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Siloxane bond formation by heterofunctional condensation of alkoxysilane and halogenosilane. Application to the preparation of copoly(tetramethyl-*p*-silphenylenesiloxane-dimethylsiloxane)

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Abstract

Siloxane linkages are formed non-hydrolytically by the reaction of dihalogenosilanes with either dibenzylether, or dibenzyloxysilanes and dibenzhydryloxysilanes. The heterocondensation reaction is activated in the presence of NaI (in acetonitrile) or fluoride anions. This offers an alternative copolymerization route to the usual dehydrocondensation of SiOH-terminated species. Thus, the title copolymer was prepared by reaction of equimolar amounts of $Me_2Si(OCHPh_2)_2$ and 1,4-bis(chlorodimethylsilyl)benzene at 100°C. The ^{29}Si NMR spectrum supports a quasi-random sequence in the copolymer. Thermal stability is similar to that reported for an alternating microstructure, as inferred from thermogravimetric analysis.

Key words: Siloxane; Polymer

1. Introduction

The largescale production of polysiloxanes is based upon the ability of silanols, readily obtained by hydrolysis of organochlorosilanes [1,2], to self-condense. Copolymers, whether or not they contain only siloxane units, may be prepared by the dehydrocondensation of SiOH-terminated monomers. However, polycondensation, which should normally lead to the random arrangement of the different units along the chain, may result rather in blocklike-disordered chains, due to the different reactivities of the differently substituted silicon centres. A similar route is followed to build up block copolymers from SiOH-terminated oligomers. However, condensation catalysts are needed, which also catalyse redistribution of siloxane bonds in the presence of water which is released during the course of the reaction [3]. Thus, block lengths cannot be assumed from the degree of oligomerization of the starting disiloxanol.

Nonhydrolytic processes to obtain copolymers with a definite structure have aroused some interest [4]. A survey of reactions in which water is not directly involved is given in reference 2. Most of them concern the condensation of a silanol group with another function (chloride, alkoxide, ester, amide). However this is restricted to disilanols which do not spontaneously self-condense. Thus high-molecular-weight silarylene-siloxane copolymers with exactly alternating structure have been prepared by the step-growth polycondensation of arylenedisilanols with diaminosilanes or bis(ureido)silanes [5]. Another possible nonhydrolytic route is illustrated by the ring-opening polyreaction of hexamethylcyclotrisiloxane in toluene with methanol (or water) as an initiator and a biscatecholsiliconate as a catalyst [6].

An alternative nonhydrolytic route to SiOSi linkage is the heterofunctional condensation of organohalogenosilanes and organoalkoxysilanes with release of alkyl halide [7,8].

$$\equiv SiOR + XSi\equiv \longrightarrow \equiv SiOSi\equiv + RX$$

R = Et; X = Cl; catalyst = $FeCl_3$; 100°C [7]; R = Me; X = Br; 150°C [8].

The basic reaction consists of the nucleophilic cleavage of an OR bond and therefore electronic effects at the

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carbon centre are expected to prevail over those at the silicon. We have reported that tertiary and benzylic carbon groups, which are able to stabilize a carbocation, react much more rapidly than primary and secondary groups [9a]. Cognate reactions in which the driving force is the high stability of the Si–O bond have found application in organic chemistry for deoxygenation of alcohols, ethers and carbonyl compounds by halogenosilane reagents [10–15], such as iodotrimethylsilane [16].

$$ROR' + Me_3SiX \longrightarrow RX + R'OSiMe_3$$

$$R'OSiMe_3 + Me_3SiX \longrightarrow R'X + Me_3SiOSiMe_3$$

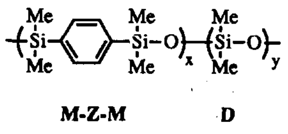
R' = alkyl or aryl

In previous work we used this type of reaction as a novel nonhydrolytic sol-gel route to silica and various metal oxide gels [9].

$$MX_n + n/2\ R\text{–}O\text{–}R \longrightarrow MO_{n/2} + n\ RX$$

$$M(OR)_n + MX_n \longrightarrow 2\ MO_{n/2} + n\ RX$$

Our objective here was to apply this process to the preparation of polysiloxanes. First, we experimented with reactions of methylphenyldihalogenosilanes ($PhMeSiX_2$, X = Cl, Br) with dibenzyl ether as oxygen donor. Then we extended the process to the preparation of copolysiloxanes by polycondensation of dichlorosilanes ($R^1R^2SiX_2$) and dialkoxysilanes ($R^3R^4Si(OR)_2$). Finally this route was applied to the preparation of poly(tetramethylsilphenylenesiloxane-dimethylsiloxane) (Scheme 1) by polycondensation of $ClMe_2Si$-p-$C_6H_4SiMe_2Cl$ and $Me_2Si(OR)_2$.



