Translated from *Uspekhi Khimii* 59 1492–1521 (1990) U.D.C. 541.64

Polycondensation and polyaddition processes using silylated monomers

A L Rusanov
A N Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow

ABSTRACT. Polycondensation and polyaddition reactions using silylated monomers are reviewed. Means of obtaining silylated nucleophilic monomers and the influence of silylation on the reactivity of nucleophiles containing amine, hydroxyl and thiol groups have been analysed. It has been shown that in many cases the use of silylated monomers enables polycondensation processes to be carried out under mild conditions to give high molecular systems.

The bibliography contains 88 references.

Contents

I. Introduction 868
II. Polycondensation reactions using silylated nucleophiles 868
III. Polycondensation reactions in the presence of silylating agents 881

I. Introduction

Polycondensation chemistry has been enriched in the last two decades by a series of new processes which significantly broaden the scope of linear polycondensation and polycyclocondensation. These include 'direct' polycondensation,[1,2] 'activated' polycondensation,[3] polycondensation using phase transfer catalysts,[4] reductive polyheterocyclisation,[5,6] etc. Polycondensation processes using silylated monomers,[7–10] also called 'silylated' polycondensation,[10] must be included. 'Silylated' polycondensation, like 'direct'[1,2] and 'activated'[3] polycondensation is based on a change, usually an increase, in the reactivity of one of the monomers participating in the reaction, however, in contrast to the processes mentioned above, 'silylated' polycondensation assumes a change of reactivity in electrophilic and nucleophilic monomers including diamines, bis-phenols, bis-thiophenols and multifunctional systems.[10]

This approach was used for the first time in synthetic chemistry by Klebe and collaborators[7,8] from the middle sixties to the beginning of the seventies and has been taken up once more in the last 5–10 years. Some achievements in the area of 'silylated' polycondensation have been considered,[7–10] however none of these reviews gives a complete picture of the achievements of this rapidly developing area of polycondensation. The present review is required to fill this gap.

II. Polycondensation reactions using silylated nucleophiles

1. Methods of obtaining silylated nucleophilic monomers

The silylation of nucleophilic monomers reduces to the protection of labile hydrogen atoms in their functional groups by tris-(hydrocarbonyl)silyl residues, most frequently by trimethylsilyl or dimethylphenylsilyl groups.

The most widespread method of silylating nucleophiles is treatment of them with chloro-tris(hydrocarbonyl)silane, most frequently with chlorotrimethylsilane in inert solvents in the presence of acceptors of the hydrogen chloride released

$$HX{-}Ar{-}XH + 2Cl{-}SiR_3 \xrightarrow{-2HCl} R_3Si{-}X{-}Ar{-}X{-}SiR_3,$$

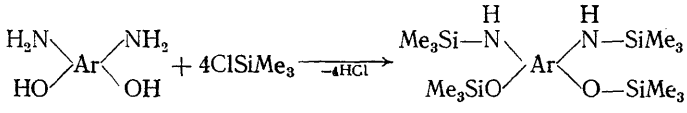
$$X = {-}NR'{-},\ {-}O{-},\ {-}S{-};\ R' = {-}H,\ -C_6H_5$$

This method has been used successfully for the silylation of primary diamines,[11–13] secondary diamines,[12–14] bis-phenols[15–17] and bis-thiophenols.[18] The silylation of secondary diamines, bis-phenols and bis-thiophenols leads to a bis-silylated product while analogous conversions of primary diamines may, depending on the conditions of carrying out the reaction, lead to the preparation of both bis-silylated[11–13] and *N,N,N',N'-tetrakis*-silylated diamines[19]

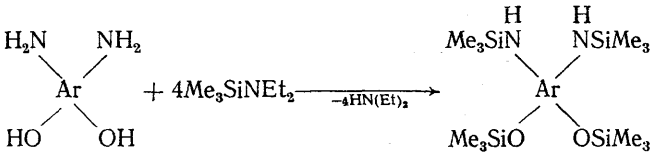
$$Me_3SiN(H){-}Ar{-}NSiMe_3(H) \leftarrow H_2N{-}Ar{-}NH_2 \rightarrow$$

$$\rightarrow (Me_3Si)_2N{-}Ar{-}N(SiMe_3)_2.$$

The same method of silylation was successfully used for obtaining *N,N',O,O'-tetrakis*-(trimethylsilyl)-bis(*o*-aminophenols)[20]



An alternative method of silylating bis-(*o*-aminophenols) is based on the use of trialkylsilyldialkylamines,[21–24] particularly of trimethylsilyldiethylamine in place of chlorotrimethylsilane



The last method has several significant advantages over silylation with chlorotrimethylsilane, such as reaction being effected in an excess of trialkylsilyldialkylamine in the absence of solvent and HCl

acceptor since the reaction byproduct is diethylamine. It is interesting to note[24] that on silylation of aminophenols the phenolic hydroxyls reacted first which made possible the isolation and characterisation of the *o*-, *m*- and *p*-isomers of the following series of compounds:

$$Me_3SiOC_6H_4\overset{H}{N}H_2,\quad Me_3SiOC_6H_4\overset{H}{N}SiMe_3,\quad Me_3SiOC_6H_4N(SiMe_3)_2.$$

Finally, silylated bis-phenols are obtained by treating various bis-phenols with hexamethyldisilazane in inert solvents[16]

$$HO—Ar—OH + Me_3Si\overset{H}{N}SiMe_3 \xrightarrow[-NH_3]{} Me_3SiO—Ar—OSiMe_3.$$

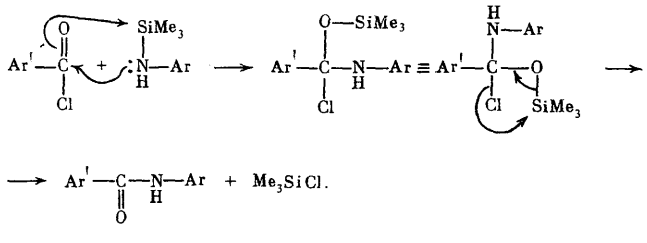
The same approach was used to obtain silylated derivatives of hydroxybenzoic acids[16]

$$HO—Ar—\overset{O}{\overset{\|}{C}}—OH + Me_3Si\overset{H}{N}SiMe_3 \xrightarrow[-NH_3]{} \rightarrow Me_3SiO—Ar—\overset{O}{\overset{\|}{C}}—OSiMe_3.$$

2. Reactivity of silylated nucleophilic monomers

As mentioned above the silylation of nucleophilic monomers is accompanied by a change in their reactivity. This problem has been considered in greatest detail when applied to silylated primary amines which possess an increased reactivity in reactions with carboxylic acid chlorides. The high reactivity of *N*-silylated amines may be explained by means of the mechanism presented below.[25]

It is a characteristic of organosilicon compounds that Si atoms have a high affinity for oxygen, and for fluoride and chloride ions and also that a carbocation in a position 3 to silicon may be stabilised by the $\sigma-\pi$ effect of the latter. A two-stage addition-elimination mechanism has been proposed for the nucleophilic substitution of acyl in acid chlorides by an *N*-trimethylsilylated amine allowing for these special features of organosilicon compounds[25]



In the first stage of the reaction, attraction of the carbonyl oxygen of the acid chloride for the Si atom of the *N*-silylated amine facilitates nucleophilic attack by the nitrogen atom of the latter on the carbonyl carbon of the acid chloride, with subsequent rapid formation of a tetrahedral intermediate. In the second stage of the process elimination of a chloride ion from the intermediate is facilitated by the presence of the Si atom in the β-position which leads to rapid formation of amide together with chlorotrimethylsilane.[25]

The reactivity of *S*-trialkylsilated thiophenols may approach the reactivity of *N*-silylated amines.[18] Silylation of a hydroxyl group leads to its protection from electrophilic attack[8,26] as a result of the strong affinity of silicon for oxygen.

The reactivity of *S*-trimethylsilylbenzenethiol (I), *N*-trimethylsilylaniline (II) and *O*-trimethylsilylphenol (III) towards electrophiles has been compared.[18] It was found that the relative reactivities of these compounds on reaction with benzoyl chloride is expressed in the series (II) > (I) > (III) and in reaction with 1-chloro-2,4-dinitrobenzene in the series (I) > (II) > (III). *O*-Trialkylsilated phenols (trialkylsilyloxybenzenes) may react with such electrophiles as acid halides and activated organic halides only in the presence of chloride or fluoride ion

$$Ar—O—SiMe_3 + X^{\ominus} \rightarrow Ar—O^{\ominus} + Me_3SiX.$$

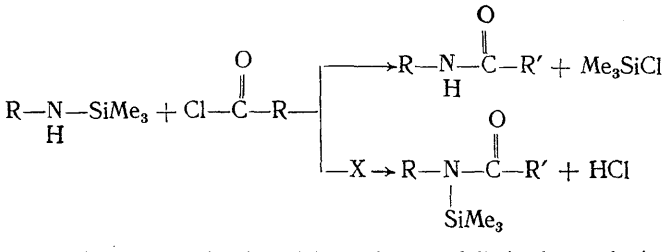
The silylation of such tetrafunctional nucleophiles as bis-(*o*-aminophenols) leads, in full agreement with that mentioned above, to activation of amino and deactivation of hydroxyl groups,[20] which facilitates[27,28] the selective execution of the first stage of polycyclocondensation and permits avoidance of gel formation.

3. Condensation and addition polymers based on silylated diamines

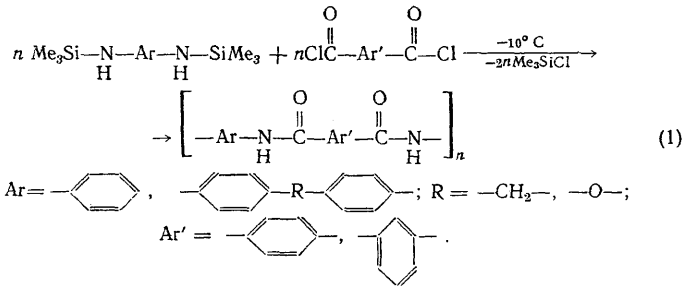
As was shown above *N*-trialkylsilylated amines are some of the most reactive organosilicon compounds. They react with various electrophiles such as acid chlorides and anhydrides, isocyanates, benzyl halides, aldehydes, etc.[8] All these reactions have been used to obtain nitrogen-containing condensation and addition polymers.[10]

a) Synthesis of polyamides

It is known[29] that on reacting *N*-trimethylsilyl-protected amines with carboxylic acid chlorides, amides are formed with the elimination of chlorotrimethylsilane as byproduct and not trimethylsilylamides with elimination of hydrogen chloride as a byproduct



This amidation reaction is widely used successfully in the synthesis of polyamides. Thus high molecular aromatic polyamides have been obtained[25,30] by the interaction of *N,N'*-disilylated aromatic diamines with diacid chlorides of aromatic dicarboxylic acids under low temperature polycondensation conditions in solution

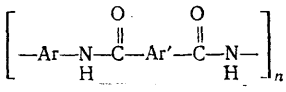


(1)

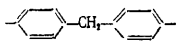
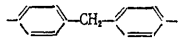
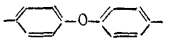
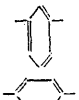
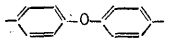
Comparison of the polyamidation process being considered with the traditional method of synthesis of aromatic polyamides, viz. reaction of diamines with diacid chlorides of dicarboxylic acids,[31–33] using the synthesis of poly-(*p*-phenyleneterephthalamide) as example, showed[30] that *N,N'*-disilylated *p*-phenylenediamine

reacts much more rapidly with terephthaloyl chloride. Polyamides with higher viscosity characteristics are obtained. Some results of syntheses of aromatic polyamides are shown in Table 1.

