Trimethylsilylation of Mineral Silicates

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ABSTRACT

The application of the technique of trimethylsilylation
to mineral silicates is reviewed. Information can be
obtained on the molecular size distribution of the silicate
anions and also on the aluminium distribution in a silicate
backbone. Examples of the use of trimethylsilylation in
the structural determinations of silicates include examination
of sodium silicates and their solutions, calcium silicates,
various glasses, cements and concretes. Included within
the review is a discussion of the attempts to prepare new
polyorganosiloxane materials. Trimethylsilylation of certain
micas, for example, give polyorganosiloxane fluids and greases;
and attempts to physically and chemically modify the
polyorganosiloxane products are also reviewed.

INTRODUCTION

The trimethylsilylation of mineral silicates involves the
removal of ionic sites (and associated cations) and their
replacement by trimethylsilyl groups.

$$\geqslant Si - O^{\ominus}M^{\oplus} \longrightarrow \geqslant Si - O - SiMe_3$$
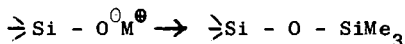
Interest in this subject area results from two objectives:-
(a) the determination of new information on silicate structures
and

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(b) the preparation of new polyorganosiloxane materials.

Silicate anions occur in sizes ranging from small molecules containing one silicon atom up to macromolecules of infinite size. These macromolecules are composed of building units of the general formula

$$({}^-O)_n Si(O_{\frac{1}{2}})_{4-n}$$

n = 0,1,2,3 or 4

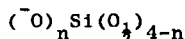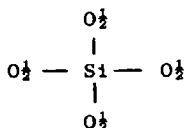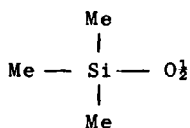The macromolecular silicate anions may be single chains, double chains, sheets or various irregular assemblies. Successful trimethylsilylation of all these arrays gives rise to polyorgano-siloxanes composed of mainly monofunctional (M) and quadrifunctional building units (Q).

$$
\begin{array}{cc}
\begin{array}{c}
O\frac{1}{2} \\
| \\
O\frac{1}{2} \!-\! Si \!-\! O\frac{1}{2} \\
| \\
O\frac{1}{2}
\end{array}
&
\begin{array}{c}
Me \\
| \\
Me \!-\! Si \!-\! O\frac{1}{2} \\
| \\
Me
\end{array}
\\
\text{Quadrifunctional (Q)} & \text{Monofunctional (M)}
\end{array}
$$

In the search for additional information on silicate structures it was hoped that the polyorganosiloxanes prepared by the trimethyl-silylation of the silicate anion would reproduce exactly the back-bone structure of the silicate used i.e. only the replacement of ionic sites occurs. If this hope were realised then the molecular size distribution of the polyorganosiloxane products would be exactly the same as the molecular size distribution of the silicate being examined. Although X-ray crystallography and related techniques give very detailed information on the relative positions of the atoms in silicate structures these techniques are unable to give information on the overall size of the silicate anions. Silicates cannot directly be dissolved in solution without molecular break-down and thus cannot be examined directly in solution by the techniques of polymer physics; however the trimethylsilylated derivatives may be quantitatively analysed by a variety of techniques including hplc, glc, mass spectrometry, nmr and thermal analysis.

Inorganic polymers have recently received much attention and books by Ray on Inorganic Polymers [1] , Wilson and Crisp entitled Organolithic Materials [2] , Holliday on Ionic Polymers [3] and Carraher on Organometallic Polymers [4] give a broad introduction to this general area. This review is the first to concentrate solely on the trimethylsilylation of mineral silicates, the equally important area of grafting organic groups to mineral silicates will be dealt with in a future review.

THE TRIMETHYLSILYLATION REACTION

The two fundamental techniques for mineral trimethylsilylation
have been called the Lentz [5] and the 'direct method' attributed
to Gotz and Masson [6] ; the "Lentz technique" consists of slurrying
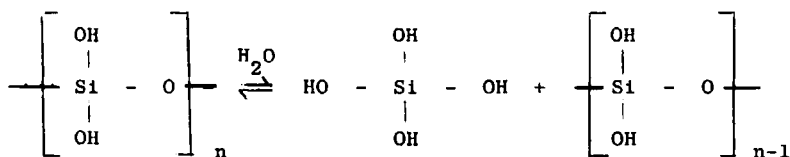the mineral with water for 1 h before adding the two-phase reaction
mixture of ice, concentrated hydrochloric acid, propan-2-ol and
hexamethyldisiloxane; the mixture is then stirred for 48 h at room
temperature and then filtered. The acid/water phase leaches the
cations from the mineral and a silicic acid is formed; this
silicic acid is capped by the trimethylsilylating agent which is
formed by the breakdown of the hexamethyldisiloxane in the presence
of hydrochloric acid. The function of the propan-2-ol is to increase
the solubility of the silylating agent in the water. The various
reaction sequences may be described as follows:-

$$
\begin{bmatrix} & O^{\ominus}M^{\oplus} & \\ -\!\!\!\!\!- & Si & -\; O -\!\!\!\!\!- \\ & O^{\ominus}M^{\oplus} & \end{bmatrix}_n \quad \xrightarrow[\text{Cation removal}]{H_2O/HCl} \quad \begin{bmatrix} & OH & \\ -\!\!\!\!\!- & Si & -\; O -\!\!\!\!\!- \\ & OH & \end{bmatrix}_n + 2nM^+
$$