Scheme 1.

2. Experimental section

All manipulations were carried out under dry dinitrogen, in oven-dried glassware. Solvents were distilled from appropriate drying agents prior to use.

2.1. NMR spectroscopy

^1H NMR spectra were recorded on a Bruker AW80 spectrometer. ^{29}Si NMR spectra were recorded using Bruker AC200 or AC250 spectrometers with $CDCl_3$ as a solvent and internal standard. Chemical shifts are given in ppm downfield from TMS. An inverse-gated decoupling sequence was used, under the quantitative conditions reported by Williams and co-workers [3]: 45° flip angle, 5 s delay and addition of chromium(III) acetylacetonate as a relaxation agent.

2.2. Gel permeation chromatography

Polymer molecular weights were determined by gel permeation chromatography (GPC) in tetrahydrofuran (flow rate 1 ml/min) using a Waters apparatus (Ultrastyragel columns, 100, 500, 1000 and 10000 ångström, pump EF410, refractive index detector) calibrated with polystyrene standards.

2.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out using a Netzsch STA409 thermobalance. Typically, about 20 mg of sample was heated in an alumina crucible from room temperature to 1200°C at 10 K min^{-1} in a stream of argon or air.

2.4. Dihalogenosilanes

Chlorosilanes Me_2SiCl_2 and $MePhSiCl_2$ were kindly provided by Rhône-Poulenc, and were distilled over magnesium turnings prior to use. $MePhSiBr_2$ was prepared by bromination in refluxing EtBr of $MePhSiH_2$, itself obtained by reduction of $MePhSiCl_2$, according to reference 16: boiling point 105°C/12 mmHg (70% yield). 1,4-bis(chlorodimethylsilyl)benzene was obtained by chlorination at 0°C of HMe_2Si-p-C_6H_4-$SiMe_2H$ prepared according to the literature [18]: $ClMe_2Si$-p-$C_6H_4SiMe_2Cl$: boiling point 108–110°C/1.5 mmHg (64% yield).

2.5. Dialkoxysilanes

$Me_2Si(OEt)_2$ was used as received from Janssen. $Me_2Si(OCH_2Ph)_2$, $Me_2Si(OCHPh_2)_2$, and $MePhSi(OCHPh_2)_2$ were prepared by alcoholysis of the parent chlorosilanes in the presence of pyridine (procedure adapted from reference 19).

In a typical experiment, 92 g of Ph_2HCOH (0.5 mol) were mixed with 40.4 ml of pyridine (0.5 mol), then added dropwise to a solution of 30.3 ml of Me_2SiCl_2 (0.25 mol) in ether (400 ml) chilled to 0°C. After heating under reflux for 8 h, the solution was filtered to eliminate pyridinium hydrochloride. The solvent was pumped off and crystallization from hot hexane afforded 86.3 g of $Me_2Si(OCHPh_2)_2$ (81% yield): m.p. = 69–70°C. ^1H NMR (CCl_4): δ 7.20 ppm (20H); 5.75 ppm (2H); 0.05 ppm (6H). ^{29}Si NMR ($CDCl_3$): δ -2.35 ppm.

$Me_2Si(OCH_2Ph)_2$: b.p. = 160°C/16 mmHg (70%). ^1H NMR (CCl_4): δ 7.30 ppm (10H); 4.74 ppm (4H); 0.16 ppm (6H). ^{29}Si NMR ($CDCl_3$): δ -1.09 ppm.

$MePhSi(OCHPh_2)_2$: m.p. 72–73°C (97% yield). ^1H NMR (CCl_4): δ 7.15–7.80 ppm (25H); 5.75 ppm (2H); 0.15 ppm (3H). ^{29}Si NMR ($CDCl_3$): δ -16.20 ppm.