Table 1. Viscosity characteristics of aromatic polyamides of formula



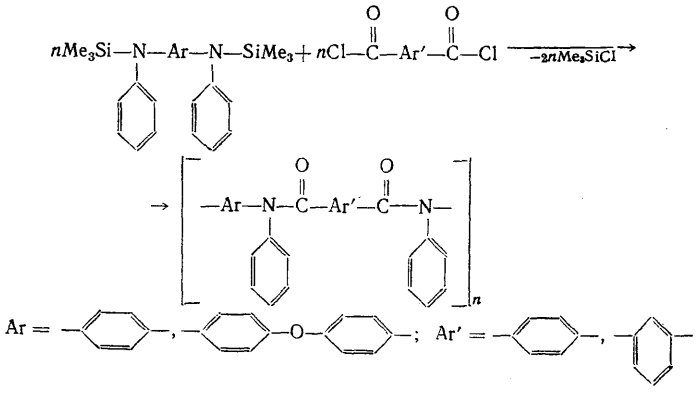
(Ref.25)

Ar	Ar′	η_{inh}, dlitre g^{-1}, conc. H_2SO_4, 30 °C	
		from *N*-silylated diamines	from unsilylated diamines
		2.45	1.03
		3.19	0.94
	 *	7.41	3.23
		2.41	1.19
		2.54	1.15
		3.21	1.40
		3.97	2.10
		3.99	1.50

Note. Polymerisation was carried out in *N*-methyl-2-pyrrolidone (NMP) containing LiCl, at −10 to −5 °C for 5 h.
*Polymerisation was carried out in a mixture of NMP and hexamethylphosphoramide (HMPA) containing LiCl at −10 to −5 °C for 12 h.

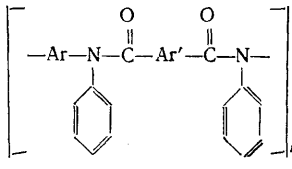
Analysis of the data shown in Table 1 indicates that without exception polyamides are obtained with significantly higher viscosity characteristics from silylated diamines than from free diamines.

The use of silylated diamines is particularly expedient in those cases when high molecular compounds cannot be obtained from free monomers of this class. The preparation of high molecular polyamides based on weakly basic diamines, which have low reactivity, is extremely problematical. The *N*-silylation of such diamines is a reliable method of activating them[12,13,34] and may be illustrated using aromatic *N,N′*-diphenyl-substituted diamines as an example.[13,34,35] These compounds, being extremely low in reactivity, are activated by silylation to such an extent that their reaction with diacid chlorides of aromatic dicarboxylic acids under high temperature polycondensation conditions in tetramethylene sulphone leads to the formation of high molecular poly-(*N*-phenyl)amides:[13,34,35]

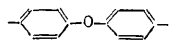
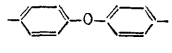


Some characteristics of the poly-(*N*-phenyl)amides synthesised are given in Table 2.

Table 2. Conditions of synthesis and viscosity characteristics of poly-(*N*-phenyl)amides of general formula



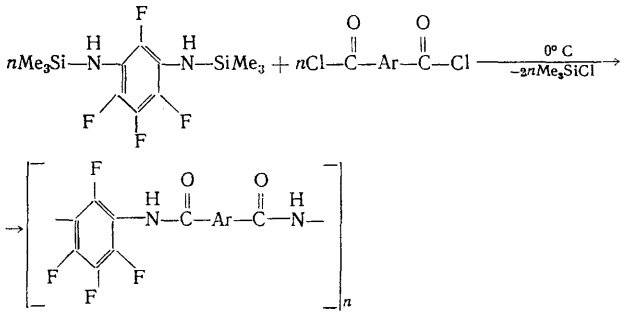
(Refs.13, 34)

Ar	Ar′	Polycondensation conditions		η^*_{inh}, dlitre g^{-1}	T_g^{**}, °C
		T, °C	time, h		
		160	24	1.65	225
		200	6	2.21	255
		160	24	1.24	195
		200	24	1.35	215

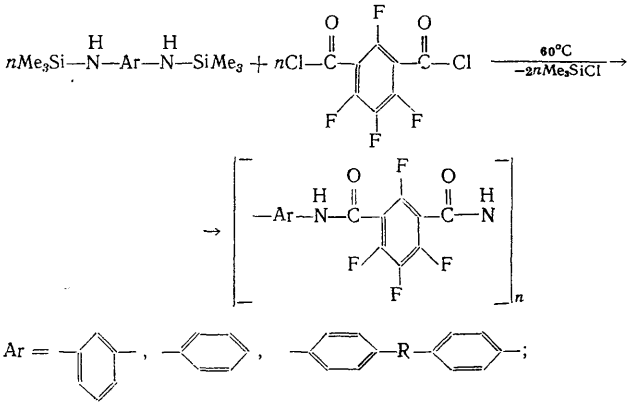
*η_{inh} was measured in H_2SO_4 at 30 °C and a concentration of 0.5 g dlitre^{-1}; **T_g was determined by differential thermal analysis (DTA) at a heating rate of 10 °C min^{-1}.

Analysis of the data given in Table 2 indicates that, as in the processes considered above for unsubstituted polyamides, the use of *N*-silylated diamines made it possible to obtain systems with extremely high viscosity characteristics. The poly-(*N*-phenyl)amides synthesised had T_g 195–255 °C. They dissolved in various solvents, including dimethylformamide (DMF), *m*-cresol and chloroform.

Tetrafluoro-*m*-phenylenediamine is a diamine with low basicity. It too may be activated by silylation.[36] High molecular fluorine-containing polyamides are obtained by reacting its *N,N'*-bis-trimethylsilylated derivative with diacid chlorides of aromatic dicarboxylic acids under low temperature polycondensation conditions in solution



It is interesting to note that silylated aromatic diamines form high molecular polyamides even on reaction with the poorly reactive diacid chlorides of aromatic dicarboxylic acids. The preparation of fluorine-containing polyamides by reaction of *N*-silylated aromatic diamines with tetrafluoroisophthaloyl chloride under low temperature polycondensation conditions in solution is an example[37]

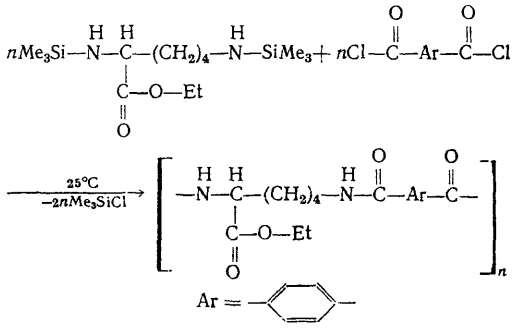


Ar = ;

R = —O—, —CH_2—.

Fluorine-containing aromatic polyamides obtained by a scheme analogous to this possessed η_{inh} equal to 0.43 dlitre g^{-1} and T_g equal to 245–280 °C (Table 3).

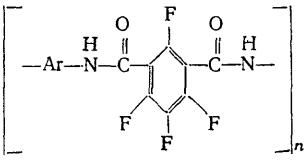
In addition to aromatic systems, aliphatic-aromatic polyamides have also been obtained based on *N*-silylated diamines. In particular high molecular aliphatic-aromatic polyamides are obtained by the polycondensation of *N*-silylated lysine with the diacid chloride of an aromatic dicarboxylic acid:[38]

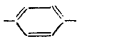
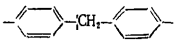
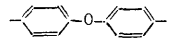


Polyterephthalamides obtained from *N*-silylated lysine possessed η_{sp} = 1.02 [hexamethylphosphoramide (HMPA)].[38]

The interaction of silylated diamines with diacid chlorides according to Scheme (1) may be effected not only in solvents but also under conditions of solvent-free vacuum 'deposition' polycondensation (from the gas phase) making it possible to obtain thin films on appropriate substrates.[39] Thin polyamide films may also be obtained using unsilylated diamines[40,41] however a temperature of the order of 100 °C is required to remove the HCl formed during the reaction. On using *N*-silylated diamines the solvent-free vacuum 'deposition' polycondensation from the gas phase takes place at temperatures of the order of 60 °C with separation of neutral chlorotrimethylsilane. Metallic plates capable of erosion may be used as substrates and are coated with thin polyamide films. It is interesting to note that poly-*p*-phenyleneterephthalamide (Kevlar), usually a highly crystalline polymer, applied using silylated diamine, forms an amorphous transparent film.

Table 3. Some characteristics of polyamides of general formula

 (Ref.37)

Ar	η^{*}_{inh}, dlitre g^{-1}	T^{**}_{g} °C
	0.43	245
	0.56***	275
	0.63	280
	0.82	280

Note. Polyamide synthesis was effected in chloroform containing triethylamine hydrochloride at 60 °C for 6 h.

* η_{inh} was measured for 0.5% solutions in DMA at 30 °C;

** determined by DTA at ΔT = 10° min^{-1} (air);

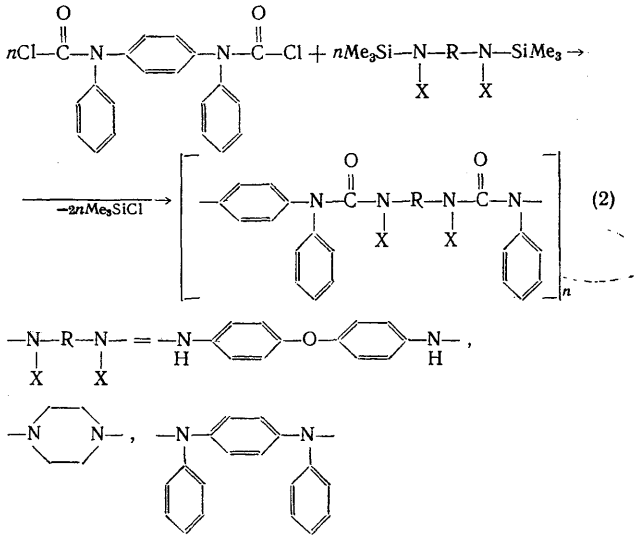
*** polycondensation was carried out at 0 °C for 6 h.

'Activated' polycondensation reactions[3] have been used for obtaining polyamides in addition to the reactions of silylated diamines with diacid chlorides. In particular silylated diamines react with bis-(2,4-dinitrophenyl) esters of dicarboxylic acids.[38] These processes, accompanied by the separation of *O*-silylated 2,4-dinitrophenol as a byproduct, are examples of polycondensation reactions using both activated nucleophiles and electrophiles. The examples given above demonstrate the application of polycondensation with silylated diamines to the efficient preparation of various polyamides.

b) Synthesis of polyureas

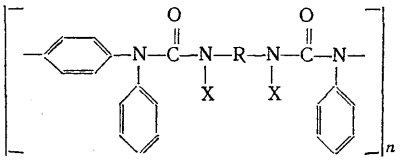
Silylated diamines have been used for obtaining polyureas by applying both polycondensation[12] and polyaddition[42] processes.

In particular, the reaction of *N,N'*-di(trimethylsilylated) aromatic diamines with *N,N'*-dichloroformyl-*p*-dianilinobenzene[12] proceeded according to Scheme 2 and *N*-phenylated polyureas were partially or completely obtained. Conditions of syntheses and individual characteristics are given in Table 4.