$$
Me_3SiOSiMe_3 \quad \xrightarrow{H_2O/HCl} \quad 2Me_3SiOH
$$

$$
\begin{bmatrix} & OH & \\ -\!\!\!\!\!- & Si & -\; O -\!\!\!\!\!- \\ & OH & \end{bmatrix}_n \quad \xrightarrow{Me_3SiOH} \quad \begin{bmatrix} & SiMe_3 & \\ & O & \\ -\!\!\!\!\!- & Si & -\; O -\!\!\!\!\!- \\ & O & \\ & SiMe_3 & \end{bmatrix}_n + H_2O
$$
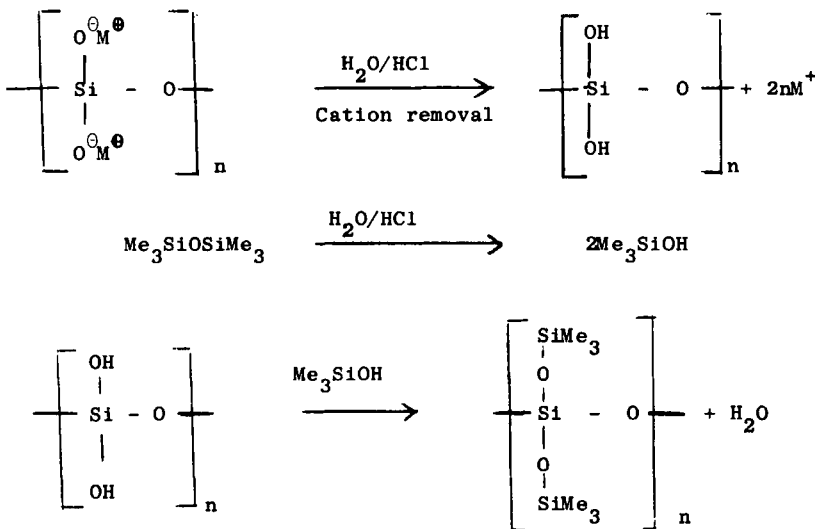
Many workers have found that trimethylsilylation does not always
proceed to completion thus in the final product some unreacted
silanol groups may be found. As a result the derivatization has
been completed by treating the initial product with Amberlyst 15
(an ion exchange resin) in the presence of hexamethyldisiloxane.
This converts the residual silanol groups to their trimethylsilyl
analogues. The application of the trimethylsilylation technique
to the determination of the molecular size of silicate anions
depends on the assumption that the value of n does not change

during the course of the reaction. Unfortunately, the polysilicic
acids in acidic aqueous solutions are liable to various polymer-
isation/depolymerisation equilibria as follows:-

$$\left[\begin{array}{c} OH \\ | \\ Si - O \\ | \\ OH \end{array} \right]_n \underset{\rightleftharpoons}{\overset{H_2O}{}} HO - \begin{array}{c} OH \\ | \\ Si - OH \\ | \\ OH \end{array} + \left[\begin{array}{c} OH \\ | \\ Si - O \\ | \\ OH \end{array} \right]_{n-1}$$

The Gotz and Masson direct method was developed in an attempt to
suppress this side reaction by reducing the amount of free
hydrochloric acid and water available by using trimethylchlorosilane
instead of hexamethyldisiloxane. Hence it is particularly
applicable to those minerals containing appreciable amounts of
water of crystallisation. In the initial publications [6,7,8]
describing their method Gotz and Masson reported its application
to, for example, olivine (an orthosilicate) and hemimorphite
(a pyrosilicate); the former gave an 88% yield of QM_4 and the
latter a 94% yield of Q_2M_6 in accurate reflections of the original
silicate structures.
Dent Glasser and Sharma [9,10] applied trimethylsilylation to a
study of sodium silicates and concluded that Lentz's method is more
suitable for the study of solutions, probably because the large
quantity of hydrochloric acid used rapidly reduces the pH to a
point where these polymerisation/depolymerisation equilibria are
relatively slow.
     Various different groups of workers have tried various reaction
techniques to minimise the opportunities for silicic acid inter-
mediates to undergo side-reactions. The equilibrium constants
of these reactions are strongly dependent on pH and the reaction
rates have a minima between pH 2 and 3; attempts to minimise these
side reactions therefore involve control of pH and a reduction of
the time needed for trimethylsilylation. In order to accelerate
the trimethylsilylation reaction Garzo et al [11] used weakly
acidified bistrimethylsilylacetamide (BSA) as the trimethylsily-
lating agent and replaced propan-2-ol by acetone. Acetone was
added in such an amount that the reaction mixture appeared to be
a single homogeneous phase after the addition of the BSA solution.
In order to demonstrate that side reactions were not occurring
four main components of silicic acid solutions (QH_4, Q_2H_6, Q_3H_8 and
Q_4H_8) were first determined by means of ^{29}Si nmr spectroscopy.
These results were in acceptable agreement with the glc results
obtained after BSA silylation of the same sample. To provide
further justification of their technique Garzo et al studied the
application of their technique and that of the Lentz and the Gotz-
Masson techniques to the study of mono- and disilicic acid solutions.