2.6. Other reagents

Tetrabutylammonium fluoride (1 M solution in THF), NaI, and dimethylbenzyldodecylammonium chloride were purchased from Aldrich, Janssen and Fluka, respectively. $PhCH_2Cl$ was purchased from Prolabo, $PhCH_2Br$ from Janssen, Ph_2CHCl from Merck, and Ph_2CHBr from Aldrich.

2.7. Reactions of dihalogenosilanes with dibenzylether and with dialkoxysilanes

Equimolar amounts of reagents were put in sealed tubes and heated at 100°C. No solvent was used, except for experiments carried out in acetonitrile. In some runs, tetrabutylammonium fluoride (1% mol with respect to dichlorosilane) or NaI (stoichiometric amount with respect to SiCl functions) were added. The tubes were opened under N_2. The reactions were followed by ^1H NMR spectroscopy. Reactive end groups were quenched by treating with an excess of methylmagnesium bromide in ether. CH_3NO_2 was used (about 10 ml per g of polymer) to extract the lower-molecular-weight fraction. The supernatant higher-molecular-weight fraction was separated by centrifugation. Several washings (monitored by GPC) were needed to obtain a good purification. The residual solvent was pumped off before further characterization by GPC and ^{29}Si NMR spectroscopy.

2.8. Preparation of poly(tetramethyl-p-silphenylene-siloxane-dimethylsiloxane)

This was prepared using the above procedure. 7.4 g of the copolymer whose characteristics are given below were obtained from 14.34 g of $Me_2Si(OCHPh_2)_2$ and 8.89 g of $ClMe_2Si$-*p*-$C_6H_4SiMe_2Cl$ (78% yield).

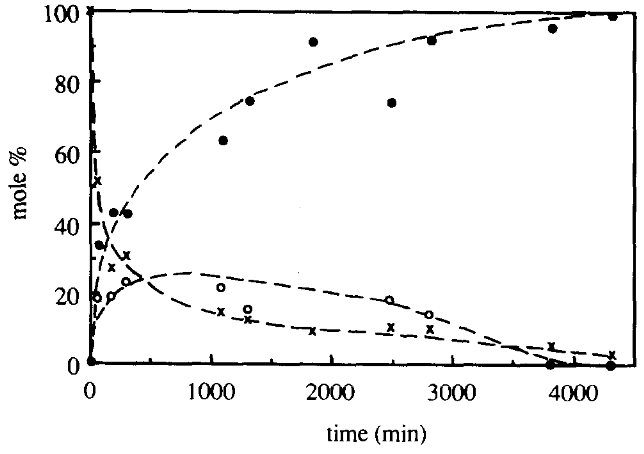


Fig. 1. ^1H NMR monitoring of the reaction of $MePhSiBr_2$ with $PhCH_2OCH_2Ph$: •: $[PhCH_2Br]$; ×: $[PhCH_2OCH_2Ph]$; o: $[\equiv SiOCH_2Ph]$ (mol % errors estimated at ±5%).

3. Results

3.1. Reactions of organodihalogenosilanes with dibenzylether

The reaction of dibromomethylphenylsilane with an equimolar amount of benzyl ether at 100°C in a sealed tube was complete within 72 h. Cyclotri- and cyclotetra-siloxanes were formed, along with other siloxane oligomers as inferred from gel permeation chromatography (GPC) and ^{29}Si NMR spectroscopy.

$$n\,(PhCH_2)_2O + n\ MePhSiBr_2 \longrightarrow 2n\ PhCH_2Br + (MePhSiO)_n$$

The reaction was followed by ^1H NMR spectroscopy (Fig. 1). The intermediate formation of $SiOCH_2Ph$ groups was detected. Accordingly, benzyl bromide arose from two types of reaction, which are both competitive and consecutive.

$$\equiv Si\text{–}Br + (PhCH_2)_2O \longrightarrow \equiv Si\text{–}OCH_2Ph + PhCH_2Br$$

$$\equiv Si\text{–}Br + \equiv Si\text{–}OCH_2Ph \longrightarrow \equiv Si\text{–}O\text{–}Si\equiv + PhCH_2Br$$

Moreover, in the absence of solvent the volume was not constant and the medium drastically changed in the course of the reaction. Therefore no reasonable estimates of rate laws and activation parameters could be made.