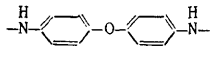
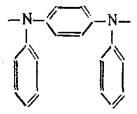


(2)

Table 4. Conditions of synthesis and some characteristics of polyureas of general formula



(Ref.12)

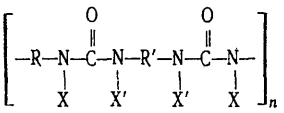
–N–R–N– (X, X)	Polycondensation conditions*			Properties of polymers	
	solvent	*T*, °C	time, h	yield, %	η_{inh}, dl·g^{-1}**
	*sym*-TCE	120	5	80	0.13
	anisole	120	5	80	0.19
	o-dichlorobenzene	120	5	78	0.12
	nitrobenzene	120	5	80	0.19
	sulpholan	120	5	88	0.22
	"	120	24	88	0.27
	"	180	5	79	0.09
	sulpholan	80	24	92	0.22***
	"	120	3	85	0.21***
	"	160	24	85	0.35***
	"	200	24	82	0.26***
	sulpholan	190	24	75	0.08
	"	220	5	76	0.09
	"	220	24	82	0.13
	"	250	24	70	0.09

* Polycondensation was carried out by reacting 1 mmole *N,N'*-dichloroformyl-*p*-dianilinobenzene with 1 mmole silylated diamine in 3 ml solvent in a stream of N_2;

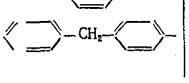
** viscosity was measured for 0.5% solutions in NMP at 30 °C;

*** viscosity was measured in conc. H_2SO_4.

Table 5. Thermal characteristics of polyureas of general formula



(Ref.12)

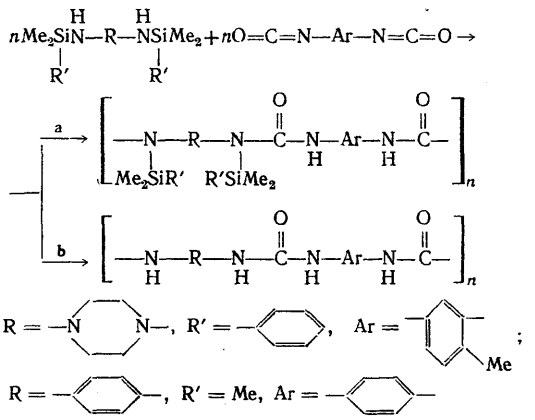
R	R'	X	X'	T_{dec}, °C* in air	T_{dec}, °C* in N_2
			H	265	295
		»	H	385	420
		»		520	520
	»	H	H	335	340

* T_{dec} is temperature at which polymer mass has lost 10% (TGA, ΔT = 10 °C min^{-1}).

As follows from analysis of the data given in Table 4 high molecular polymers were obtained in only one case, however the favourable influence of silylation of amines was recorded in the viscosity characteristics of the polyureas. Polymers with significantly lower viscosity characteristics were obtained from unsilylated diamines. The completely and partially phenylated polyureas obtained from silylated aromatic diamines dissolved readily in organic solvents such as dimethylacetamide (DMA), tetrahydrofuran (THF) or *m*-cresol and surpassed significantly in solubility the unsubstituted aromatic polyureas and also polymers from silylated piperazine, which are crystalline systems.

The introduction of phenyl substituents in place of comparatively labile hydrogen atoms into polyureas increases not only the solubility but also the thermal stability of these systems (Table 5) which is in agreement with the results of investigations on various classes of heterochain and heterocyclic polymers.[43]

An additional method of synthesising polyureas using silylated diamines was described by Klebe in 1964.[42] It was shown that addition of *N,N'*-disilylated diamines to a diisocyanate led to the preparation of *N*-silylated polyureas which were readily methanolised into unsubstituted polyureas



The polyaddition reaction occurs under homogeneous conditions even on carrying it out in non-polar solvents (Table 6) due to the lower polarity of *N*-silylated polyureas compared to unsubstituted polyureas.[44]

Table 6. Synthesis of aromatic polyureas in various solvents.[44]

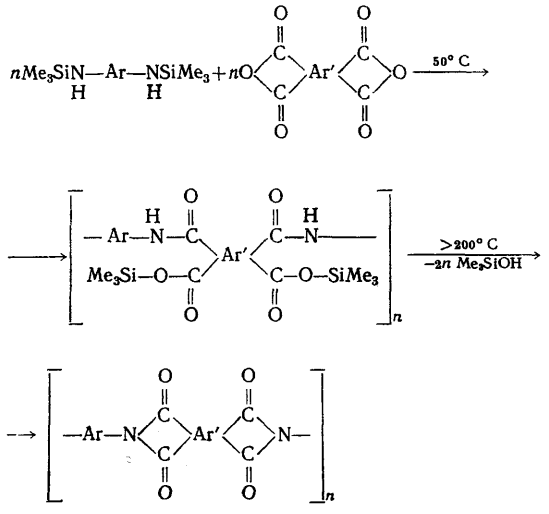
Solvent	η_{inh}, dlitre g^{-1}
DMSO	0.54
Tetramethylenesulphone	0.60
Tetrachloroethane (TCE)	0.91
Anisole	0.77
Nitrobenzene	0.65
Toluene	0.74

Note. Reaction of *N,N'*-bis(trimethylsilyl-substituted 4,4'-diaminodiphenylether was carried out at 100 °C for 10 h; viscosity was measured for 0.5% solutions in conc. H_2SO_4 at 30 °C.

It should be mentioned that polyureas obtained by the methanolysis of *N*-silylated polymers are characterised by low crystallinity and good solubility in organic solvents in difference to polyureas obtained by the usual method (diamines with diisocyanates).

c) Synthesis of polyimides

By analogy with the widespread two-step method of synthesis of polyimides[45–50] their preparation from silylated diamines occurs through the formation of intermediate polymers which are converted thermally into the desired systems.[51,52] The polyaddition of *N*-silylated aromatic diamines to dianhydrides of aromatic tetracarboxylic acids occurs with ring fission of the latter with the formation of trimethylsilyl esters of polyamidoacids which then form imides at a temperature >200 °C with the separation of trimethylsilanol



The presence of trimethylsilyl groups in the polyamidoacid esters determines the significantly greater stability of these polymers compared to unsubstituted polyamidoacids and also their increased solubility in non-polar solvents. The latter circumstance enables the synthesis of similar polymers not only in dipolar aprotic solvents of the type of DMA and *N*-methylpyrrolidone (NMP) but also in ethers or hydrocarbons. In several cases these processes are accompanied by precipitation of the polyamidoacid from solution (Table 7), however polyamidoacids with high inherent viscosities were obtained in practically all the solvents tested (Table 7).

Table 7. Synthesis of polyamidoacids in various solvents.[52]

Solvent	η_{inh}, dlitre g^{-1}	Reaction conditions
DMA	1.77	P
NMP	1.46	P
bis-Methoxyethyl ether	0.92	P
1,4-Dioxan	0.80	P
THF	0.97	P
Chloroform	0.99	P
Acetonitrile	0.88	O
Nitrobenzene	0.81	O
Toluene	0.92	O

Note. Synthesis of polyamidoacids was carried out by reacting *N,N'*-bis-(trimethylsilyl)-substituted bis-(4-aminophenyl)ether with pyromellitic anhydride at 20 °C for 1 h and then at 50 °C for 12 h; inherent viscosities were measured for 0.5% solutions in DMA at 30 °C; P denotes reaction in solution; O denotes formation of solid during reaction.

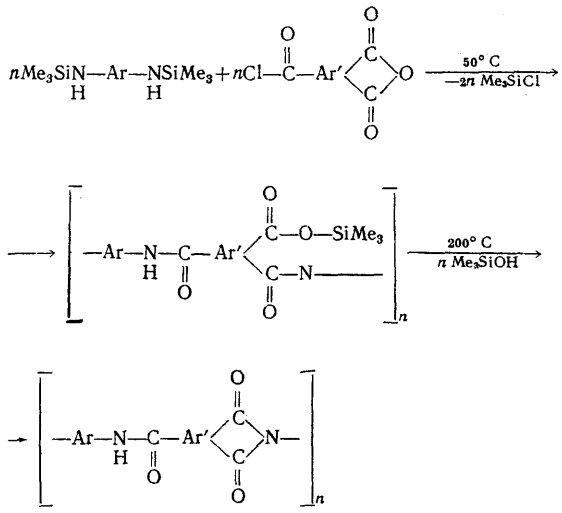
The thermal conversion of silylated polyamidoacids into polyimides occurs slowly and completion of imide formation requires higher temperatures compared with the cyclisation of unsubstituted polyamidoacids.

A single-stage process for synthesising polyimides using *N*-silylated diamines[53–55] has been applied to obtain polyimides containing residues of aliphatic diamines and polyimides difficult to obtain as high molecular systems from unsubstituted aliphatic diamines.[54] In addition these processes were used successfully to obtain polynaphthylimides distinguished by an enhanced stability towards hydrolysis.[56]

The synthesis of polyimides using *N*-silylated diamines, as when using unsubstituted diamines, may (by analogy with that suitable for polyamides[39] considered above) be used for applying thin films to appropriate substrates using solvent-free vacuum 'deposition' polycondensation from the gas phase.[57–59] In the first stage of applying thin polyimide films, the aromatic diamine and dianhydride are applied to the substrate under high vacuum which is then heated to effect imide formation.

Polycondensation using *N*-silylated diamines may also be used when appropriate with derivatives of aromatic polycarboxylic acids containing various electrophilic functional groups. Thus the

interaction of 4-chloroformylphthalic anhydride with *N,N'*-bis-(trimethylsilyl)-substituted 4,4'-diaminodiphenyl ether proceeded through a polycondensation/polyaddition reaction with the formation of the trimethylsilyl esters of polyamidoacids[60]



Results of the synthesis of intermediate polymers in various solvents are given in Table 8.

Table 8. Synthesis of copolyamido-amidoacids in various solvents.[60]

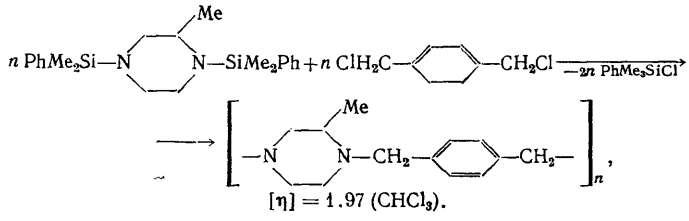
Solvent	η^{*}_{inh}, dlitre g^{-1}	Reaction conditions
DMA	1.82	P
NMP	1.48	P
Acetonitrile	1.14	O
Nitrobenzene	1.21	O
bis-Méthoxyethyl ether	1.00	O
1,4-Dioxan	0.75	O
THF	0.94	O
Chloroform	0.59	O
Benzene	0.57	O

Note. Synthesis was effected by reacting *N,N'*-bis-(trimethylsilyl)-substituted 4,4'-diaminodiphenyl ether with 4-chloroformylphthalic anhydride at −5 °C for 1 h and then at 50 °C for 4 h.
* Inherent viscosities were measured for 0.5% solutions in NMR at 30 °C.

As is seen from Table 8 only reactions in NMP and DMA media proceed homogeneously. Nonetheless polymers were obtained in practically all solvents with comparatively high solution inherent viscosity. The silylated intermediate polymer may be converted into a polyamidoimide by thermal treatment under the same conditions used in the synthesis of polyimides.

d) Synthesis of polyamines

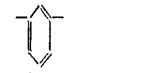
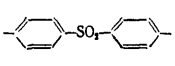
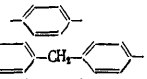
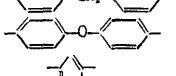
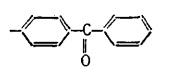
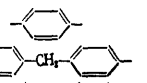
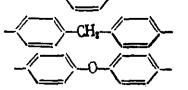
In spite of the fact that alkyl halides are aminolysed with difficulty compared with carboxylic acid chlorides, they may also interact with *N*-silylated amines.[8] According to Klebe[14] benzyl chloride reacts with *N*-silylated amines at temperatures >100 °C forming benzylamines and trialkylsilyl chloride in quantitative yield. Ammonium salts and cyclic sulphone catalytically increase the rate of the process. This reaction was extended to the synthesis of polyamines which are difficult to obtain as high molecular compounds by the reaction of diamines with dihalo compounds because of side reactions. Polycondensation of reactive dihalides of the benzyl chloride type with *N*-silylated piperazine, carried out in bulk at 150 °C, led to the formation of a high molecular polyamine[14]



$[\eta] = 1.97$ ($CHCl_3$).

