of this method.

Photosensitive polymers. An interesting study designed to create photo-sensitive (photodegradable) polymers has been carried out.[130–132] 1,2-Bis(*p*-aminophenyl)tetramethyldisilane was synthesised by the reaction of 1,2-dichlorotetramethyldisilane with 4-[*N*,*N*-bis(trimethylsilyl)amino]phenyl-lithium:

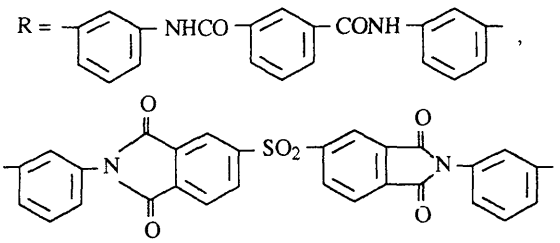


Polyamides ($\eta_{log} \leqslant 0.7$ dl g^{-1}) and polyimides ($\eta_{log} \leqslant 0.84$ dl g^{-1}), which undergo photodegradation on UV illumination, were synthesised by the polycondensation of the above diamine with dicarboxylic acid dichlorides[130] and the dianhydride of di(3,4-dicarboxyphenyl) sulphone[131] respectively.

The same workers proposed also an alternative method of synthesis of photo-sensitive polyamides and polyimides ($\eta \leqslant 0.59$ dl g^{-1}), in which the silylated amino-groups are directly involved in the chain propagation process:[132]

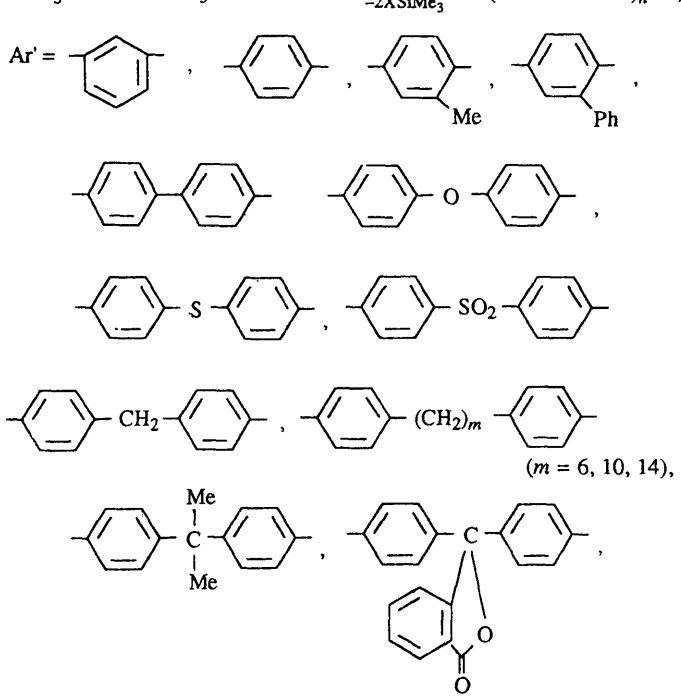


where X = NEt_2, HN—Ph;

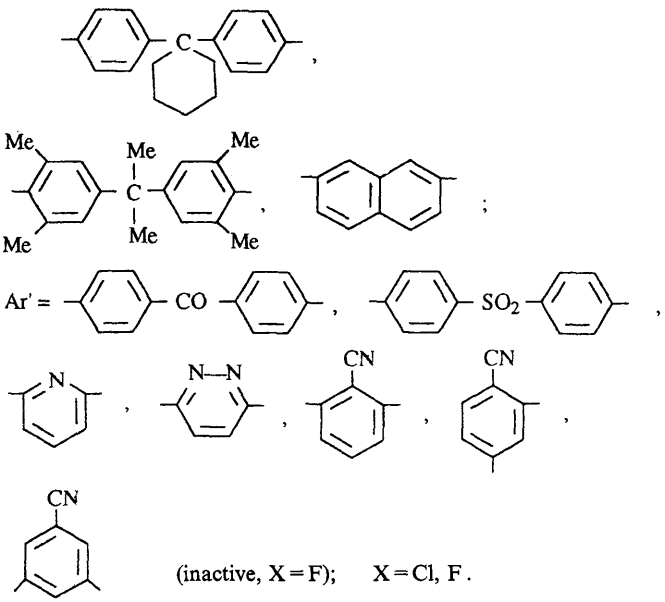


Polymers based on monomers with a O(S)—Si bond

Polyethers. Kricheldorf and co-workers obtained high-molecular-weight ($\overline{M}_W \leqslant 2 \times 10^5$) simple homopolymers and copolymers by the reaction of silylated bisphenols with activated (with the aid of a heterocycle or the electron-accepting CO_2 and SO_2 groups) aromatic difluoro(chloro)-compounds:[24,25,31,35,38,39,48,133–136]