Freshly prepared (lifetime 1 min) mono- and disilicic acid solutions
were chosen for the silicate systems, it was assumed that hydrolysis
(leading to monosilicic acid) or condensation (leading to di-,
trimeric or higher silicic acids) takes place to only a small
extent within 1 min. Thus nearly 100% of the weighed silica is
expected to appear as QM_4 (monosilicic acid sample) and Q_2M_6

(di-silicic acid samples) and all other components indicate hydrolysis
or condensation during the silylation process. The Garzo technique
gave 77% of the silica occurring as QM_4 from the monosilicic acid

solution and 84% of the silica occurring as Q_2M_6 from the disilicic

acid solutions. Garzo et al concluded that the application of the
Gotz and Masson technique to these solutions appeared to promote
condensation reactions and the Lentz technique to favour the hydrolysis
of Q_2M_6 species. Both techniques promoted cyclisation whereas the

Garzo method seems to suppress all of these disturbing effects to
a reliable extent. They also concluded that incomplete silylation
allowed a formation of Q_2M_5H and Q_3M_7H only if Lentz or Gotz and
Masson techniques' were used.
   Sharma and Hoering [12] have developed anhydrous methods for
trimethylsilylation in order to reduce side reactions; 60-80% yields
of dimer, cyclotetramer and linear trimer were obtained from the
corresponding silicates i.e. hemimorphite, laumontite and
natrolite by reacting finely ground minerals with a large excess of
trimethylchlorosilane and hexamethyldisiloxane solvent; anhydrous
methanol saturated with dry hydrogen chloride and Amberlyst 15 ion
exchange resin were added to provide acidity.
After sixteen hours reaction trimethylsilylation was incomplete
and free OH groups were still present in the products. Derivatisation
was completed by stirring the reaction product with hexamethyldisiloxane
in the presence of the ion exchange resin. A second method which did
not give such good results involved stirring the mineral with a
large excess of trimethylchlorosilane and hexamethyldisilazane in
the solvent hexamethyldisiloxane. A small quantity of water was
then added slowly. Water reacts rapidly with the silylating agent
to yield hydrogen chloride and ammonium chloride which leaches the
metallic ions from the mineral. Derivatisation was again completed
by stirring the reaction product with hexamethyldisiloxane in the
presence of the ion exchange resin.
   The use of Amberlyst 15 has been reported by many workers
however, it has been noted [11, 13] that some of the high molecular
weight products will redistribute on prolonged exposure to an
Amberlyst 15/hexamethyldisiloxane mixture. Masson [14] has shown
that Q_3M_6 is converted to Q_3M_8 on stirring with Amberlyst 15 for

several days at room temperature and has suggested derivatisation
using trimethylgermylchloride as an alternative. The interference
caused by the formation of isopropoxy derivatives in the trimethyl-
silylation of natrolite has been extensively studied by combined
gas chromatography – mass spectrometry [15]. In the absence of
side-reactions the natrolite structure should give solely octakis-

(trimethylsiloxy)trisiloxane by cleavage at the Al-O-Si sites;
however siloxane cleavage and rearrangement give a wide range of
linear and cyclic products. A range of various trimethyl siloxy
and monoisoproxy derivatives were obtained, the most complicated
product was decakis(trimethylsiloxy)tetrasiloxane and the simplest
tris(trimethylsiloxy)monoisopropoxysilane.

CHARACTERISATION AND QUANTITATIVE ANALYSIS OF TRIMETHYLSILYLATED DERIVATIVES

The products of trimethylsilylation consist of QM units which
may be bonded together to give a wide range of molecular possib-
ilities. Separative methods involve the use of various chromato-
graphic methods; gas liquid and thin layer chromatography for the
lower molecular weight range and gel permeation chromatography
for the higher ranges.

Early methods were based on a column of SE30 on Chemisorb W
80-100 mesh with a temperature programmed rise at 8 $^{\circ}$C min^{-1} from
50 $^{\circ}$C to 260 $^{\circ}$C, with nitrogen being used as the carrier gas. These
methods allowed analysis of the derivatives from QM_4 up to Q_4M_{10}.
Masson[13] and Sharma [12] have both reported conditions for the
detection of species up to Q_6M_{12}. The former either using SE30
on Chemisorb W or a 25m x 0.27 mm glass capillary column coated
with OV 101, the latter using Dexsil 300, a silicone-carborane
copolymer, for column packing. Model compounds Q_nM_{2n+2}
(n = 1-4) Q_3M_6, Q_4M_8, Q_6M_{10}, Q_7M_{10}, Q_8M_8 and $Q_{10}M_{10}$ have been
prepared by trimethylsilylation, the products separated by tlc
and then the molecular weights and stoichiometry of the compounds
were established by mass spectrometry and combustion analysis[16].
These model compounds were then chromatographed by Garzo et al
[11, 16] using in separate experiments a glass capillary column
and three packed columns all analyses being performed using a
Perkin Elmer Model 900 gas chromatograph equipped with a flame
ionization detector.

Retention indices were measured by the simultaneous injection
of the sample compound, two suitable dimethylsiloxane chain oligomers
$[(CH_3)_3SiO_{\frac{1}{2}}]_2$ $[(CH_3)_2SiO]_n$, and methane; the homologous series of
dimethylsiloxane oligomers were used as secondary standards for the
retention index determinations. Retention characteristics depend
mainly on the number of M groups located on the surface of a
molecule while the size and structure of the molecular skeleton
have only minor effects. The relationship found between the
retention indices and molecular structure was suggested to be a
basis for the correct chemical and structural identification of
unknown peaks.

Glasser [17] and also Cook [18] have used gel permeation
chromatography (gpc) to obtain the molecular weight distributions

of higher molecular weight fractions. In the case of Cook a Waters
Associates Model 501hplc was used with three μ-styragel columns
with permeability ranges 10^2, 5 x 10^2 and 10^3 Å, each having a
plate count greater than 3000. Samples were injected as solutions
in chloroform each containing benzene as an internal standard.
Peaks were determined using refractive index and ultraviolet 254 nm
detectors. The instrument was calibrated with polystyrene standards.
Unfortunately no high molecular weight standards for the trimethyl-
silylated esters of silicic acid exist and the only suitable
commercially available standards are either polystyrene or poly-
glycol, both very different chemically from the polymers under
investigation. With this reservation Cook [18] reported that the
highest molecular weight material derived by the trimethylsily-
lation of a biotite mica was greater than 110,000 on the polystyrene
scale.