No reaction was observed with the parent dichlorosilane under the same conditions. However, in the presence (1%) of tetrabutylammonium fluoride, which is known to promote nucleophilic substitutions at silicon [20,21], 75% of $PhCH_2Cl$ was formed after 6 days of reaction at 100°C. Another efficient activator is NaI/CH_3CN, which promotes the *in situ* formation of iodosilane [14,16]. In this case 88% of $PhCH_2I$ was formed after 15 days at room temperature.

3.2. Reactions of organodihalogenosilanes with dialkoxysilanes

The reaction of dibenzyloxydimethylsilane with methylphenyldichlorosilane in the presence of NaI and in CH_3CN as a solvent afforded copolysiloxanes (number- and weight-average molecular masses 3960 and 6510, respectively) in poor yield (13%, after separation of the lower-molecular-weight fraction with CH_3NO_2). The polycondensation was improved by a more reactive alkoxy derivative, dibenzhydryloxymethylphenylsilane $MePhSi(OCHPh_2)_2$, in the absence of NaI and without solvent at 100°C in a sealed tube. The reaction was complete within 240 min with dimethyldichlorosilane, as well as with methyldichlorosilane or methylphenyldichlorosilane (Fig. 2). No enhancement of the reaction rate was observed in the presence of anhydrous (dimethylbenzyldodecyl)ammonium chloride.

This indicates that the nucleophile concentration does not affect the kinetics.

It is not clear whether the alkyl halide by-products are able to cleave siloxane linkages, thus causing a redistribution of the molecular weights, but attempts failed to cleave siloxane bonds in octamethylcyclotetrasiloxane by action of $PhCH_2X$ or Ph_2CHX (X = Br or Cl) at 100°C.

After heating an equimolar mixture of $MePhSiCl_2$ and $MePhSi(OCHPh_2)_2$ in acetonitrile for 7 d under reflux, the unreacted Cl groups were quenched with methyl magnesium bromide. The ^{29}Si NMR spectrum indicated the presence of 39% of $Me_2PhSi(OCHPh_2)$ (arising from $MePhSi(OCHPh_2)Cl$) and 20% of $MePhSi(OCHPh_2)_2$ plus Me_3PhSi (corresponding to the starting materials) along with oligomers. The formation of $MePhSi(OCHPh_2)Cl$, the major monomeric species, indicates that exchange between SiOR and SiCl functions [22] competes with the condensation reaction.

3.3. ^{29}Si NMR investigation of a poly(methylphenylsiloxane-dimethylsiloxane)

A copolymer containing both MePhSiO (designated D^{Ph}) units and Me_2SiO (designated D) units was prepared from methylphenyldichlorosilane and dibenzhydryloxydimethylsilane and investigated by ^{29}Si NMR spectroscopy. The study was performed on the high-molecular-weight fraction isolated after extracting with CH_3NO_2 (32% yield; number- and weight-average molecular masses, 9940 and 34260, respectively). The NMR data (Table 1) are obviously not consistent with the alternating microstructure expected in the absence of exchange reactions (only two signals would be observed). Actually they are close to the NMR pattern reported for a poly(methylphenylsiloxane-dimethylsiloxane) with a random distribution of D and D^{Ph} monomeric units [23].

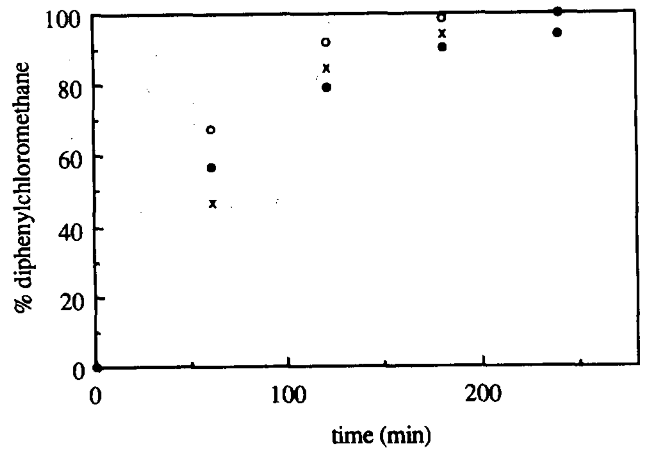


Fig. 2. ^1H NMR monitoring of the reactions of $MePhSi(OCHPh_2)_2$ with ●: Me_2SiCl_2, ×: $MeHSiCl_2$ and ○: $MePhSiCl_2$ (mol % errors estimated at ±5%).