(*m* = 6, 10, 14),



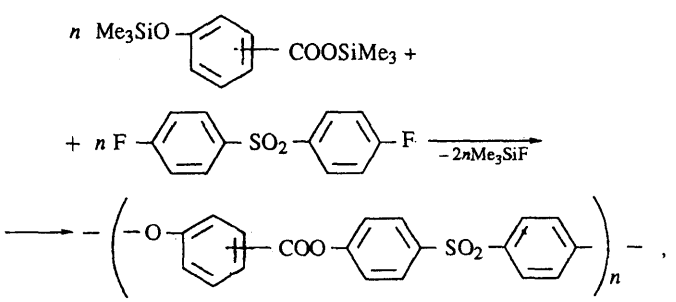
(inactive, X = F); X = Cl, F.

The polycondensation of silylated bisphenols with activated aromatic difluoro-compounds proceeds at elevated temperatures ($\leqslant$340 °C) in bulk. The silylated oxygen in bisphenols can be activated by inorganic anions (F^-, Cl^-, CO_3^{2-}), the use of fluorides (KF, CsF) producing the best results.

Polycondensation with participation of activated aromatic chloro-compounds also proceeds in solution in methylpyrrolidinone in the presence of K_2CO_3. On the whole, in the reactions indicated aromatic fluoro-compounds are much more reactive than their chloro-analogues, as in the reactions with alkali metal phenoxides.[137,138]

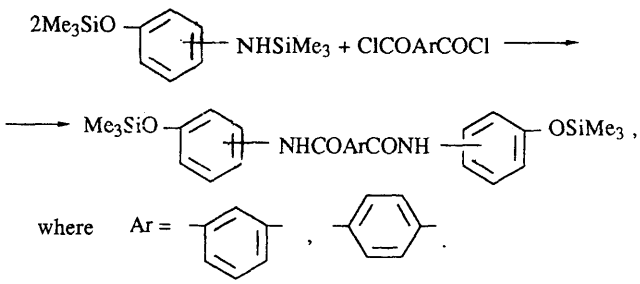
The proposed methods of synthesis of aromatic polyethers, involving the evolution of volatile products (Me_3SiF, Me_3SiCl), have advantages over the traditional method of their synthesis by the polycondensation of alkali metal bisphenoxides with activated aromatic dihalo-compounds in solution (in DMSO, methylpyrrolidinone, etc.).[137,138] The main disadvantage of the traditional method consists in the necessity to eliminate large amounts of metal salts (low-molecular-weight polycondensation side products) from the polyethers.

Polymers containing ether and ester linkages in the main macromolecular chains have been obtained by the reaction of silylated *m*- and *p*-hydroxybenzoic acids and di(4-fluorophenyl) sulphone:[48]



$\bar{M}_n \leq 20\,000$.

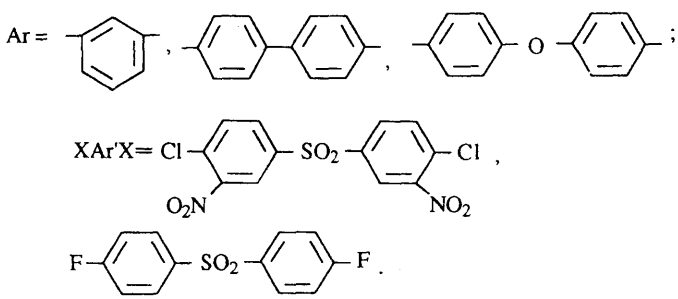
Using the different reactivities of *O*- and *N*-silylated functional groups, regular polyamides containing ether linkages have been synthesised.[139] Silylated diphenyldiamides were obtained initially by the reaction of *N,O*-bis(trimethylsilyl)-3-(or 4-)aminophenol with acid dichlorides under mild conditions. The diamides were then condensed with activated aromatic difluoro-monomers:



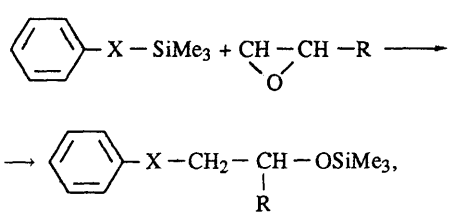
Polysulphides have also been synthesised by the reaction of *S,S'*-bistrimethylsilylated dithiophenols with aromatic dihalo-compounds:[140]

$$n\,Me_3Si-SArS-SiMe_3 + n\,XAr'X \xrightarrow[-2nMe_3SiX]{} -(-SArSAr'-)_n-,$$

where



We may note that silylated phenols and thiophenols may be alkylated also with the aid of epoxy-compounds. The oxiran ring is then inserted (and opened) between the Si and O(S) atoms:[68]



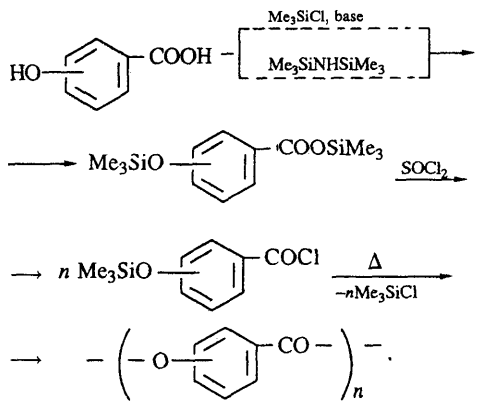
where X = O or S.

Polyesters. Kricheldorf and co-workers[30,32–34,49,141] developed a method of synthesis of polyarylates which serves as an alternative to the procedure for the arylation of silylated acids described above. It consists in the interaction of silylated phenols with acid chlorides at elevated temperatures in bulk or in a high-boiling solvent:

$$\sim ArOSiMe_3 + ClCOAr'\sim \xrightarrow{200-300^\circ C} \sim ArOCOAr'\sim ,$$

According to the authors, "silylated polyesterification" is especially useful in the synthesis of AB-polyesters, because monomers are partly volatilised in the AA–BB polycondensation, which leads to the breakdown of stoichiometry.

The silylated aromatic OH groups are inert to acid chlorides in a neutral medium and at moderate temperatures. This made it possible to synthesise the chlorides of trimethylsiloxybenzoic acids:

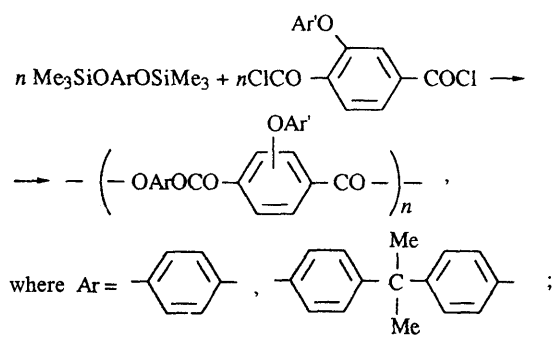


The polycondensation of trimethylsiloxybenzoic acid in bulk in the temperature range 200–300 °C leads to the synthesis of polyesters with $\overline{M}_n$ = 12000–13000; in solution in the presence of pyridine (a nucleophilic catalyst), much worse results are achieved ($\overline{M}_n \leqslant 2300$).[33]

The new scheme for the synthesis of aromatic AB-polyesters also has an advantage over the thermal polycondensation of acetoxybenzoic acids[30] and over direct polycondensation in the presence of phosphorus compounds as condensing agents.[33]

By selecting appropriate conditions (redistilled trimethylsilyl ester of *p*-trimethylsiloxybenzoic acid in the persence of an excess of $SOCl_2$, polycondensation in Marlotherm S), it was possible to increase $\overline{M}_n$ for the polyester to 200000.[34]

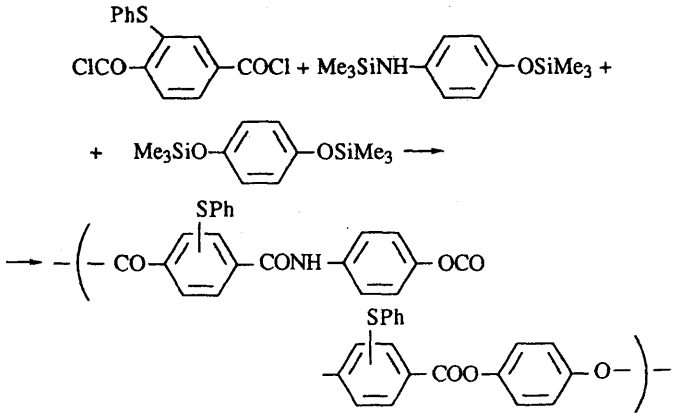
Using the silylated polyesterification method, thermotropic polyarylates were synthesised from aryloxyterephthalic acid:[52,72,146]