    Glasser et al have used gpc to study derivatives from sodium
silicate solutions. The calibration curves were constructed using
a combination of polydimethylsiloxane fractions and polystyrene
standards. Gpc depends on the effective hydrodynamic volume of
the molecules and Glasser et al realised that these calibrations
were not strictly accurate. Derivatives of Si_4O_{12} and Si_8O_{20} were
prepared with reasonable purity and gpc gave apparent molecular
weights for these that were 10% low; indicating that their
method of calibration was not grossly wrong. Recently Shimono
and co-workers [19] have successfully separated QM_4, Q_2M_6 and the
M_8 isomers Q_3M_8 and Q_4M_8 from the trimethylsilylation of
hemimorphite using Bio-beads S-X1 as the support and chloroform
isopropanol as eluent.

    The simplest derivatives can of course be unambiguously
characterised after separation simply by elemental analysis and
molecular weight determinations, however, it is of course much more
difficult to determine the structure where the molecular size
allows different possibilities for the ways in which Q and M may
be bonded together. To provide a basis for the study of the more
complicated derivatives Harris and Newman [20] have studied the
^{29}Si and ^{13}C nmr of various derivatives. They have reported the
relative ^{29}Si chemical shifts for trimethylsilylated silicate
derivatives as follows:-

Compound	M – units ppm from QM_4		Q-units ppm from QM_4	
	on Q^1	on Q^2	Q^1	Q^2
Q_2M_6	0.30	–	-2.38	–
Q_3M_8	0.23	0.55	-2.64	-5.06
Q_4M_8	–	1.52	–	-3.65

These results indicate that the Q unit region of ^{29}Si nmr
spectrum is more useful than the M unit region for quantitative
analysis of a mixture because the Q unit shifts are dispersed over
a range 3 times as wide. In particular the Q units of the dimer
and trimer should definitely be resolvable where the M units
attached to these units may not be distinguished. They studied
the trimethylsilyl derivatives of wollastonite and also pseudo-
wollastonite and concluded that the structures of the original
silicates were not retained , although the original structures
do clearly influence the product distribution; they also concluded
that ^{29}Si can be a useful technique in the analysis of such
products provided that all samples are studied at the same concen-
tration in the same solvent; and that it is convenient to relate
chemical shifts to those of the corresponding QM_4 groups. In a
further paper [21] Harris in collaboration with Glasser,
Lachowski and Jones used these techniques to study the products
of the trimethylsilylation of tetramethylammonium silicate which
contained a compound of formula $C_{30}H_{90}O_{21}Si_{18}$ and showed that the
structure of this compound was related to a double four-membered
cage Q_8M_8 by the replacement of one Si-O-Si bridge by trimethyl-
siloxy units to give Q_8M_{10}.

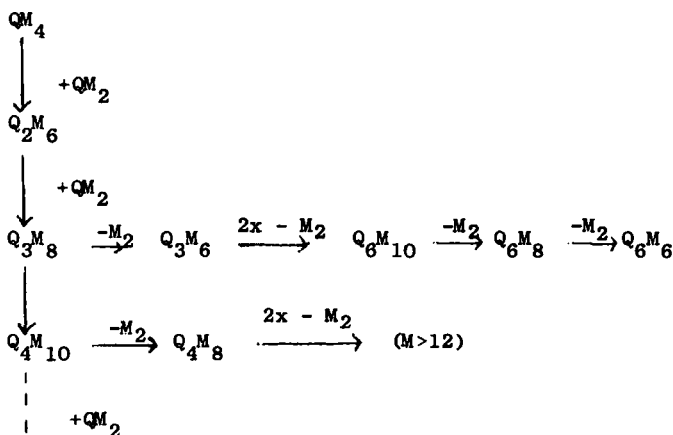EXAMPLES OF STRUCTURAL EXAMINATION USING TRIMETHYLSILYLATION

Study of Sodium Silicates

     As one example of the applicability of his technique Lentz
presented the results of a study of the trimethylsilylation of
sodium silicates and their solutions. In his original paper
Lentz [5] was well aware of the occurrence of side reactions but
nevertheless felt that valuable information could be obtained in
spite of this limitation. Thus for example only 43.5% of the
silicate was recovered as QM_4 from a 1 M sodium orthosilicate
solution with a Na:Si ratio of 4:1, he argued that although this
may be a true reflection of the content of the solution some of
the silicate solution is polymeric because (i) such a low yield
was never obtained with an orthosilicate mineral, (ii) a 9.6%
yield of a cyclic tetramer derivative is an improbable product of
a reaction if the solution is entirely monomeric and (iii) higher
yields of orthosilicate derivative were found as the concentration
of sodium was decreased.
     As described in earlier sections of this review the study of
sodium silicate solutions has provided a vehicle for the develop-
ment of techniques which give derivatives providing a truer
reflection of the structure of the original solutions. Glasser
et al [9,17] agreed with the observations of earlier workers that
the degree of polymerisation increases with increasing concentration
and decreasing soda:silica ratio. Their results were consistent
with the view that cross-linking is a major factor as the degree

of polymerisation is increased. Of those species positively
identified only the monomer, dimer and trimer were linear, the
tetramer and hexamer were cyclic and the Si_8O_{21} derivative was
thought to be either a cage with one of the edges opened, or a
cage of four or five membered rings. Glasser and Lachowski [22]
have established that changes in pH and concentration of sodium
silicate alters the degree of polymerisation of the silicate
species as measured by trimethylsilylation. The structure of
the polymeric species formed in solution was the subject of a
second paper which established the following rules:-
(i) connectivity is maximised consistent with a lower ring
size of four tetrahedra, (ii) all tetrahedra in a given
species show as nearly as possible the same degree of connectivity
[23].
        Garzo et al[11] in their work also reported the formation
of non-linear species. They suggested the following pathways
for the formation of the more complicated derivatives formed
using either the Lentz or the Gotz and Masson techniques.