TABLE 1. ^{29}Si NMR pattern of poly(dimethyl-methylphenyl)siloxane

Sequence [a]	Chemical shift (ppm)	Integration %	Total % of D and D^{Ph} units
D^{Ph}-*D*-D^{Ph}	−19.4	15.3	
D^{Ph}-*D*-D	−20.6	25.4	52.9
D-*D*-D	−21.9	12.2	
D-D^{Ph}-D	−34.73	14.6	
D^{Ph}-D^{Ph}-D	−34.19	21.7	47.1
D^{Ph}-D^{Ph}-D^{Ph}	−33.67	10.8	

[a] D = Me_2SiO; D^{Ph} = MePhSiO.

3.4. Preparation, structural analysis and thermal stability of poly(tetramethyl-p-silphenylenesiloxane-dimethylsiloxane)

The title copolymer (Scheme 1) was prepared by reaction of equimolar amounts of dibenzhydryloxydimethylsilane $Me_2Si(OCHPh_2)_2$ (D units) and 1,4-bis(chlorodimethylsilyl)benzene $ClMe_2Si$-*p*-C_6H_4-$SiMe_2Cl$ (MZM units) at 100°C under ambient pressure. The condensation reaction was complete within 20 h as judged by ^1H NMR spectroscopy. The crude product was washed with CH_3NO_2 to isolate the high-molecular-weight fraction (78% yield; number- and weight-average molecular masses, 17900 and 51800, respectively [24*]. The relative integrations of ^1H and ^{29}Si NMR signals are consistent with equimolar amounts of the two monomer units. The ^{29}Si NMR spectrum is shown in Fig. 3. The peaks at −1.20 and −2.52 ppm arise from M units, and those at −19.47, −20.64 and −21.63 ppm are due to D units. The assignments to the different sequences were based on reference 3 (Table 2). Using the statistical approach proposed by Harwood and Ritchey [25] (assuming a Bernoullian law), the microstructural parameters were calculated from the relative integrations [23,26] (Table 3). The run number R, that is the average number of monomer sequences in a copolymer per 100 monomer units, is related to the occurrence of linkages A–B and B–A in a copolymer containing X_A and X_B mole fractions of A and B units, respectively.

$$\%AA \text{ links} = \%A - \%AB \text{ links} = 100.X_A - R/2;$$

$$\%BB \text{ links} = \%B - \%BA \text{ links} = 100.X_B - R/2;$$

$$\%(AB + BA) \text{ links} = 2(\%AB \text{ links}) = 2(\%BA \text{ links}) = R.$$

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* Reference number with an asterisk indicates a note in the list of references.

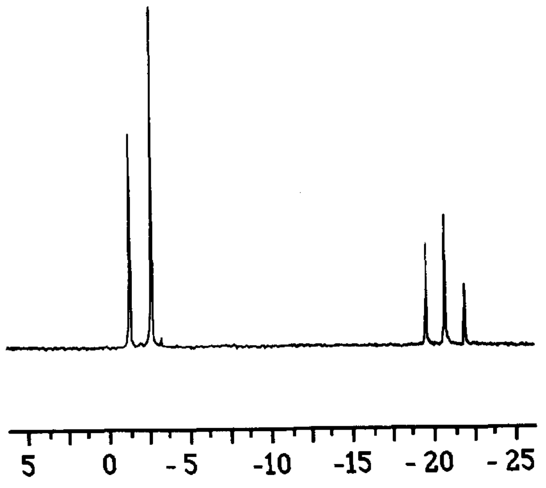


Fig. 3. ^{29}Si NMR spectrum of copoly(tetramethyl-*p*-silphenylenesiloxane-dimethylsiloxane).