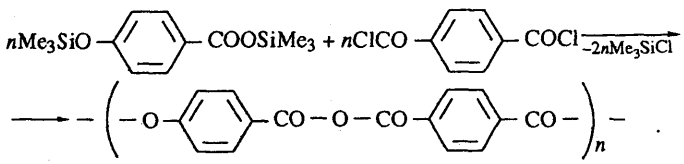
Ar' = Ph, PhOPh, $PhOC_6H_4Cl$, $PhOC_6Cl_5$.

Polyarylates with higher viscosities were obtained by the above method in many instances than in the traditional low-temperature polyesterification of bisphenols by acid dichlorides in the presence of pyridine or in the high-temperature polycondensation of aryloxy-terephthalic acids with acetylated bisphenols. The advantage of the new scheme is the small contribution of the anthrone formation side reaction.[24,49,141]

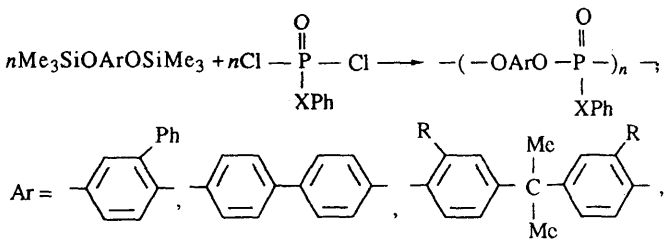
Using silylated 4-aminophenol as the comonomer, thermotropic polyamidoesters have been synthesised:[24]



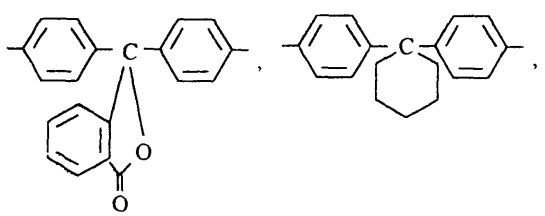
The polycondensation of terephthaloyl chloride with a silylated hydroxyacid afforded thermotropic polyester anhydrides:[24]



Stepwise heating of silylated bisphenols with phenyl phosphorodichloridate and phenyl phosphonodichloridate in the presence of benzyltriethylammonium chloride as the catalyst afforded fire-resistant poly(phenyl phosphates) and poly(phenyl phosphonates) with $M_n \leqslant 20\,000$:[36,37]

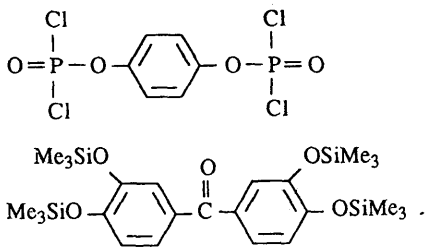


(R= H, Mc, Cl, Br),



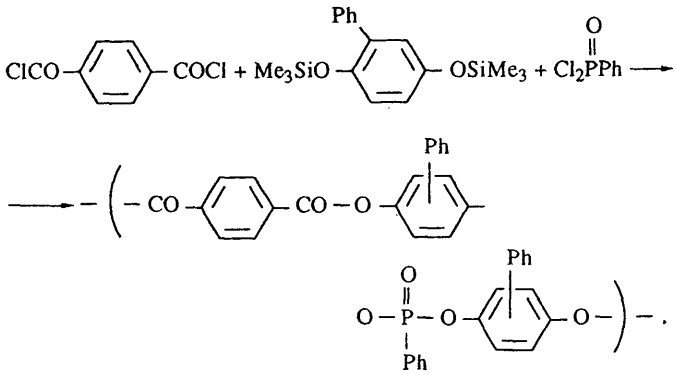
X = bond, O.