QM_4

$\downarrow$ $+QM_2$

Q_2M_6

$\downarrow$ $+QM_2$

Q_3M_8 $\xrightarrow{-M_2}$ Q_3M_6 $\xrightarrow{2x\ -\ M_2}$ Q_6M_{10} $\xrightarrow{-M_2}$ Q_6M_8 $\xrightarrow{-M_2}$ Q_6M_6

$\downarrow$

Q_4M_{10} $\xrightarrow{-M_2}$ Q_4M_8 $\xrightarrow{2x\ -\ M_2}$ (M>12)

$\vdots$ $+QM_2$

Although in their paper they described these molecules in their
fully trimethylsilylated form they did point out that the
condensation steps would involve the protonated forms and that
some of the trimethylsilyl groups are probably hydroxyl groups.
        The degree of polymerisation of polysilicic acids in
magnesium silicates has also been studied by the trimethyl-
silylation of the silicic acid produced by the acid hydrolysis
of the silicates. The results showed that some 76-82% of
the derivative consisted of insoluble polysilicic acids,
which suggested that when silicates are hydrolysed in gastric
juice most of the silicic acids produced lead to insoluble
silica gel [24] .

Analysis of glasses

The structure of glass as a three dimensional polymer has
been investigated by the trimethylsilylation method. The earliest
application of the Lentz technique [5] was in a study of the
silicate structure [25] and the effect of time and temperature
on the silica distribution in borate glasses [26]. The results
suggested a random distribution of silica tetrahedra in a glassy
boric oxide matrix; the method also enabled an estimate of the
time taken to establish the melt equilibrium. The application
of a modified Gotz and Masson technique to glass-type samples
PbO.SiO$_2$ [27] showed that glassy 2PbO . SiO$_2$ and each of the
three main crystalline polymorphs are characterised by its own
specific silicate anion distribution. The agreement between
paper chromatography which can identify the higher molecular
weight derivatives and the corrected TMS results were good.
However, Nakumura in a study of PbO.SiO$_2$, and 2ZnO.SiO$_2$ suggested.
that further development of the trimethylsilylation technique
was needed before its reliability could be established [28].
The glc data obtained appeared to be dependent on the
experimental procedure adopted e.g. the amount of water added
or the method of shaking whilst temperature was found to have
no significant effect on the QM_4/Q_2M_6 ratio. Trimethylsiloxy
groups have been added on to the surface of titanium dioxide or
cobalt blue and the resulting materials were stable up to 300 ^{o}C
[29].
An extensive review of polymer mass distribution of silicate
glasses included trimethylsilylation as a useful additional
technique to traditional methods [30,31]. The effect of heating
lead orthosilicates at 500 ^{o}C for different times has been
carefully investigated [32]. Initially the dimer concentration
increases reaching a maximum after 30 minutes and then decreases
continually with time, the monomer concentration also decreases
noticeably with heat treatment duration. Diffractograms showed
that the heat treated samples gradually crystallised to include
tetramers at high concentration. Lunar samples have also been
analysed by trimethylsilylation and the orthosilicate derivative
was found ,agreeing with the modal analysis which showed a
significant proportion of olivine [33,34]. Trimethylsilylation
of augite and enstatite did not yield significant amounts of
silicate ions, this showed that the ions observed did not arise
from the decomposition of pyroxenes. Discussion of the differences
between the Apollo 11 and 12 samples were given. The minor
constituent $Si_4O_{12}^{8-}$ led to speculation of yet undetected mineral
phases with discrete silicate frameworks as microlites or crypto-
crystallites in the shocked partially melted minerals and glasses
in lunar fines. Interestingly enough there seemed to be little
or no $Si_4O_{12}^{8-}$ from Apollo 14 samples compared with the Apollo 11 and
12 fines [34].
Currell et al [35] have shown that the presence of other
metal ions in a silicate influence the yield and structure of poly-

organosiloxane derivatives from glasses. In a study of calcium
aluminosilicate glasses the yield of soluble polymer produced
was related to the % Al_2O_3 present. Evidence for SiF bonds has
been presented by Masson [37] in a study of a glass $3PbO.PbF_2.SiO_2$
where trimethylsilylation gave evidence for $[SiO_4]^{4-}, [Si_2O_7]^{6-}$ and
$[Si_3O_{10}]^{8-}$ as well as a number of mono, di and trifluorosilicate
ions. The results provide direct experimental evidence for
discrete silicate and fluorosilicate ions in the glass, in line
with polymer theory predictions.

The Analysis of Dioptase

      The trimethylsilyl derivative of dioptase $Cu_6Si_6O_{18}6H_2O$ was
expected to be the monocyclic hexamer $Si_6O_{18}[Si(CH_3)_3]_{12}$ but
gas chromatographic [12] analysis revealed three bicyclohexamers.
Earlier Gotz and Masson [36] had given a peak temperature of
289 °C for the monocyclic hexamer, however Hoebbel [16] suggested
that this was low and that the peaks obtained between 291 - 293 °C
correspond to bicycloisomers of Q_6M_{10} caused by intermolecular
condensation or cyclization.
The results obtained by Masson [13] are given overleaf.