TABLE 2. ^{29}Si NMR pattern of copoly(silphenylenesiloxane-siloxane) and statistical abundance of each sequence

Sequence [a]	Chemical shift (ppm)	Integration %	Statistical abundance D = A; MZM = B
MZM-*D*-MZM	−19.47	15.23	$p_{AB}^2 \cdot X_A$ [b]
MZM-*D*-D	−20.64	25.93	$2p_{AB} \cdot p_{AA} \cdot X_A$
D-*D*-D	−21.63	11.11	$p_{AA}^2 \cdot X_A$
MZ*M*-MZM	−1.20	18.93	$p_{BB} \cdot X_B$
MZ*M*-D	−2.52	28.80	$p_{BA} \cdot X_B$

[a] D = Me_2SiO; M-Z-M = $-OMe_2Si$-*p*-C_6H_4-$SiMe_2$-. [b] Terms p are the probabilities of occurrence of each linkage. X_A and X_B are the mole fractions of A and B in the polymer (52.3% and 47.7%, respectively, based on the integration of D and M signals).

TABLE 3. The number average sequence lengths, probabilities of various linkages and experimental run number R of copoly-(silphenylenesiloxane-siloxane) (based on ^{29}Si NMR spectroscopy [19–21])

D units (A = D)	M units (B = MZM)
$X_A = 0.523$ [a]	$X_B = 0.477$ [a]
$l_A = 1.9$	$l_B = 1.7$
$p_{AA} = 0.46$	$p_{BB} = 0.40$
$p_{AB} = 0.54$	$p_{BA} = 0.60$
$R = 56.4 \pm 1$	$R = 57.6 \pm 1$

[a] X_A and X_B are the mole fractions of A and B in the polymer. l_A and l_B are the number average sequence lengths: $l_A = 200 \cdot X_A / R$ and $l_B = 200 \cdot X_B / R$. Terms p are the probabilities of occurrence of each linkage.

In fact, the experimental run number was found to be close to 57; it would be 50 for a purely random distribution, and 100 for a perfectly alternating microstructure. The number-average sequence lengths were 1.9 and 1.7 for D and MZM monomeric units, respectively. With a perfect random distribution an average value of 2 would be found (1 with a regular alternating pattern).

Thermogravimetric analyses (TGA) under argon and air (Figs. 4 and 5) indicated that the thermal stability of the quasi-random copolymer was similar to that of previously reported (*p*-silphenylenesiloxane-siloxane) copolymers [27,28], including the alternating copolymers [29].

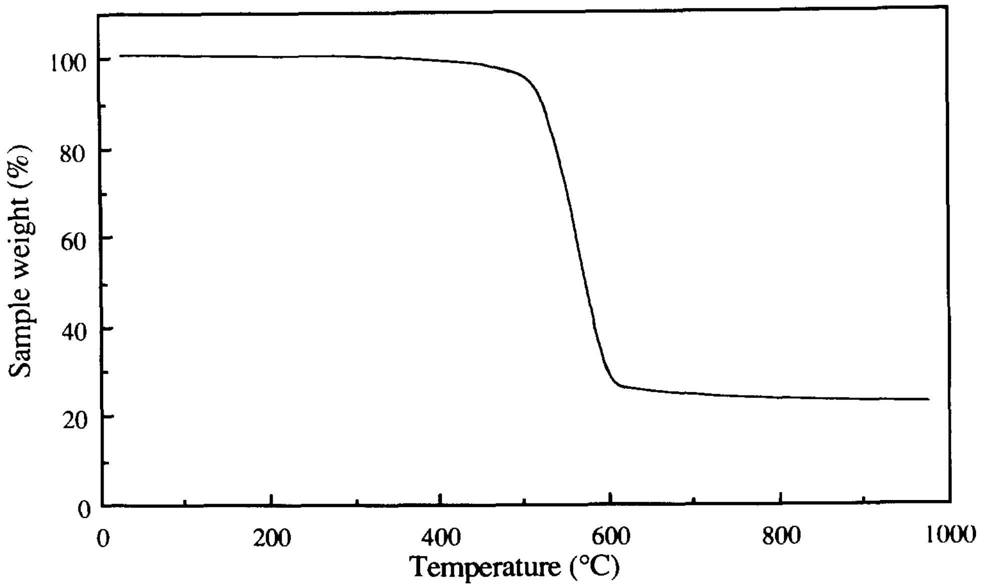


Fig. 4. Thermogravimetric analysis under argon of copoly(tetramethyl-*p*-silphenylenesiloxane-dimethylsiloxane) (heating rate 10 K min^{-1}).