"Cross-linking" tetrafunctional compounds have also been used in the synthesis of phosphorus-containing polyesters, but the reaction yielded polymers with lower viscosity characteristics:

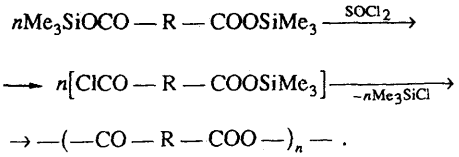


According to the author,[37] this is associated with the involvement of the tetrafunctional monomers in side reactions.

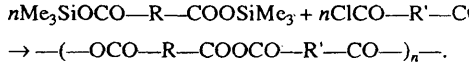
Thermotropic copolymers of terephthalic and phenylphosphonic acid have been synthesised:[24]



Polyanhydrides. The synthesis of polyanhydrides ($\eta_{int} \leqslant 0.6$ dl g^{-1} in chloroform) by the polycondensation of bistrimethylsilylated dicarboxylic acids with $SOCl_2$ in the presence of benzyltriethylammonium chloride as the catalyst has been described:[142]



Polyanhydrides can also be synthesised by the reaction of bistrimethylsilylated dicarboxylic acids with acid dichlorides, similarly to the synthesis of polyester anhydrides described above:

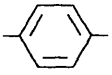


The "silylated polyanhydrides formation" reactions can be useful for the synthesis of new polyanhydrides promising as biodegradable polymers.[121–123]

Polyesterurethanes. Under certain conditions, silylated alcohols and phenols react with carboxylic acid chlorides whilst remaining inert to isocyanate groups. This feature has been used[29] to synthesise diesterdiisocyanates in accordance with the scheme

$$2OCN(CH_2)_mCOCl + Me_3SiOROSiMe_3 \longrightarrow$$

$$\longrightarrow OCN(CH_2)_mCOOROCO(CH_2)_mNCO;$$

R = $(CH_2)_4$, ; m = 2, 3, 5.

Polyesterurethanes with a regular structure have been synthesised from diesterdiisocyanates. We may note that the above monomers are of interest for the synthesis of regular polyesterureas and polyamidoesters.

Polycondensation *in situ*

Polycondensation reactions in which the silylating agent is added directly to a mixture of the biselectrophile and bisnucleophile are examined below. Under these conditions, one of them gives rise to a silylated derivative, which then reacts *in situ* with the monomer of the opposite kind.

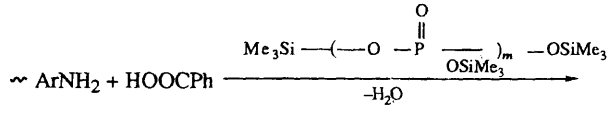
Modification of the bisnucleophile. Kaneda and co-workers[143,144] proposed a simplified method of synthesis of polyamides which does not require the preliminary synthesis and purification of silylated diamines. The diamine is subjected to polycondensation with an acid dichloride in amide solvents (HMPA, DMA, methylpyrrolidinone) at 0 °C in the presence of Me_3SiCl. This entails the silylation of the amino-groups of the diamine, which reacts *in situ* with the acid chloride. The addition of Me_3SiCl makes it possible to obtain polyamides with higher molecular weights ($\eta_{log} \leqslant 6.68$ dl g^{-1}) than in the case where salts such as LiCl ($\eta_{log} \leqslant 3.9$ dl g^{-1}) or $CaCl_2$ ($\eta_{log} \leqslant 4.48$ dl g^{-1}) (polyamides based on 3,9-diaminophenanthridinone and terephthaloyl chloride) are used.

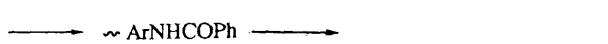
Direct polycondensation. A method of synthesis of polyamides by the polycondensation of diamines and dicarboxylic acids or *p*-aminobenzoic acids in the presence of $SiCl_4$ as the condensing agent has been proposed (in this case both the biselectrophile and the bisnucleophile may be activated simultaneously):[145–147]

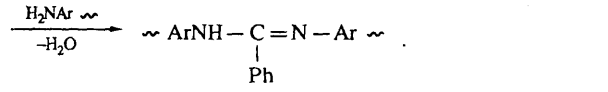
$$n H_2NArNH_2 + n HOOCAr'COOH + {}^n/_2 SiCl_4 \rightarrow$$
$$\rightarrow -(-NHArNHCOAr'CO-)_n- + (SiO_2)_{n/2} + 2n HCl.$$

It is of interest that SiO_2 is formed in these processes as a side product. This leads to the prospect of obtaining filled materials directly during synthesis.