Table 9. Conditions of synthesis and viscosity characteristics of aromatic polyamines of general formula

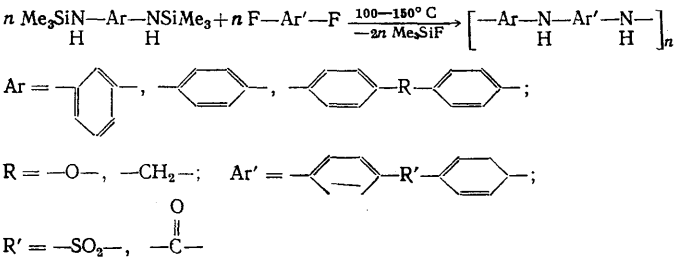
$$\left[-Ar-\underset{H}{N}-Ar'-\underset{H}{N}-\right]_n$$ (Ref.61)

Ar	Ar'	Polycondensation conditions* (temperature/time, °C/h)	η_{inh}, **dlitre g^{-1}
		100/7—150/14	0.62
	»	150/12	0.57
	»	150/12	0.42
	»	100/7—150/14	0.60
		100/24—240/48***	0.55
	»	220/48***	0.37
	»	100/24—240/48	0.45
	»	150/48	0.66

*Polycondensation was carried out in the presence of KF;
**inherent viscosities were measured for 0.5% solutions in NMP at 30 °C;
***polycondensation in tetramethylenesulphone.

A similar substitution reaction occurs on treatment of activated haloaromatic compounds with *N*-silylated aromatic amines. In this way secondary aromatic amines were formed together with

trimethylsilyl halides.[61] Correspondingly new aromatic polyamines were successfully obtained from activated aromatic difluoro compounds and *N*-silylated aromatic diamines[61]



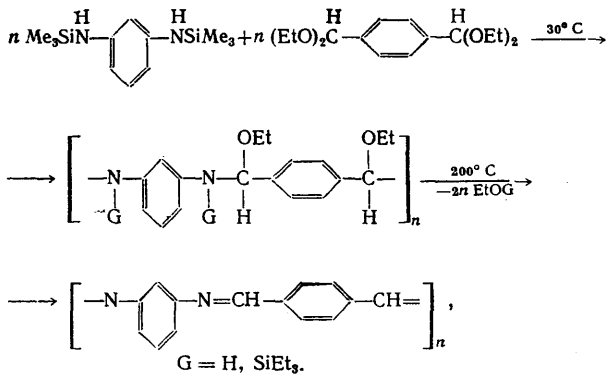
The polycondensation reaction was carried out in DMSO in the presence of fluorine-containing catalysts (KF, CsF) at 100–150 °C. Polyamines with comparatively high viscosity characteristics were obtained as a result (Table 9).

The presence of a catalyst is essential to obtain high molecular polyamines. The use of the corresponding dichlorides in place of activated aromatic difluorides led to the preparation of only low molecular polymers. Introduction of a nitro substituent into aromatic dihalo compounds increased their reactivity and led to the formation of polyamines with higher inherent viscosities. These aromatic polyamines dissolved readily in organic solvents like NMP and had $T_g \sim 200$ °C. They are potential engineering plastics.[61]

At the same time they may readily be reduced to the corresponding poly-(*o*-amino)amines[5,6,61–65] which in their turn may be used to obtain a large range of heterocyclic polymers[65]

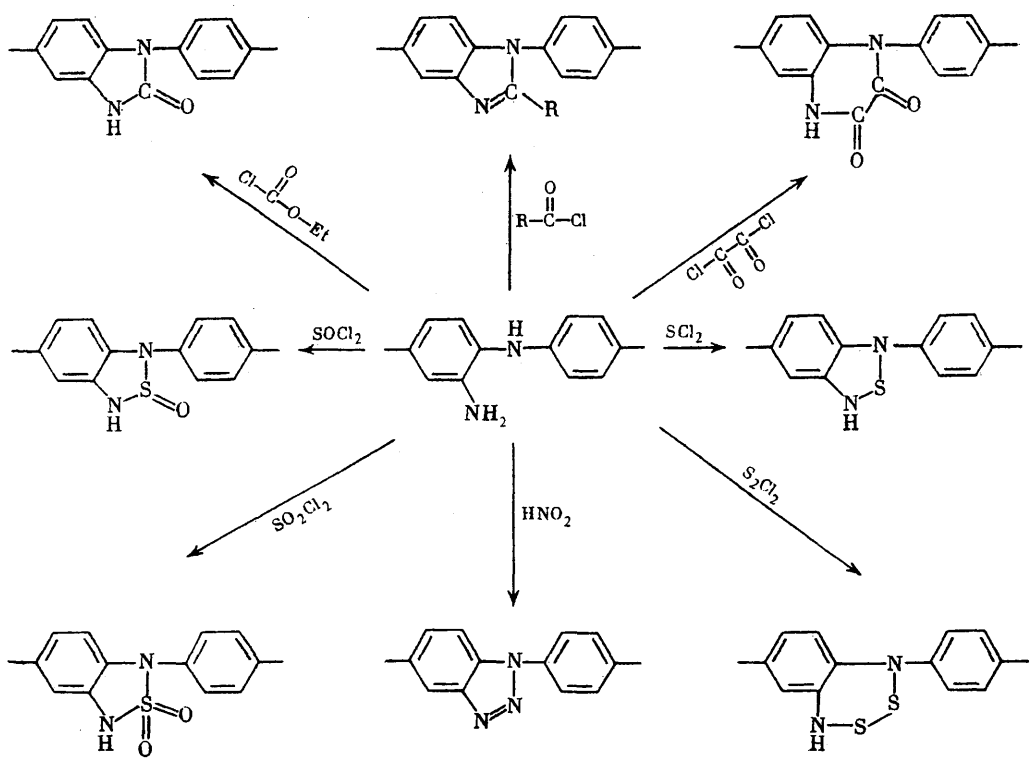
e) Synthesis of polyazomethines

The majority of aromatic polyazomethines are not obtained as high molecular compounds because of their insolubility and infusibility. Kurosaki and collaborators[16,66] have intensively investigated reactions to obtain aromatic polyazomethines and found new synthetic routes to these systems using *N*-silylated aromatic diamines. One method led to the polycondensation reaction of *N,N'*-bis-(trimethylsilyl)-substituted aromatic diamines with aromatic bis-(diethylacetals) in NMP leading to an intermediate polymer which was soluble in organic solvents. This was reprocessed into films by conversion at 200 °C into insoluble polyazomethines[66]

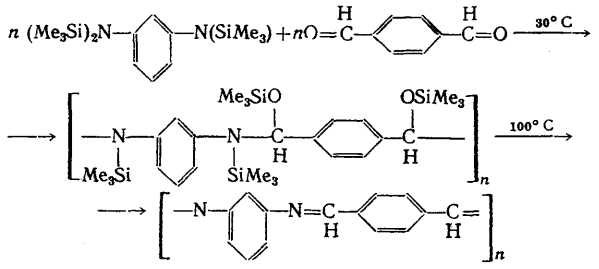


G = H, $SiEt_3$.

Another method is the polyaddition of *N,N,N',N'-tetrakis*-(trimethylsilyl)-substituted aromatic diamines with aromatic dialdehydes in NMP with the formation of soluble intermediate polymers, with



subsequent conversion (thermal) into insoluble polyazomethine films[19]



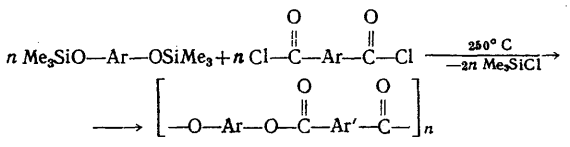
Similar intermediate polymers were formed in both cases in the first stages subsequently undergoing β-elimination with the formation of azomethine bonds in the main macromolecule chains.

4. Polymers based on *O*-silylated bis-phenols

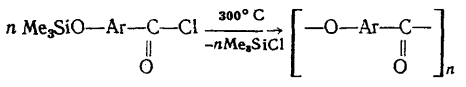
The possibility of using *O*-silylated bis-phenols to obtain high molecular compounds has been studied in detail by Kricheldorf and collaborators[15–17,67–70] who synthesised high molecular polyesters and polyethers based on these monomers.

a) Synthesis of polyesters

The possibility was shown in 1979 of synthesising polyaryl esters from *O*-silylated bis-phenols and diacid chlorides of dicarboxylic acids[15]



or from trimethylsilyloxybenzoyl chlorides

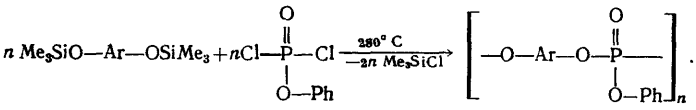


by polycondensation in bulk at 200–300 °C.

The drawback of the thermal polycondensation of two different monomers (A–A and B–B types) such as *O,O'*-trimethylsilyl-substituted 2,2-bis-(4-hydroxyphenyl)propane and isophthaloyl chloride is the possibility of distilling or subliming out the more volatile monomer which disturbs the stoichiometry of the starting materials and leads to a reduction in the degree of polymerisation. This drawback is eliminated in the homocondensation of monomers of the A–B type such as trimethylsilyloxybenzoyl chloride. The molecular weight of a polymer obtained from a *m*-hydroxybenzoic acid derivative (type A–B) was greater than that of a polymer from *O*-silylated bis-phenol and isophthaloyl chloride. Thus the silylation method is useful for the high temperature preparation of polyarylates from monomers of type A–B.

The homocondensation reaction of *m*- and *p*-silyloxybenzoyl chlorides has been carried out in bulk and in solution.[67,68] Polycondensation of *m*-trimethylsilyloxybenzoyl chloride in bulk at 250 °C led to the preparation of a polyaryl ester of molecular weight 10000–14000,[67] while polycondensation of the *p*-isomer in a high boiling solvent at 320 °C led to the preparation of a polymer of molecular weight 20000–50000.[68] In the latter case crystalline oligomers separated from solution in the first stage of the polycondensation, the molecular weight of which continued to grow on heating. Polycondensation was accelerated by such catalysts as triethylamine hydrochloride and benzyltriethylammonium chloride leading to polyaryl esters with large molecular weights.