4. Discussion

Two types of reaction take place between alkoxysilanes and halogenosilanes: an exchange reaction and a heterofunctional condensation reaction, the former appearing to be the faster. The first step, common to both reactions, involves the reversible coordination of the oxygen atom of the alkoxide on the electrophilic silicon atom of the halogenosilane [16,21]. At this stage, the rapid scrambling of alkoxy and halide functions takes place [22], either via a four-centre concerted mechanism (Scheme 2, intermediate *a*), or via the formation of an intermediate ion pair (intermediate *b*, but most unlikely with X = Cl [21]). Hence the exchange of functions leads to halogeno-alkoxy derivatives $R_2SiX(OR')$, whose heterocondensation results in the quasi-random microstructure of the copolymers.

Condensation and formation of alkyl halide results from nucleophilic attack of the halide on the carbon centre adjacent to the oxygen atom. The increasing reactivity from OCH_2Ph to $OCHPh_2$ alkoxy group, related to the increased resonance, is consistent with an S_N2, an S_N1, as well as a concerted mechanism [30]. However, the fact that the addition of chloride anions does not affect the reaction rate is consistent with an S_N1 mechanism or more probably, in the absence of dissociating solvent, a four-centre broadside attack (concerted mechanism, Scheme 3). The formation of alkoxide from halogenosilane and ether proceeds similarly, through the coordination of ether to the silicon

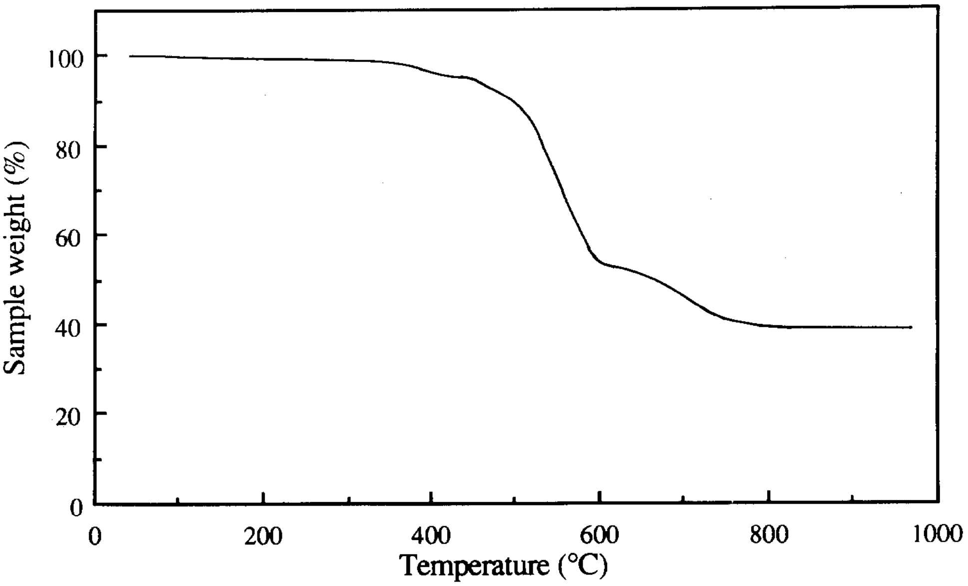
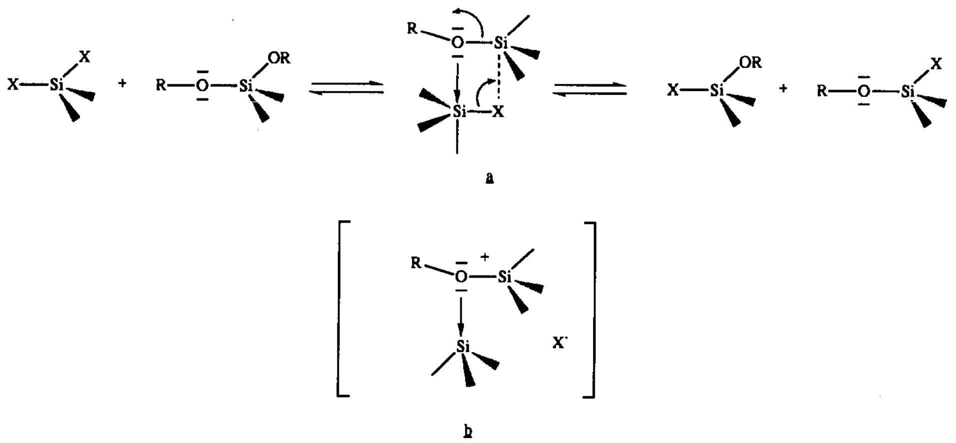
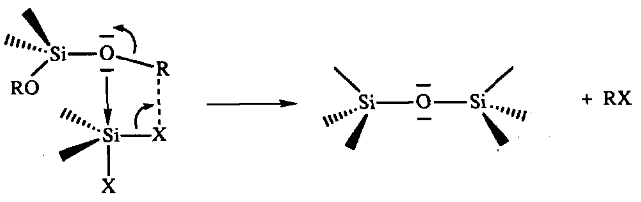