Poly(trimethylsilyl phosphate) has also been used as the condensing agent:[148]







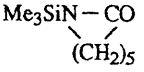
This agent exerts such a powerful dehydrating effect that an amidine bond is formed from the amide and amine groups. The interaction of diamines with benzoic acid (which behaves as a bifunctional monomer in the processes indicated) yielded polyamidines.

The syntheses described in this Section illustrate a variety of direct polycondensation—a new promising method of synthesis of heterochain polymers.[149,150]

(b) Polymerisation

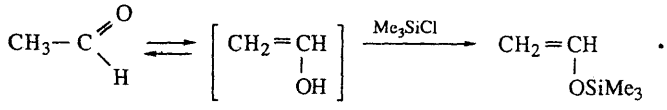
Polymerisation of heterocycles

The silyl protecting group has been used in the synthesis of polycarbohydrates by polymerisation with the opening of the ring in the corresponding anhydro-sugars. For example, the reaction of t-butylchlorodimethylsilane and 1,5-anhydro-β-D-xylofuranose afforded 1,5-anhydro-2,3-di-*O*-(t-butyldimethylsilyl)-β-D-xylofuranose, whose polymerisation in the presence of BF_3 or $SbCl_5$ yielded high-molecular-weight polymers containing the 1,5-α- and 1,5-β-furanose fragments.[151] A polysaccharide with free hydroxy-groups, capable of further polymer-analogue transformations, was obtained by the desilylation of the polymer indicated.

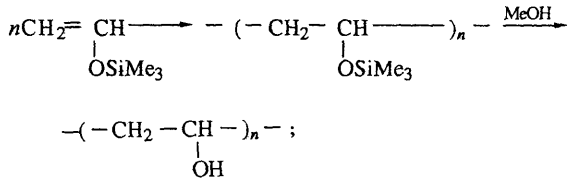
N-Trimethylsilylated lactams have also been used in the synthesis of polymers. In particular, it has been established that *N*-trimethylsilyl caprolactam  accelerates the anionic polymerisation of ε-caprolactam.[152]

Timethylsilated compounds are also effective as catalysts of the polymerisation of heterocycles. It has been shown[153] that trimethylsilylated acids, in particular, trimethylsilyl triflate ($CF_3=SO_3SiMe_3$) and bistrimethylsilyl sulphate ($Me_3SiOSO_2OSiMe_3$) initiate the polymerisation of lactones. Polycaprolactone with a molecular weight of 60 000 (degree of conversion 70–90%) has been obtained by treatment with trimethylsilyl triflate in 1,2-dichloroethane at 50 °C.

Polymerisation of silyl ethers of enols. An elegant method of synthesis of poly(vinyl alcohol) from acetaldehyde has been proposed.[154] The *O*-trimethylsilyl derivative of the enolic form of acetaldehyde was synthesised initially and then trimethylsiloxyethylene was obtained:

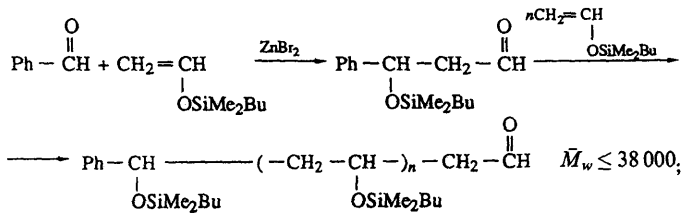


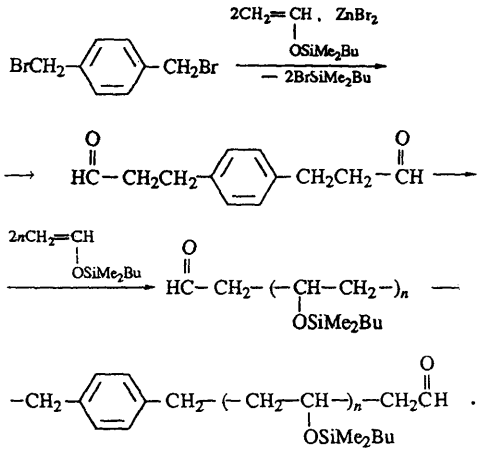
The polymersiation of the latter afforded silylated poly(vinyl alcohol). It was desilylated by adding methanol;