Derivative	Method 1a	Method 2a	Method 1b
QM_4	0.5	8.4	0.6
Q_2M_6	0.2	Tr	0.2
$Q_4M_8 + Q_3M_8$	0.6	3.3	0.4
Unknown	0.9	2.0	0.4
$Q_6M_9(C_3H_7)$	5.9		3.9
$Q_5M_{10} Q_6M_{10}$	41.3	70.9	41.4
Unknown } Unknown }	2.9	trace	2.2
Q_6M_{12} isomer 1	3.1	9.7	9.6
Q_6M_{12} isomer 2	35.8	5.6	38.7
Q_6M_{12} isomer 3	9.0		2.6

a) 24 hours Amberlyst treatment b) 168 hours Amberlyst
                                             treatment

Method 1   Dioptase (0.3g), HMD (9 cm^3) and IPA (1 cm^3) were
stirred together at room temperature, chlorotrimethylsilane
(2 cm^3) was added and the stirring continued for ca 17h. The HMD
layer was removed and chlorotrimethylsilane removed. The residue
was stirred with Amberlyst 15.

Method 2   Dioptase (0.3g), HMD (9 cm^3) IPA (6 cm^3) , H$_2$0(4 cm^3)
and concentrated HCl (37% 4 cm^3) were stirred together for
ca 20 h at room temperature. Separation as in 1.
The table shows that the addition of Amberlyst 15 has an effect
on the derivatives obtained, this has been discussed elsewhere
in this review. Trimethylsilylation of dioptase by method 1 gives
three isomers of both Q_6M_{12} and Q_6M_{10}.   Acidification of the
reaction medium results in a decrease in the yield of Q_6M_{12} and
an increase in Q_6M_{10}. Gotz and Masson [36] and Hoebbel [16]
using more acidic conditions found the Q_6M_{10} but little or no
Q_6M_{12}.

These results suggest that the following rearrangement may occur.
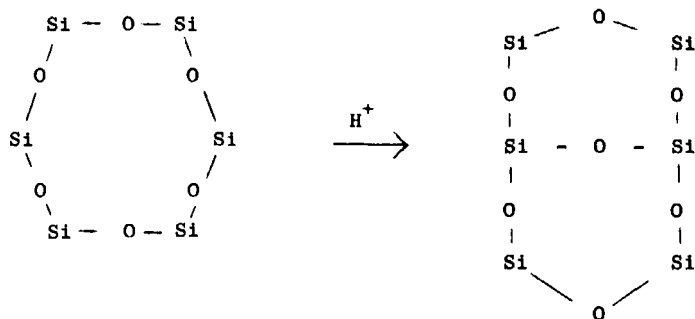
Intermineral Conversion

     Masson and co-worker   [38] have used the TMS technique to
look at intermineral conversion, hemimorphite Zn$_4$(OH)$_2$Si$_2$O$_7$.H$_2$O
loses water between 175-600 $^\circ$C and changes to a modified hemi-
morphite Zn$_4$(OH)$_2$Si$_2$O$_7$ which has Si$_2$O$_7^{6-}$ as the main structural

unit. Heating between 600 - 630 ^{o}C causes dehydroxylation and
yields a material with an orthosilicate structure identical to
β-ZnSiO$_4$ described by Taylor. This work confirmed by trimethyl-
silylation that at temperatures >835 ^{o}C βZn_2SiO_4 is converted to

α Zn_2SiO_4 without change in the orthosilicate nature of the

materials.

The Analysis of Cements, Concretes and Calcium Silicates

Lentz applied his original silylating study to cement paste
[39] tobermorite [40] and also to study the effect of carbon dioxide
on silicate structures in portland cement paste [41] . This work
complemented the acid molybdate method and thin layer chromato-
graphy [42,43] which had been pioneered by Wieker [44], further
work on this including modifications to the tlc technique has been
reported by Tamas [45] .

The major silicate structures found in the cement samples
analysed by Lentz varied with time and consisted of an ortho-
silicate, a pyrosilicate and a polysilicate of unknown molecular
configuration. Small quantities of a trisilicate and a cyclic
tetrasilicate were also detected. In an attempt to further
investigate the nature of the polymerised structures formed in
aged cement pastes, tobermorite $Ca_5(Si_6O_{18}H_2).4H_2O$ and wollastonite

were analysed by the trimethylsilylation technique. The results
indicate that on the basis of the trimethylsilylation technique
there is only limited similarity between the mineral tobermorite
and the calcium silicate hydrate in portland cement paste.
These original papers have been followed by investigations into
(i) the side effects that occur during the derivatisation and
(ii) attempts to improve the derivatisation procedure.
Two model compounds for the silicate structures in cement have
been investigated by Currell [46] .

Akermanite ($Ca_2MgSi_2O_7$) and β-dicalcium silicate (Ca_2SiO_4)
were trimethylsilylated under a whole variety of conditions;
the results showed that the ratio of QM_4 and Q_2M_6 varied with

reaction time, temperatures and concentrations of the reactants.
Frazier [47] had previously noted that the yield of QM_4 altered

by replacing hexamethyldisiloxane with trimethylchlorosilane as
the silylating species. Komatsu and co-workers [48] have used the
Lentz technique as a means of determining the growth of siloxane
units in calcium silicate.

Glasser and Lachowski [49] investigated the hydration of

$3CaO.SiO_2$ pastes at 25 ^{o}C by a variety of techniques and suggested

a mechanism for gradual polymerisation of silicates in cements.

The trimethylsilylation technique used in this study was
introduced by Tamas, Sarkar and Roy [50] which is the preferred
method for calcium silicates. Lachowski [51] has compared the
methods of Lentz [39] ;Gotz and Masson[6] ; and Tamas Sarkar and
Roy [50]; for the derivatisation of cement pastes.

Reagents/Author	Lentz (I)	Gotz/Masson (II)	Tamas et al (III)
Hexamethyldisiloxane	10 ml	9 ml	5 ml
Propan-2-ol	15 ml	0.8 ml	0
Hydrochloric acid	7.5 ml	0	0
Deionised water	6.3 ml	0.2 ml	0
Trimethylchlorosilane	0	2 ml	5 ml
Dimethylformamide	0	0	10 ml

Sample size of silicate 10 mg: mixtures stirred before addition
of silicate
                I (60 mins) II (0 mins) III (15 mins).
Post   treatment with Amberlyst 15.