Fig. 5. Thermogravimetric analysis in air of copoly(tetramethyl-*p*-silphenylenesiloxane-dimethylsiloxane) (heating rate 10 K min^{-1}).



Scheme 2.



Scheme 3.

atom, followed by the nucleophilic displacement at carbon by the halide. The back reaction (*i.e.* the cleavage of siloxane bond by $PhCH_2Cl$) appears negligible.

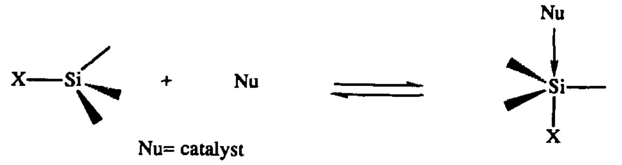
$$RX + \equiv Si{-}O{-}Si\equiv \not\longrightarrow \equiv SiOR + \equiv SiX$$

In contrast the reactions involving benzaldehyde were reported to reach equilibrium [12].

Every factor which enhances the coordination of the lone pair of the oxygen atom of alkoxysilane or ether favours nucleophilic displacement, by weakening the OR bond and withdrawing the electron density from the α-carbon (Scheme 3). Thus, the increase in the rate of condensation from bromo- to chloro-silanes may be related to the higher apicophilicity of bromine, that is the ability of the Si–Br bond to lengthen under the influence of an attacking nucleophile, and should accordingly lead to the pentacoordinate structure [31].

Similar explanations may be proposed for the activation by fluoride or NaI/CH_3CN. Thus, fluoride anions are known to catalyze nucleophilic attack at silicon [20,21] by forming complex anions (Scheme 4) in which the positive charge on the silicon atom is increased with respect to the tetracoordinate state (the electronic density being transferred to the equatorial and axial substituents) [32]. The sodium iodide/CH_3CN couple associates two activating processes. Acetonitrile acts as a nucleophilic catalyst, and the Si–Cl bond is converted into a more polarizable Si–I bond (Scheme 5) [16].

The usual preparations of (*p*-silphenylene/siloxane) copolymers involve the condensation reaction of *p*-phenylenedisilanol and the appropriate disilanol [28], diaminosilane, or bis(ureido)silane [5]. The polycondensation of alkoxysilanes and halogenosilanes is an alternative. In this work, our starting materials were 1,4-bis(chlorodimethylsilyl)benzene and dibenzhydryloxydimethylsilane. The former is easy to synthesize and is less sensitive to moisture than aminosilanes. The rather low degree of polycondensation obtained should be improved in a stepwise polyreaction monitored by GPC or ^1H NMR, as described by Dvornic and Lenz [5c]. Degradative side reactions [33] resulting from the alkyl halide by-products and limiting the chain growth do not occur.



Scheme 4.

The properties of block copolymers of poly(dimethylsiloxane) and poly(tetramethyl-*p*-silphenylenesiloxane) depend upon the composition and average sequence lengths of the soft dimethylsiloxane segments and the hard crystalline silphenylene blocks [34]. The exactly alternating silarylene-siloxane microstructure was proposed as the optimum combination of low-temperature flexibility and high thermal stability [5b]. The rigidity of every second unit should hinder the formation of cyclic degradation products by intramolecular exchange of Si–O bonds, involving the folding back of the chain, which is typical of siloxane chains above 300°C. The present work indicates that a quasi-random silphenylenesiloxane-siloxane copolymer exhibits a comparable stability. Additional work showing that intermolecular thermal rearrangements explain this will be reported elsewhere [35].

Acknowledgment

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