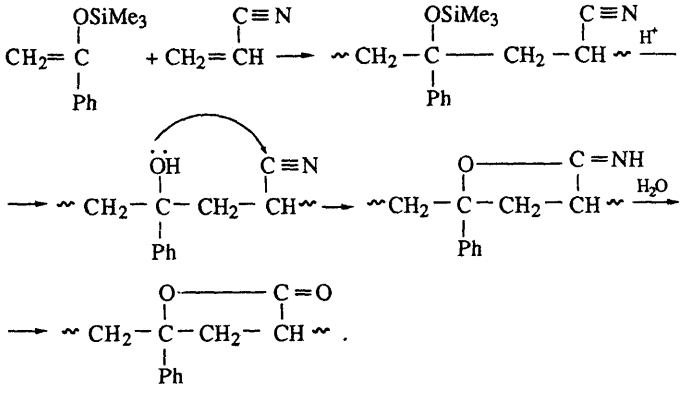
$$[\eta]^{30}_{H_2O} \leq 0.6 \text{ dl g}^{-1}.$$

This interesting procedure was developed in a study[53] whose authors achieved the synthesis of silylated poly(vinyl alcohols) in accordance with one of the schemes presented below (the polymer formation process proceeds via the mechanism of aldol condensation):



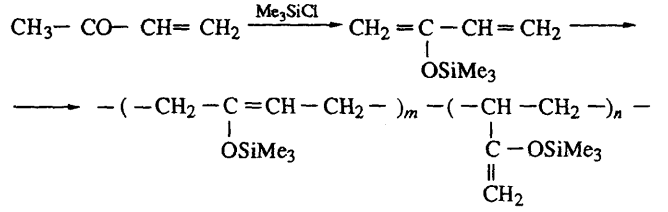


α-Trimethylsiloxystyrene, its polymers, and its copolymers with styrene[155] and acrylonitrile[156] were synthesised from acetophenone. In the latter case, in the presence of a proton, there is possibility of cyclisation with formation of a five-membered lactone:

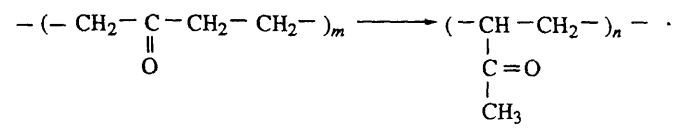


Lactone-containing polymers are of intereest, for example, as carriers for the covalent immobilisation of various substances. In this case, there is no need for the additional activation of the polymer, because it is known that five-membered lactones exhibit an enhanced reactivity and readily interact with aliphatic amino-groups.[157]

An interesting method of synthesis of polyolefins containing ketone groups in the main and side chains of the macromolecules has been proposed.[158] 2-Trimethylsiloxybuta-1,3-diene was obtained initially by silylating methyl vinyl ketone and its polymerisation or copolymerisation with unsaturated monomers led to polymers with 1,4- and 3,4-units:



Desilylation of the polymers by treatment with HCl or NBu_4F results in the formation of polyketones:



These are of interest, for example, as photodegradable materials.

Interesting examples of the use of silyl compounds as initiators of the polymerisation of unsaturated compounds exist. Thus metallo-derivatives of silylamines $(Me_3Si)_2NM$ (where M = Li or Hg) catalyse the polymerisation of vinyl monomers,[1] lithium derivatives exhibiting a high catalytic activity; the catalytic activity of the corresponding amide complex of mercury is less marked. Polymers resistant to fungi have been obtained using the above initiators.

Silyl compounds can also be used to protect catalytic systems. For example, silylamines having the general formula

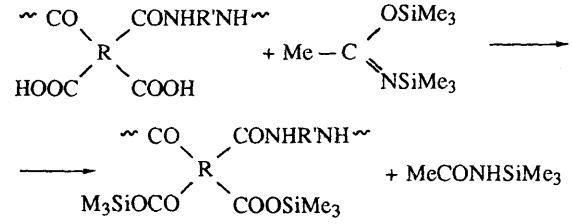
$$R_aSiH_b(NR^1R^2)_c,\ a=1,\ 2,\ 3;\ b=0.01;\ c=1,\ 2;\ a+b+c=4$$

are used as additive neutralising compounds which poison the anionic polymerisation of unsaturated compounds.[160]

Silylation is used to block functional groups (phenolic hydroxyls) present in the monomer itself and capable of inhibiting polymerisation, for example, the polymerisation of 4-allyl-2,6-dimethylphenol.[161]

IV. Reactions in polymer chains

An alternative method of synthesis of Si-PAA, by polymer-analogue reactions in accordance with the scheme



(apart from the silylating agent indicated in the scheme, other donors of the $SiMe_3$ group have been used) is of undoubted interest as regards the employment of the advantages of silylated polycondensation in the synthesis of polymides. Carboxylic acids are silylated more readily than the initial arylenediamines. However, such treatment of PAA at room temperature results in an effective

imide formation reaction.[75]¶ As can be seen from Table 2, best results are then achieved using *N,O*-bis(trimethylsilyl) acetamide.