        Method III has the advantages of a solvent (DMF) which
suppresses side reactions; DMF acts as a good solvent for the
calcium salts produced in the reaction. Lachowski [51] concludes
that method III gives higher, more reliable yields for those
calcium silicates which are of interest to cement chemists,
however the Ca/Si ratio needs to be fairly high. If this require-
ment is not met either the Lentz method [39] or Milestones vari-
ation [52] which uses t-butanol/salt as a method of preferentially
salting out the silicic acid into the organic phase are preferable.
        Milestone [52] has also suggested the use of γ-glycidoxy-
propyltrimethoxysilane as a suitable internal standard in the gas
liquid chromatographic analysis of QM_4 and Q_2M_6. Although it is
clear that in itself the QM_4/Q_2M_6 ratio is only giving general

information about the silicate polymerisation mechanism. The ratio
reflects at least two on-going mechanisms, the disappearance of
the anhydrous phase as well as the polymerisation of the hydrated
material [53] .
        The trimethylsilylation techniques of Lentz [39] Tamas [50]
and Milestone [52] have been applied to the analysis of creep and
dry shrinkage of calcium silicate pastes [54] and also autoclaved
lime-quartz materials [55] . There is still clearly a need for
better structural information on the high molecular weight deriv-
atives and an agreed method for the analysis of the low molecular
weight species QM_4 and Q_2M_6.

TRIMETHYLSILYLATION OF COMPLEX SILICATES

Susceptibility of Minerals to Trimethylsilylation

The applicability or otherwise of the trimethylsilylation depends in a very complicated way on the structure of the silicate mineral used. The first requirement is that the cations must be leachable by hydrochloric acid. Although the susceptibility of silicate minerals to attack by acids has been discussed by Mase [56] , Murata [57] and Petzold [58] the situation is complicated and is still incompletely understood. However some general points will be noted:

(a) according to Petzold cation removal is helped by the presence of heavy metal ions e.g. Fe,
(b) the less closely packed is the backbone the more likelihood there is of acid attack i.e. ease of access of the acid molecules.

Following cation removal the accessibility of the Si-OH sites to attack by trimethylsilanol will be the controlling factor. The size of the silicic acid molecules formed following acid removal will probably also have a major influence. In most sheet silicates which contain aluminium in the tetrahedral layer(isomorphous replacement of silicon by aluminium) the distribution of the aluminium atoms will control the size of the silicic acid molecules and is an important factor in trimethylsilylation. Currell and co-workers have investigated [59] using the Lentz technique the possibility of trimethylsilylation of a wide range of silicate minerals.

Single Chains		Group
Diopside	$CaMg(Si_2O_6)$	1
Hedenbergite	$CaFe(Si_2O_6)$	2
Hypersthene	$(Mg,Fe)_2(Si_2O_6)$	3
Bronzite	$(Mg,Fe)_2(Si_2O_6)$	1
Wollastonite	$Ca(SiO_3)$	2
Double Chains		
Anthophyllite	$(Mg,Fe)_7(Si_8O_{22})(OH)_2$	1 and 2
Tremolite	$Ca_2Mg_5(Si_8O_{22})(OH)_2$	1

Sheets

Daphnite	$(Fe,Al)_6(Si,Al)_4O_{10}(OH)_8$	3
Vermiculite	$(Mg,Fe,Al)_3(AlSi_3O_{10})(OH)_2$	2
Prehnite	$Ca_2Al_2(Si_3O_{10})(OH)_2$	1
Apophylite	$Ca_4K(Si_4O_{10})_2F.8H_2O$	2
Biotite	$K(MgFe)(AlSi_3O_{10})(OH)_2$	3
Phlogopite	$KMg_3(AlSi_3O_{10})(OH)_2$	1 and 3
Talc	$Mg_3(Si_4O_{10})(OH)_2$	1
Kaolinite	$Al_4(Si_4O_{10})(OH)_8$	1
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	1 and 2
Margarite	$CaAl_2(Al_2Si_2O_{10})(OH)_2$	1 and 3
Thuringite	$FeAl(Al_2Si_2O_{10}(OH)_2(MgFe)_3$ $(OH,O)_6$	1 and 3

Note:

Group 1 products whilst soluble in the reaction media were on examination shown to be unreacted minerals.

Group 2 products were insoluble in the reaction media and were on examination shown to be partially trimethylsilylated.

Group 3 products were soluble in the hexamethyldisiloxane layer and are fully trimethylsilylated.

Note that in the case of Margarite and Thuringite Group 3 products only were obtained with reaction temperatures of 75° Group 1 products only at ambient reaction temperature ; also Phlogopite only gave Group 1 at ambient and a mixture of 1 and 3 at 75 $^{\circ}C$.