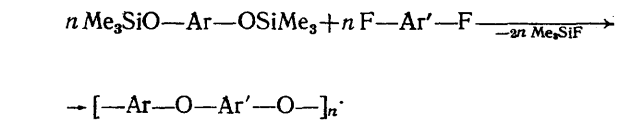
O-Silylated bis-phenols also react with aryl phosphodichloridates with the formation of aromatic polyphosphates which are polyesters in the wide sense of the word[69,70]



Polycondensation in bulk was carried out at 180–300 °C in the presence of catalytic amounts of benzyltriethylammonium chloride. Polyphosphates of molecular weight up to 12000 were obtained in this way.

b) Synthesis of polyethers

The possibility of using *O,O'*-bis-trimethylsilylated bis-phenols to obtain polyethers in addition to polyesters has been investigated.[16,17,71,73] Activated difluoro-aromatic compounds were selected as comonomers of silylated bis-phenols



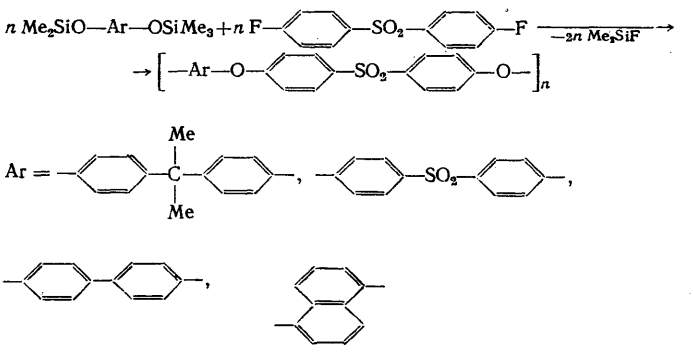
The use of the corresponding derivatives of the diphenylsulphone[16] and benzophenone[17] series as activated difluoro-aromatic compounds enabled the preparation valuable poly(ether sulphones)[16,72] and poly(ether ketones).[17,73]

These polymers are usually obtained by high temperature polycondensation of bis-phenols with activated dihalo-aromatic compounds in solutions of alkali metal salts.[74–78] The main drawback of these processes is the need to purify the desired polymers from reaction by products, viz. metal salts, and also from the expensive high boiling solvents used in obtaining them.

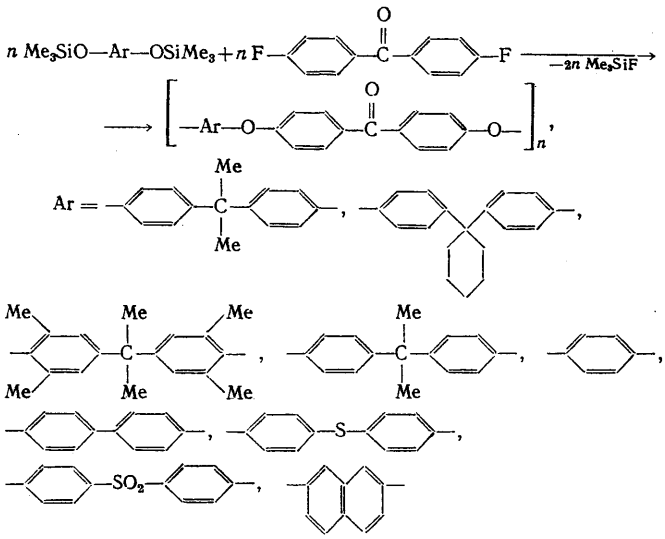
The use of silylated monomers enables polymers to be obtained which require no purification from large amounts of metal salts.

The reduction in reactivity of silylated bis-phenols requires the synthesis of polyesters to be conducted at elevated temperatures using catalysts such as KF and CsF.

The interaction of *O,O'*-trimethylsilyl-substituted bis-phenols with 4,4'-difluorodiphenylsulphone, which was carried out in bulk at temperatures up to 340 °C (Table 10), led to the preparation of poly(ether sulphones) with molecular weights reaching 17500.[16]

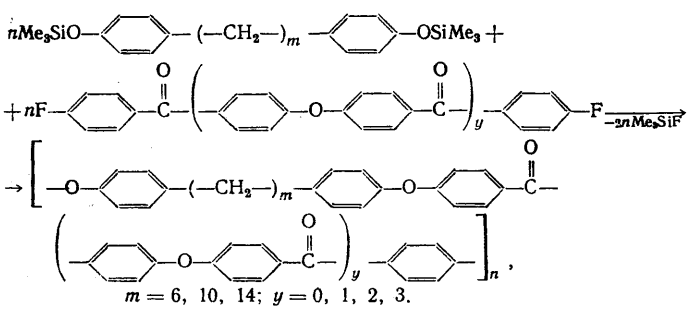


The reaction of *O,O'*-dimethylsilylated bis-phenols with 4,4'-difluorobenzophenone[17] leading to polyetherketones was effected under analogous conditions.



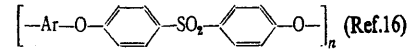
Some characteristics of the poly(ether ketones) obtained are shown in Table 11.

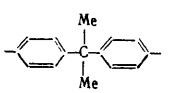
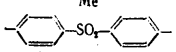
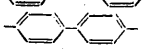
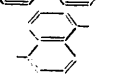
As continuation of these investigations the synthesis of fatty aromatic poly(ether ketones) with alternating aliphatic 'looseners' (spacers) and aromatic ether ketone blocks has been effected[73]



$m = 6, 10, 14; y = 0, 1, 2, 3.$

Table 10. Conditions for polycondensation of 4,4'-difluorodiphenylsulphone with *O,O'*-trimethylsilyl-substituted bis-phenols and some characteristics of the poly(ether sulphones) obtained of general formula



Ar	Polycondensation conditions		Yield, %	T_g, °C
	temperature, °C	time, h		
	180/320	0.5/2.5	98	185—195
	270/320/340	0.5/0.5/2.0	97	240—245
	250/320	0.5/2.5	95	240
	250/320	0.5/2.5	93	227

The poly(ether ketones) obtained in this way were crystalline substances, not forming mesophases.

2,6-Difluoropyridine is another activated difluoro-aromatic compound reacting with silylated bis-phenols[71]

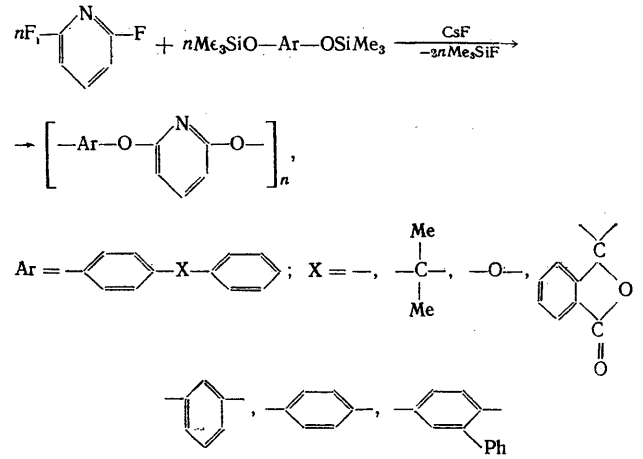
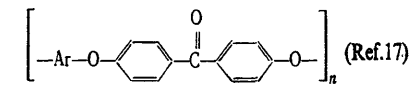
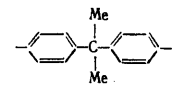
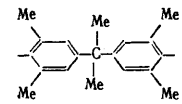
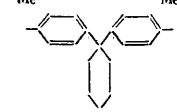
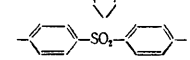
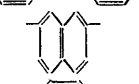
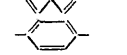
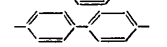


Table 11. Some characteristics of poly(ether ketones) of general formula



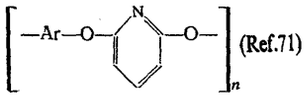
Ar	η^*_{rel}	$\overline{M}_n^{**}$	$\overline{M}_w^{***}$	T_g^{****}, °C	Mp^{****}, °C
	1.11	11 500	60 000	151—153	—
	1.06	1 700	3 200	143—145	—
	1.09	9 000	40 000	173—175	—
	1.46	7 000	—	184—186	—
	—	нр	нр	152—154	241—243
	2.21	—	—	—	343—345
	1.85	—	—	—	420—422

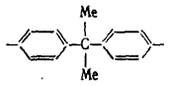
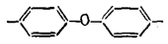
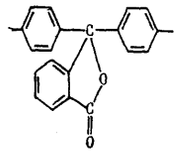
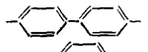
*Measured for 1% solutions in H_2SO_4 at 25 °C; **measured by osmometry in chloroform; ***measured by GLC in THF; ****determined by DSC at a temperature rise rate of 20° min^{-1}.

These processes are carried out in bulk at a maximum temperature of ~300 °C using CsF as catalyst by analogy to the synthesis of polyethers mentioned above (Table 12). As a result of

the low boiling point of 2,6-difluoropyridine (123 °C) a portion of it is removed from the reaction. Consequently the polycondensation processes were carried out with a small excess of 2,6-difluoropyridine (Table 12).

Table 12. Conditions of preparation and some characteristics of polyethers of general formula


(Ref.71)

Ar	Excess of 2,6-difluoro-pyridine, mol.	Yield, %	η_{inh}, dlitre g^{-1}
	0	99	0.25
	1.0	96	0.41
	3.0	96	0.47
	0	96	0.20
	1.0	97	0.42
	1.0	98	0.50
	0	91	0.45
	1.0	94	1.00
	—	96	1.40
	1.0	60	0.51

*Measured for solutions (c = 2 g litre^{-1}) in a mixture of dichloromethane–formic acid–trifluoroacetic acid (molar ratios 70:10:20) at 25 °C.

The conditions for carrying out the reaction of 2,6-difluoropyridine with silylated bis-phenols and the viscosity characteristics of the polyethers obtained are shown in Table 12.

As is seen from Table 12 the polyethers were obtained in almost all cases in yields exceeding 90% and with η_{inh} lying at 0.20–1.40 dlitre g^{-1}. The best viscosity characteristics were inherent in the film-forming polyether obtained from *O,O'*-disilylated phenylhydroquinone.

The molecular weight and thermal characteristics of the products of interaction of 2,6-difluoropyridine with silylated bis-phenols are shown in Table 13.

In addition to the homopolymeric polyesters the synthesis has been undertaken of copolymeric structures using an equimolar mixture of 2,6-difluoropyridine with 4,4'-difluorobenzophenone or 4,4'-difluorophenylsulphone as electrophilic comonomers[71]

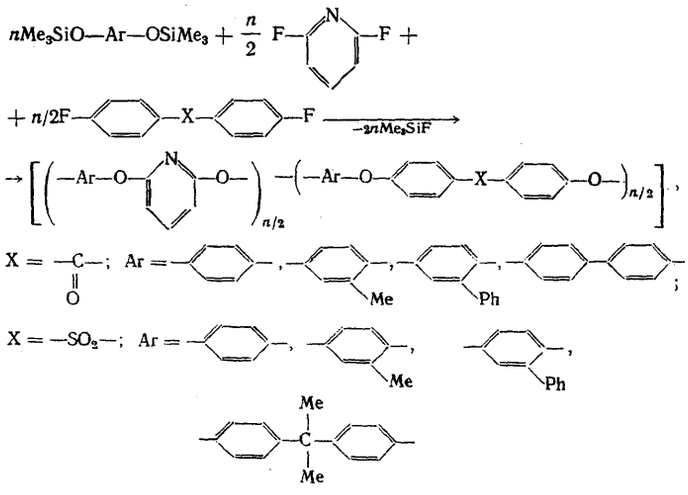
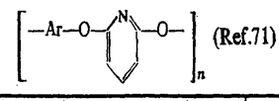
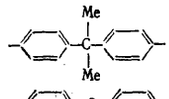
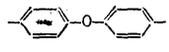
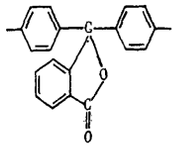
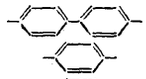
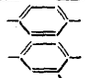


Table 13. Properties of polyethers of general formula


(Ref.71)

Ar	η^{*}_{inh}, dlitre g^{-1}	$M_w 10^{-3}$ mol	T_g**, °C	M.p.**, °C	Temperature for mass loss °C, %		
					5	10	50
	0.133	95	108	—	442	462	520
	—	—	90	—	419	445	550
	0.128	—	195	—	458	469	570
	нр	—	119	253	430	458	620
	нр	—	100	272	360	430	555
	0.140	1200	71	—	425	451	485
	0.223	2900	116	—	445	460	560

*Measured for solutions in dichloromethane (c = 2 g litre^{-1}); ** date of DSC at heating rate 20° min^{-1}.