An advantage of silylating agents in imide formation processes is that, in contrast to, for example, carboxylic acid anhyrides and tertiary amines, which are effective only when used in combination with one another, there is no need for a second agent when silazanes and silylamides are employed. In addition, the cyclisation of PAA takes place successfully in the presence of equivalent amounts of silazanes. Whereas the attainment of optimum results with mixtures of anhydrides and tertiary amines requires an appreciable excess of the components of the catalytic system. The silylation of polyamide chains has also been achieved.[163]

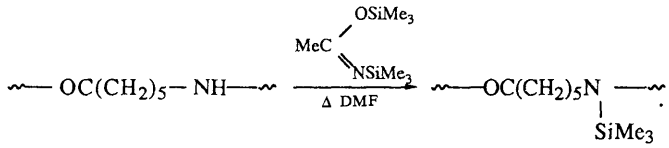


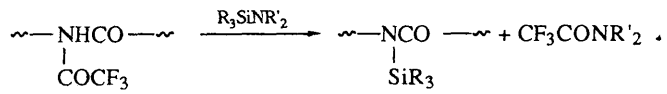
Table 2. Synthesis of polyimides by cyclising PAA in the presence of silylating agents.[75]

PAA base	η_{lg} for PAA, dl g^{-1}	Silylating agent	η_{lg} for the polymide dl g^{-1}
p-Phenylenediamine and 3,3-bis(3',4'-dicarboxyphenyl)phthalide	1.22	*N,O*-bis(trimethylsilyl)acetamide	0.95
	0.99	$Me_3SiCl+NEt_3$(1 : 1)	0.32
Anilinofluorene and bis(3,4-dicarboxyphenyl) oxide	1.10	*N,O*-bis(trimethylsilyl)acetamide	0.90
	0.64	$Me_3SiCl+NEt_3$ (1 : 1)	0.21

As a result of sharp decrease in the number of intermolecular hydrogen bonds, silylated polyamides are soluble in many organic solvents and are suitable for conversion into various articles and for studies by the gel-chromatographic methods. They can be regarded also as polymeric reagents—effective donors of the silyl group.

The conversion of polyamides into a soluble form by silylation has advantages over another known method—chain trifluoroacetylation, because certain *N*-trifluoroacetates, for example those of poly-α-aminoacids, are readily degraded.[164]

We may note that the polyamide derivatives indicated can undergo interconversions. For example, *N*-trifluoroacetyl derivatives of polyamides, which are effective trifluoroacetyl group transferring agents, can be converted into the corresponding silylated derivatives on treatment with silazanes:



¶ It is not clear why Greber and Darms[162] nevertheless obtained Si-PAA under analogous conditions, although they do note that the cyclisation of the latter takes place more readily than that of PAA.

Instances of the use of silylated amines instead of free bases in polymer-analogue reactions of polymers are known. Thus, in order to suppress aldol condensation, trimethylsilylated amines were used[165] to convert poly(methyl methacrylate) into the corresponding amide by the aminolysis of ester side groups.

V. Conclusion

There is evidently no need to conclude the review by listing anew and discussing the advantages and characteristics of the employment of the silylation method in polymer chemistry. One can only draw the reader's attention to the steady and extremely marked enhancement of interest in this approach, which has been expressed both by an increase in the number of publications and reviews on this question and also by the application of silylation to the synthesis of new poymers which are relatively difficult to obtain by means of traditional polymer formation reactions. At the same time, it is essential to note that so far the "silyl" method has not reached the stage of its industrial use as regards its application to polymers. This is apparently partly due to the fact that a successful compromise between the chemical, technological, economical, and ecological problems arising when silylated monomers and reagents are employed in the synthesis of polymers has not been found. However, one may assume that, as the process is improved and some kind of unique possibilities of the latter are discovered, it will become more than a purely preparative method for the synthesis of monomers and polymers with a specified combination of properties.

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