As follows from the data presented in Tables 14 and 15 polymers were obtained by copolycondensation possessing fairly high η_{inh} (0.44–1.56 dlitre g^{-1}) in combination with T_g lying within the limits 118–147 °C.

c) Synthesis of copolymers containing ether and ester groups

In addition to the synthesis of polyethers and polyesters the silylated monomers have been used for making high molecular compounds containing both ether and ester groups.[16] The reaction of di-methylsilylated *m*- and *p*-hydroxybenzoic acids with 4,4′-difluorodiphenylsulphone has been carried out for this purpose:[16]

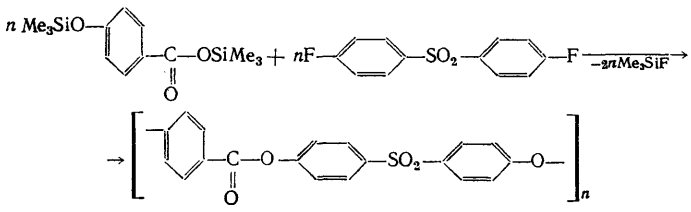


Table 14. Yields and some properties of copolymers obtained by thermal condensation of 2,6-difluoropyridine with 4,4′-difluorobenzophenone and silylated bis-phenols.[71]

bis-Trimethylsilylated bis-phenols	Yield, %	η^*_{inh}, dlitre g^{-1}	T_g, °C
HO–⟨⟩–OH	87	1.05	120**
HO–⟨⟩(Me)–OH	89	0.70	118
HO–⟨⟩(Ph)–OH	97	0.44	123
HO–⟨⟩–⟨⟩–OH	95	нр	128***

* Measured in a mixture of dichloromethane, formic and trifluoroacetic acids (70 : 10 : 20) c = 2 g litre^{-1} at 25 °C;
** after annealing at 180 °C for 1 h, m.p. = 278 °C;
*** m.p. = 293 °C.

Table 15. Yields and properties of polyethers obtained by block copolycondensation of 2,6-difluoropyridine with 4,4′-difluorodiphenylsulphone with various silylated bis-phenols.[71]

bis-Trimethylsilylated bis-phenol	Yield, %	η^*_{inh}, dlitre g^{-1}	T_g, °C
HO–⟨⟩–OH	85	0.47	131
HO–⟨⟩(Me)–OH	89	1.19	138
HO–⟨⟩(Ph)–OH	94	1.55	147
HO–⟨⟩(Me,Me)–⟨⟩–OH	97	1.56	147

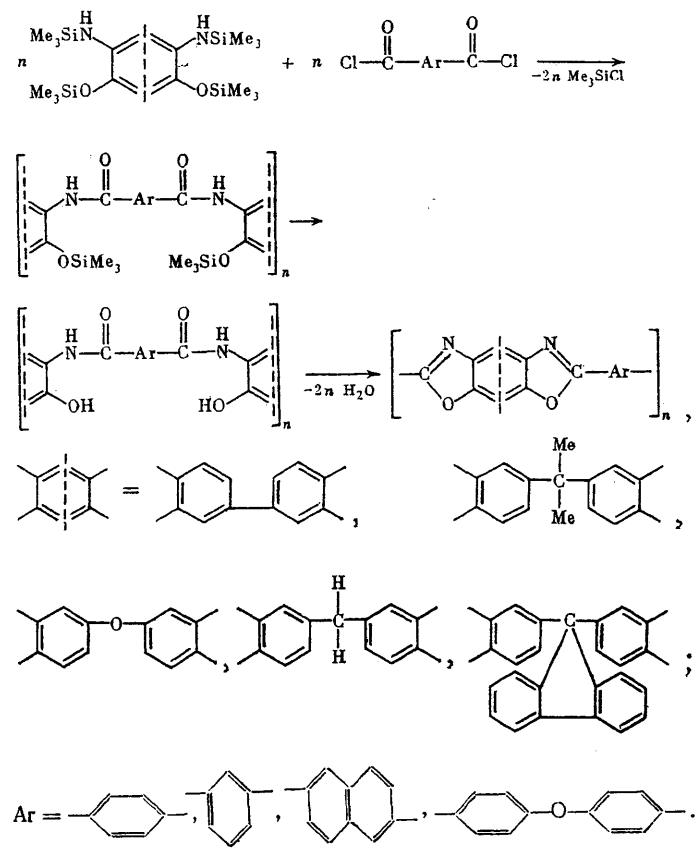
* Measured for solutions in mixtures of dichloromethane, formic and trifluoroacetic acids (70 : 10 : 20) at c = 2 g litre^{-1}.

The conditions for carrying out the polycondensation processes, yields and properties of the target copolymers are shown in Table 16.

It should be mentioned that attempts to involve activated dichloro aromatic compounds such as 4,4′-dichlorodiphenylsulphone and 4,4′-dichlorobenzophenone in reactions to obtain ester bonds proved unsuccessful. These compounds have too low a reactivity to undergo polycondensation reactions with phenolic groups rendered inert by silylation.

5. Polymers based on *N,O*-silylated aminophenols

The synthesis of polymers based on monomers containing silylated hydroxyl and amino groups is broadly represented by the synthesis of polybenzoxazoles using *N,N′,O,O′-tetrakis*-(trimethylsilyl)-bis-(*o*-aminophenols) and diacid chlorides of dicarboxylic acids.[20,22,79–81]

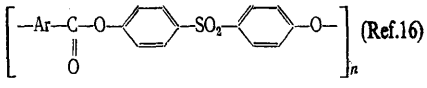


The synthesis of polybenzoxazoles based on silylated bis-(*o*-aminophenols) has been carried out by two-stage[20,79,81] and one-stage[80] methods. A detailed study of the two-stage process[20] and particularly of its first stage showed that, as in the synthesis of polyamides considered above, the use of silylated, rather than unsilylated, nucleophilic monomers led to the preparation of significantly higher molecular systems (Table 17).

The data given in Table 17 refer to poly-(*o*-hydroxy)amides devoid of silyl protection on the phenolic hydroxyls as a result of isolation from the reaction solution with methanol. Removal of silyl protection is necessary to increase the nucleophilic reactivity of the phenolic hydroxyl at the ring-closing stage. Polycyclodehydration of the poly-(*o*-hydroxy)amides thus obtained was carried out by heating at 250–260 °C in vacuum for 30 h. The polybenzoxazoles obtained

dissolved only in concentrated H_2SO_4. As a result their reprocessing into various materials such as films was effected at the stage of poly-(*o*-hydroxy)amides which are soluble in DMF, NMP, DMSO and pyridine. Some characteristics of polybenzoxazoles and films based on them are shown in Table 18.

Table 16. Conditions of carrying out block polycondensation of 4,4′-difluorodiphenylsulphone with disilylated hydroxybenzoic acids and some characteristics of the copolymers of general formula


(Ref.16)

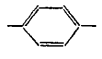
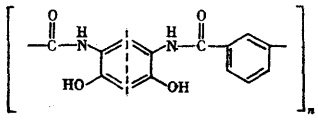
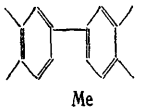
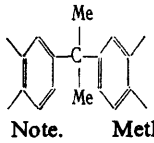
Ar	Reaction conditions		Yield, %	T_p, °C
	temperature, °C	time, h		
	250/320	0.5/2.5	91	137
	250/320	0.5/2.5	96	215

Table 17. Comparison of η_{inh} of poly-(*o*-hydroxyamides) from bis-(*o*-aminophenols) and their silylated derivatives

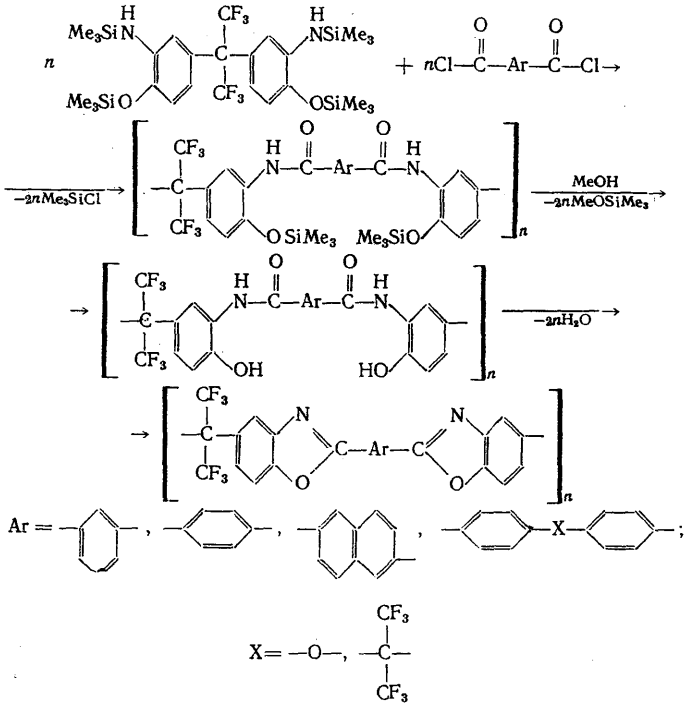

(Ref.20)

	Method A	Method B
	0.33	0.50
	0.16	0.55

Note. Method A was polycondensation using unsilylated bis-(*o*-aminophenol); method B was polycondensation using silylated bis-(*o*-aminophenol); polycondensation was carried out by reaction of bis-(*o*-aminophenol) (2.5 mmole) with isophthaloyl chloride (2.5 mmole) in DMA (5 ml) at 0–5 °C for 8 h in a stream of N_2; all polymers were obtained in quantitative yield; viscosities were measured in DMA at 30 °C and c = 0.5 g dlitre^{-1}.

The most interesting synthesis of polybenzoxazoles from silylated monomers is that based on weakly basic bis-*o*-aminophenols. One of such monomers is 2,2-bis-(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane. Further interest in the polymer based on it arises because aromatic polycondensates containing the hexafluoroisopropylidene group are characterised by a combination of enhanced solubility and good thermal characteristics.[82]

A detailed study of hexafluoroisopropylidine-containing polybenzoxazoles obtained according to:



showed that silylation of 2,2-bis-(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane led to an increase in the nucleophilic reactivity of this monomer.[20] Thus η_{inh} was equal to 0.08 dlitre g^{-1} for the polyisophthalamide based on the unsilylated monomer but η_{inh} was 0.64 dlitre g^{-1} for the poly-(*o*-hydroxy)amide based on the silylated monomer and synthesised under the same conditions.

Introduction of the hexafluoroisopropylidene grouping imparted increased solubility not only for the poly-(*o*-hydroxy)amide but also for the polybenzoxazole in full agreement with the previous report (Table 19).[82]

Viscosity and thermal characteristics of the hexafluoroisopropylidene-containing polybenzoxazoles and some strength characteristics of films based on them are shown in Table 20.

The thermal characteristics of hexafluoroisopropylidine-containing polybenzoxazoles shown in Table 20 surpass in some degree the corresponding characteristics of analogous systems obtained by reductive polyheterocyclisation.[5,6,83,84] This is in agreement with existing ideas[85] on the influence of the method of synthesis of polybenzazoles on their properties.

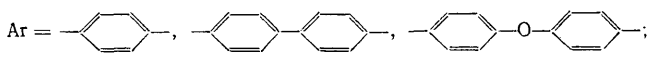
The low strength characteristics of films obtained from hexafluoroisopropylidene-containing polybenzoxazoles (Table 20) are somewhat surprising. Nonetheless these polymers are considered to be very promising thermostable polymeric materials.[20]

6. Polymers based on *S*-silylated dithiols

In spite of the fact that the reactivity of *S*-trialkylsilylated thiols is close to the reactivity of *N*-silylated amines, reactions of compounds containing an Si–S bond have been paid insignificant attention by

investigators. Nonetheless the reaction of *S*-silylated aromatic dithiols with activated dihalo aromatic compounds has been carried out:[18]

$$n\mathrm{Me_3Si{-}S{-}Ar{-}S{-}SiMe_3} + n\mathrm{X{-}Ar'{-}X} \xrightarrow[-2n\mathrm{Me_3SiX}]{} \mathrm{[{-}S{-}Ar{-}S{-}Ar'{-}]}_n,$$

Ar = ;

X = F, Cl;

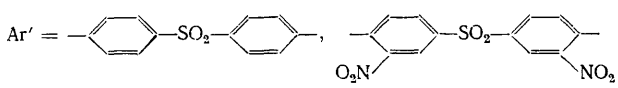
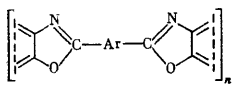
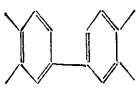
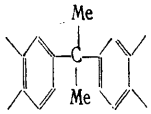
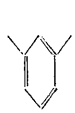
Ar′ = 

Table 18. Some characteristics of polybenzoxazoles of general formula



and polybenzoxazole films.[20]

	Ar	T_g^*, °C	T_{dec}^{**}, °C		Properties of films	
			in air	in N_2	σ_s, kg.cm^{-2}	ε_{rel}, %
		290	570	620	1980	7
		240	500	530	530	2

* Determined by thermomechanical analysis at a heating rate of 10° min^{-1} in air;

** temperature for loss of 10% initial weight (TGA, heating rate 10° min^{-1}).

The properties of the polysulphides obtained are shown in Table 21. As is seen from Table 21 aromatic polysulphides with moderate η_{inh} (0.6–0.7 dlitre g^{-1}) were obtained from the reaction (HMPA, 50 °C) of *S*-silylated dithiols with bis-(4-chloro-3-nitrophenyl)sulphone. Bis-(4-fluorophenyl)sulphone possesses little reactivity. Its reaction in solution with *S*-silylated dithiols was effected in TMS at 220 °C using CsF as catalyst. The polysulphides obtained possessed η_{inh} close to 0.3 dlitre g^{-1}.

Summing up all the above mentioned results on polycondensation and polyaddition reactions using silylated nucleophiles[10] it should be noted that:

1) silylation of nucleophilic monomers leads to compounds which are easy to purify, in particular, silylated products may be purified by distillation;

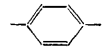
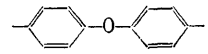
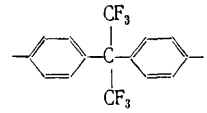
2) the majority of silylated monomers are readily soluble in organic solvents which facilitates polycondensation and polyaddition reactions in various reaction media, from low to high boiling and/or polar solvents;

3) polycondensation processes using silylated monomers may be carried out in neutral media with separation of neutral compounds as byproducts, particularly chlorotrimethylsilane, which may be used once again to obtain silylated monomers;

4) in several cases silylation of nucleophilic monomers leads to an increase in reactivity which makes it possible to carry out the synthesis of polymers under milder conditions and at higher rates. In individual cases silylation is an effective route to involve unreactive compounds in polymer synthesis;

5) the silylation of multifunctional monomers used in polyheterocyclisation reactions may lead to an increase in the difference in reactivity of neighbouring reaction centres thus enabling a smoother course for selective polyacylation.

Table 19. Solubility of hexafluoroisopropylidene-containing poly-(*o*-hydroxy)amides and polybenzoxazoles.[20]

Ar	Solubility of poly-(*o*-hydroxy)amide / Solubility of polybenzoxazole						
	NMP	DMSO	DMF	PhN	THF	Me_2CO	*o*-chloro-phenol
	++ / −	++ / −	++ / −	++ / −	++ / −	++ / −	+ / +
	++ / −	++ / −	++ / −	+ / −	− / −	− / −	− / −
	++ / −	++ / −	++ / −	++ / −	++ / −	+ / −	− / −
	++ / +	++ / −	++ / −	++ / +	++ / −	+ / −	+ / ++
	++ / ++	++ / ++	++ / ++	++ / ++	++ / −	++ / −	+ / ++

Note. (++) denotes soluble at room temperature; (+) partially soluble or swells; (–) insoluble.

The discussed merits of reactions using silylated monomers have swung the interest of investigators towards polycondensation reactions in the presence of silylated agents.

III. Polycondensation reactions in the presence of silylating agents

Since the synthesis of polymers using silylated monomers requires previous synthesis and purification of the latter a simpler way of obtaining polymers would be their synthesis in the presence of

silylating agents. Thus on reacting 3,8-diaminophenanthridine with terephthaloyl chloride in a mixture of NMP and HMPA at 0 °C in the presence of chlorotrimethylsilane, a higher molecular polyamide was obtained than in the presence of such widely used additives as LiCl and $CaCl_2$ (Table 22).

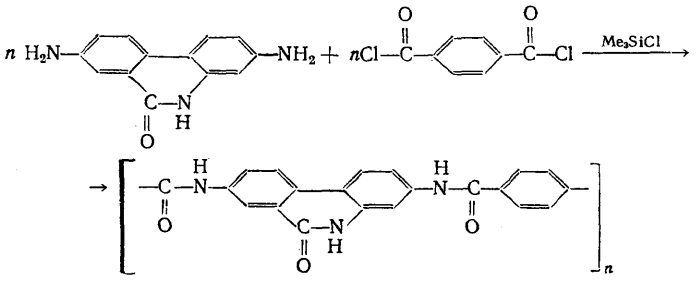
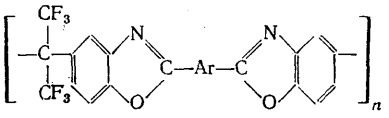
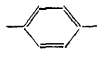
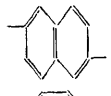
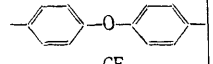
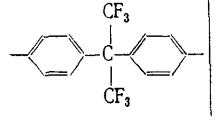


Table 20. Some characteristics of polybenzoxazoles of general formula



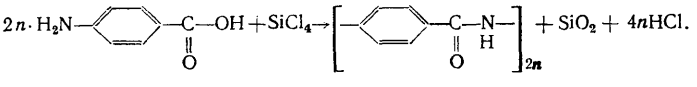
and films based on them.[20]

Ar	η_{inh}, dlitre g^{-1} (H_2SO_4, 30 °C)	T_g^*, °C	T_{dec}, °C		Properties of films	
			in air	in N_2	σ_s, $kg.cm^{-2}$	ε_{rel}, %
	—	260	530	545	—	—
	—	310	545	555	—	—
	0.76	325	540	560	930	6
	0.49	300	525	530	430	2
	0.46	295	545	555	680	3

Determined by thermomechanical analysis at a heating rate of 10° min^{-1} in air.

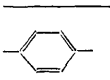
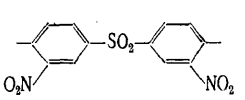
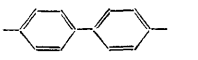
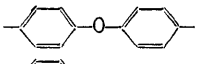
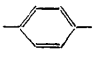
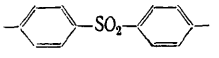
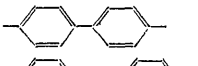
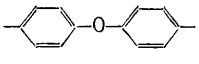
A similar approach to obtaining high molecular polyamides has been used in copolymer synthesis.[87]

Another example of carrying out a polycondensation in the presence of a silylating agent is the homocondensation of *p*-aminobenzoic acid in pyridine in the presence of $SiCl_4$.



Tetrachlorosilane has also been used as silylating agent in the reaction of *p*-phenylenediamine with terephthalic acid and of *m*-phenylenediamine with isophthalic acid.[88] The results of these processes, belonging to a variety of 'direct' polycondensation,[1,2] are shown in Table 23.

Table 21. Conditions of synthesis and viscosity characteristics of aromatic polysulphides of general formula $[-S-Ar-S-Ar'-]_n$.[18]

Ar	Ar'	Synthesis conditions			η_{inh}**, dlitre g^{-1}
		solvent	T, °C	time, h	
		HMPA	50	24	0.64
	»	ditto	50	24	0.67
	»	ditto	50	24	0.76
		TMS	220	24	0.29
	»	ditto	220	24	0.30
	»	ditto	20	24	0.30

*Solvents for polycondensation: HMPA is hexamethylphosphoramide, TMS tetramethylenesulphone; **η_{inh} was measured in HMPA at 30 °C.

Table 22. Influence of LiCl, $CaCl_2$ and Me_3SiCl in solvents on η_{inh} of poly-3,8-phenanthridinonediylterephthalamide.[86]

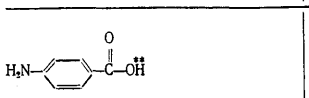
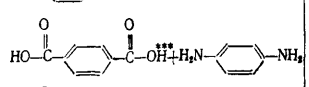
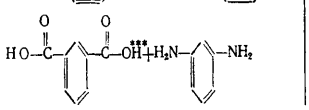
Solvent	LiCl				Me_3SiCl			$CaCl_2$
	1*	2	3	4,5	1	2	3	1
HMPA–NMP (1:1)	3.71	3.74	3.79	—	6.13	6.68	—	—
NMP–DMA (1:1)	0.83	2.62	3.91	4.01	0.74	—	1.84	4.48

*1 mole LiCl per mole diamine, etc.

As follows from the data shown in Table 23 an oligomer is obtained in 41% yield when a stoichiometric amount of $SiCl_4$ is used. On using a 20% excess of $SiCl_4$ the polyamide was obtained in quantitative yield and its molecular weight was 13 400. Polyamides with lower molecular weight characteristics were

obtained on reacting *p*-phenylenediamine with terephthalic acid. This is evidently linked with the low solubility of terephthalic acid in the reaction medium.

Table 23. Conditions of synthesis of aromatic polyamides in the presence of $SiCl_4$.[88]

Monomers	Molar ratio $SiCl_4$: :monomer	[Monomer], mol.litre^{-1}	Yield, %	[η]*, dlitre g^{-1}	M_n
	0.50	0.74	41	0.31	—
	0.62	0.67	96	1.43	1 100
	0.63	1.00	99	1.97	13 400
	0.80	0.56	94	0.60	5 300
	0.62	0.66	98	0.51	—

Note. Polycondensation was carried out at 0 °C for 24 h.

*Measured in H_2SO_4 at 30 °C; **solvent pyridine; *** solvent chlorobenzene : pyridine (2 : 1).

An interesting aspect of this synthetic method is the formation of filler materials in the reaction process. SiO_2 is formed as a result of the polycondensation.

— o0o —

It has been shown that the silylation method, particularly processes using *N*-silylated diamines, is an easy and promising route for the synthesis of high molecular condensation polymers. New polycondensation reactions using silylated monomers are at the development stage at the present time. However, in the main this area continues to remain little studied. The most characteristic distinguishing feature of the silylation method is the fact that silylated nucleophilic monomers differ markedly in reactivity from the initial nucleophiles. This method may therefore find new regions of application for making new condensation polymers and for developing new synthetic routes for obtaining various known polymers.

References

1. M Ueda *Kobunshi Kagaku,* 1986, **35** 128
2. V A Vasnev, A L Rusanov, M L Keshtov, M K Ovechkin *Itogi Nauki i Tekhniki. Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii* (Results of Science and Techniques. Chemistry and Technology of High Molecular Compounds), Izd-vo VINITI, Moscow, 1987, Vol. 23, p. 3
3. R D Katsarava *Vysokomol. Soedin., Ser. A,* 1989, **31** 1555
4. Y Imai *Yuki Gosei Kagaku Kyokaishi,* 1984, **42** 1095
5. V V Korshak, A L Rusanov, D S Tugushi *Usp. Khim.,* 1981, **50**(12) 2250 [English translation in *Russ. Chem. Rev.,* 1981(12)]
6. V V Korshak, A L Rusanov, D S Tugushi *Polymer,* 1984, **25** 1539
7. J F Klebe *Acc. Chem. Res.,* 1970, **3** 229
8. J F Klebe *Adv. Org. Chem.,* 1972, **8** 97
9. V Imai *Kobunshi Kagaku,* 1988, **37** 892
10. Y Imai, Y Oishi *Prog. Polym. Sci.,* 1989, **14** 173
11. H R Kricheldorf *Liebigs Ann. Chem.,* 1973, 772
12. Y Oishi, M Padmanaban, M-A Kakimoto, V Imai *J. Polym. Sci., Polym. Chem. Ed.,* 1987, **25** 3387
13. M Kakimoto, Y Oishi, Y Imai *Makromol. Chem. Rapid Commun.,* 1985, **6** 557
14. J F Klebe *J. Polym. Sci., Ser. A,* 1964, **2** 2673
15. H R Kricheldorf, G Schwarz *Polym. Bull.,* 1979, **1** 383
16. H R Kricheldorf, G Bier *J. Polym. Sci., Polym. Chem. Ed.,* 1983, **21** 2283
17. H R Kricheldorf, G Bier *Polymer,* 1984, **25** 1151
18. 18. A Hara, Y Oishi, M Kakimoto, Y Imai *Polym. Prepr. Jpn.,* 1987, **36** 316
19. K Miyazawa, T Munetoh, T Matsumoto, T Kurosaki *Polym. Prepr. Jpn.,* 1987, **36** 324
20. Y Maruyama, Y Oishi, M Kakimoto, Y Imai *Macromolecules,* 1988, **21** 1305
21. V V Korshak, G S Bondarevskii, P M Valetskii, et al., Authors Certificate No. 464 590 SSSR: *Byull. Izobret.,* 1975(11) 67
22. G S Bondarevskii, A I Kalachev, P M Valetskii, et al. *IV Mezhdunar. Simp. po Khimii Kremniiorganicheskikh Soedinenii* (IV International Symposium on the Chemistry of Organosilicon Compounds), Moscow, 1975, Vol. 2, Pt. 1, p. 81
23. G S Bondarevskii, A I Kalachev, P M Valetskii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1976, 920
24. A L Narkon, V I Bakhmutov, Sh A Karapet'yan, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1979, 1090
25. Y Oishi, M Kakimoto, Y Imai *Macromolecules,* 1988, **21** 547
26. G Schwarz, H Alberts, H R Kricheldorf *Liebigs Ann. Chem.,* 1981, 1257
27. V V Korshak, A L Rusanov *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1970, 289
28. V V Korshak, A L Rusanov *Polimery,* 1970, **15** 400
29. I R Bowser, P I Williams, K Kurz *J. Org. Chem.,* 1983, **48** 4111
30. Y Oishi, M Kakimoto, Y Imai *Macromolecules,* 1987, **20** 703
31. P W Morgan *Polikondensatsionnye Protsessy Sinteza Polimerov* (Polycondensation Processes in Polymer Synthesis), Khimiya, Leningrad, 1970, 448 pp [This is probably a translation of Polymer Reviews, Vol. 10 *Condensation Polymers by Interfacial and Solution Methods,* Interscience, New York, 1965, 561 pp]
32. L B Sokolov *Polikondensatsionnyi Metod Sinteza Polimerov* (The Polycondensation Method of Polymer Synthesis), Khimiya, Moscow, 1966, 332 pp
33. L B Sokolov, V D Gerasimov, V P Savinov, V K Belyakov *Termostoikie Aromaticheskie Poliamidy* (Thermostable Aromatic Polyamides), Khimiya, Moscow, 1976, 256 pp
34. Y Oishi, M Kakimoto, Y Imai *J. Polymer Sci., Polymer Chem. Ed.,* 1987, **25** 2493
35. M Sawamoto *Polymer Yearbook* (Edited by R A Pethrick), Acad. Publ., Harwood, 1989, Vol. 5, p. 165
36. Y Oishi, S Harada, M Kakimoto, Y Imai *Polym. Prepr. Jpn.,* 1987, **36** 313

37. Y Oishi, S Harada, M Kakimoto, Y Imai *LIII Chem. Soc. Jpn. Annual Meeting Prepr.*, 1986, p. 25
38. R D Katsarawa, D P Kharadze, M Sh Japaridze, et al. *Makromol. Chem.*, 1985, **186** 939
39. Y Takahashi, M Tuima, K Inagawa, et al. *LIV Chem. Soc. Jpn. Annual Meeting Prepr.*, 1987, p. 1549
40. R M Ikeda, R I Angelo, F P Boettcher, et al. *J. Appl. Polym. Sci.*, 1980, **25** 1391
41. M Tuima, Y Takahashi, K Inagawa, A Itoh *Shinku*, 1985, **28** 437
42. J F Klebe *J. Polym. Sci., Ser. B*, 1964, **2** 1079
43. V V Korshak, A L Rusanov *Usp. Khim.*, 1983, **52**(5) 812 [English translation in *Russ. Chem. Rev.*, 1983(5)]
44. Y Oishi, M Padmanaban, M Kakimoto, Y Imai *Polym. Prepr. Jpn.*, 1987, **36** 317
45. N A Adrova, M I Bessonov, L A Laius, A P Rudakov *Poliimidy—Novyi Klass Termostoikikh Polimerov* (Polyimides, A New Class of Thermostable Polymers), Nauka, Leningrad, 1968, 211 pp
46. M I Bessonov, M M Koton, V V Kudryavtsev, L A Laius *Poliimidy—Klass Termostoikikh Polimerov* (Polyimides, A Class of Thermostable Polymers), Nauka, Leningrad, 1983, 307 pp
47. C E Sroog *J. Polymer Sci. Macromol. Revs.*, 1976, **11** 161
48. P E Cassidy *Thermally Stable Polymers*, Dekker, New York, 1980, p. 163
49. K U Byuller *Teplo- i Termostoikie Polimery* (Heat-resistant and Thermostable Polymers), Khimiya, Moscow, 1984, p. 585
50. V V Korshak, A L Rusanov, I Batirov *Novoe v Oblasti Termostoikikh Poliimidov* (New Developments in Thermostable Polyimides), Donish., Dushanbe, 1986, 103 pp
51. E M Boldebuck, J F Klebe, US P. 3 303 157 (1967)
52. Y Oishi, M Kakimoto, Y Imai *LIII Chem. Soc. Japan Annual Meeting Prepr.*, 1986, p. 26
53. Ya S Vygodskii, S V Vinogradova, Z M Nagiev, et al. *Acta Polymerica*, 1982, **33** 131
54. V V Korshak, S V Vinogradova, Ya S Vygodskii, et al. *Makromol. Chem.*, 1983, **184** 235
55. Ya S Vygodskii, Z M Nagiev, V V Korshak, et al. *Acta Polymerica*, 1984, **35** 690
56. V V Korshak, S V Vinogradova, Ya S Vygodskii *Fraserforsch. Textiltechn.*, 1977, **28** 439
57. Y Takahashi, M Tuima, K Inagawa, A Itah *Shinku*, 1985, **28** 440
58. J R Salem, F O Sequeda, J Ouran, et al. *J. Vac. Sci. Technol.*, 1986, **A4** 369
59. Y Takahashi, M Tuima, K Inagawa, et al. *Polym. Prepr. Jpn.*, 1987, **36** 304
60. Y Oishi, M Kakimoto, Y Imai *Polym. Prepr. Jpn.*, 1987, **36** 315
61. Y Oishi, M Padmanabam, M Kakimoto, Y Imai *J. Polym. Prepr. Jpn.*, 1987, **36** 318
62. V V Korshak, A L Rusanov, I M Gverdtsiteli, et al. *Dokl. Akad. Nauk SSSR*, 1989, **240** 346
63. A L Rusanov, D S Tugushi, A S Shubashvili, et al., *Vysokomol. Soedin., Ser. A*, 1979, **21** 1873
64. E Hara, M Senoo, K Mori, Y Taketani, US P. 4 069 206 (1978)
65. E Hara, H Senoo, K Mori, Y Taketani, US P. 4 086 209 (1978)
66. T Munetoh, K Miyazawa, T Matsumoto, T Kurosaki *Polym. Prepr. Jpn.*, 1987, **36** 325
67. H R Kricheldorf, G Z Zang, G Schwarz *Polymer*, 1982, **23** 1821
68. H R Kricheldorf, G Schwarz *Makromol. Chem.*, 1983, **184** 475
69. H R Kricheldorf, H Koziel *J. Macromol. Sci. Chem.*, 1986, **A23** 1337
70. H R Kricheldorf *Makromol. Chem. Rapid Commun.*, 1988, **9** 217
71. H R Kricheldorf, G Schwarz, J Erxleben *Makromol. Chem.*, 1988, **189** 2255
72. H R Kricheldorf, G Bier, FRG P. 1 591 258 (1982)
73. H R Kricheldorf, U Delias *Macromolecules*, 1989, **22** 517
74. R N Johnson, A G Farnham, R A Clendinning, et al. *J. Polym. Sci., Ser. A*, 1967, **15** 2375
75. T E Attowood, D E Barr, T King, et al. *Polymer*, 1977, **18** 359
76. T E Attwood, P C Dawson, J L Freeman, et al. *Polymer*, 1981, **22** 1096
77. M J Mullins, E P Woo *J. Macromol. Sci. Rev. Chem. Phys., Ser. C*, 1987, **27** 313
78. J B Rose *High Performance Polymers: Their Origin and Development* (Edited by R B Seymour, G S Kirshenbaum), Elsevier, New York–Amsterdam–London, 1986, p. 187
79. S V Vinogradova, V V Korshak, G S Bondarevskii, et al., Authors Certificate No. 477 177 USSR; *Byull. Izobret.*, 1975(26) 69
80. V P Semenov, G M Tseitlin, P M Valetskii, et al., Authors Certificate No. 663 699 USSR; *Byull. Izobret.*, 1979(19) 82
81. Y Imai, M Kakimoto, Y Oishi, H Maruyama, Japanese P. Appln. 62-283 127; *Ref. Zh. Khim.*, 1988, 24S621 P
82. V V Korshak, I L Knunyants, A L Rusanov, B R Livshits *Usp. Khim.*, 1987, **61**( ) 489 [English translation in *Russ. Chem. Rev.*, 1987( )]
83. V V Korshak, I M Gverdtsiteli, A L Rusanov, et al., Authors Certificate No. 648 570 USSR; *Byull. Izobret.*, 1979(7) 90
84. V V Korshak, A L Rusanov, I M Gverdtsiteli *Vysokomol. Soedin., Ser. A*, 1979, **21** 1855
85. V V Korshak, G V Kazakova, A L Rusanov *Vysokomol. Soedin., Ser. A*, 1989, **31** 5
86. T Kaneda, S Ishikawa, H Dainan, et al. *Makromol. Chem.*, 1981, **183** 417
87. T Kaneda, S Ishikawa, H Dainan, et al. *Makromol. Chem.*, 1981, **183** 433
88. A Strohrige, W Heitz, G Weker *Makromol. Chem. Rapid Commun.*, 1985, **6** 111