Wollastonite was the only one of the single chain structure minerals to show some degree of trimethylsilylation. The probable reason for the relative ease of attack in the case of wollastonite is the fact that the silicate chains are less closely packed in this mineral. It should also be noted that workers at the Paint Research Association [60,61] were able to get Group 3 products by the trimethylsilylation of pseudowolloastonite and partial success in the case of Anthophyllite is possibly due to the presence of iron. The sheet silicates show an interesting variation. Kaolinite and Talc show no trimethylsilylation and the mineral is recovered i.e. they are not susceptible to the initial acid attack. Other

sheet silicates showed the formation of Group 3 or Group 2
products i.e. they were all susceptible to acid attack. Group 3
products appear to be formed when there is a certain degree of
replacement of silicon by aluminium in the silicate sheet. Thus
with very little Al in the tetrahedral sheet of Vermiculite
although the cations are removed no soluble products are
formed. Biotite, Phlogopite and Muscovite have approximate
Al:Si ratios of 1:3 while Margarite and Thuringite have
approximate Al:Si ratios of 1:1; each of these gave soluble
products. Presumably acid attack occurs at the aluminium centre
breaking the silicate sheet at these points to form fragments
small enough to allow attack by trimethylsilanol and give products
of molecular weight suitable to allow solubility in organic
solvents. To the first approximation it was reported that
average molecular weight of products could be correlated with
the distribution of aluminium in the silicate sheet. Thus
Margarite and Thuringite with high levels of aluminium in the
silicate sheet gave low molecular weight products compared with
Biotite, Phlogopite and Muscovite(with less aluminium in the
silicate sheet)which gave comparatively higher molecular weight
products. Further reports by these workers [62,63] on the
results obtained with Biotite and Phlogopite have supported this
initial conclusion but, for example, molecular weight
distributions obtained by gpc on polymers prepared from phlogopite
indicate a bimodal distribution with approximately 50% by weight
of the product in low molecular weight fragments i.e. QM_4 etc
and the rest of the product high molecular weight material with
a wide distribution. Thus the effect of aluminium distribution
on the average molecular weight is partially obscured by small
fragments breaking off from the silicic acid fragments before
complete trimethylsilylation.

        Sharma [12] suggested that aluminium is released prior to
the silicate derivatisation this is in contrast to the views of
Currell and co-workers [63] who have reported that in the reaction
of phlogopite aluminium appears to be partially retained in
preference to the potassium and magnesium although throughout
the reaction the mineral retained its original structure.
Aluminium was apparently removed from the tetrahedral layer and
moved to the octahedral sites with a compensating movement of
potassium ions to counteract the shift in charge balance in the
silicate sheet. It was suggested that at least partial trimethyl-
silylation occurs before the final breaking of the silicon/
oxygen/aluminium bonds.
Glasser [64] has applied the trimethylsilylation technique to
melilites in order to determine the Al-Si ordering by establishing
the amount of QM_4 and/or Q_2M_6 derived from one natural and five
synthetic melilites. The synthetic gehlenite - rich melilites
are appreciably but not completely disordered. The natural melilite
is well ordered, but heating at 1050 $^\circ$C introduces considerable
disorder. The Si/Al ratio has also been studied by Yokoi in
some faujasite type zeolites (Si/Al ratio : 1.20-2.65). Zeolites

have small values of Si/Al ratio (< 1.90) consist mainly of
orthosilicate and pyrosilicate ions however zeolites where Si/Al
(> 1.90) consist of three dimensional networks [65] .

Kenney et al were the first [66,67,68] to apply the technique
of trimethylsilylation to complex silicates. They used a mixture
of isopropanol, hydrochloric acid and trimethylchlorosilane.
The reaction of chrysotile asbestos with this mixture gave a
planar organosilicon polymer in fibrous form. They concluded
that half the sites available on a given sheet were occupied by
trimethylsilyl groups and that the rest were occupied by hydroxy
groups or were linked together by oxygen bridges. It was
postulated that the first stage in the reaction is the removal of
magnesium ions from the surface of the chrysotile fibres with
hydroxyl groups substituted in their place, followed by further
substitution involving trimethylsilyl groups. The resulting
individual polymer sheets which have all the trimethylsilyl groups
on one side have internal strains which cause the   sheets to
curl up into tube like ribbons. The fibres which were characterised
by detailed electron microscopy consist of bundles of rolled up
ribbons. Kenney and co-workers also applied the same reaction
mixture to the mineral apophyllite but because of the nature of the
parent sheet trimethylsilyl groups were attached to both sides
giving balanced strains and thus flat sheets.

Zapata and co-workers [71,72] applied a similar technique to
chrysotile and vermiculite this time using dimethylallylchloro-
silane as the silylation reagent, the grafting of the allyldimethyl-
silyl radical apparently proceeds more slowly than that of the
trimethylsilyl because of steric hindrance effects associated with
the bulkier alkyl group. The product was found to be rubbery, this
rubbery nature was attributed to the plasticising effect of diallyl-
tetramethyldisiloxane the removal of which by extraction destroys
the rubbery character of the material. In a later paper
Mendelovici reported on the acid and heat stability of organic
derivates of chrysotile [73] . Fripiat has [69] patented a method
for grafting hydrophobic organosilicon compounds on to the anhydrous
or hydrated calcium silicate components of cement. The corrosion
and weather resistance of the cements was improved. Other calcium
silicates, including wollastonite have been completely derivatised
to give novel polyorganosiloxanes which on the addition of clay
prior to trimethylsilylation gave mixed Si/Al derivatives.
An earlier paper by Fripiat [47] has described the methyl
derivative of chrysotile using hexamethyldisiloxane to give
a high molecular weight two dimensional organic derivative.
Linsky has also shown the possibility of forming organo-
silicon sheet polymers [70] .

Saunders, Cox and Slade in a patent [60] assigned to the
National Research and Development Corporation claimed the
preparation of a material suitable for water repellant treat-
ment prepared using a range of possible organosilyl capping
agents. A typical example describes the reaction of synthetic
wollastonite (cyclic half α form) reacted with a mixture of

concentrated hydrochloric acid, water,propan-2-ol and hexa-
methyldisiloxane followed by stirring at room temperature for
1 hour. The non-aqueous fraction after drying and distillation
at low pressure gave a colourless, mobile oil. The number average
and weight average molecular weights of the oil were
determined by gel permeation chromatography as 1610
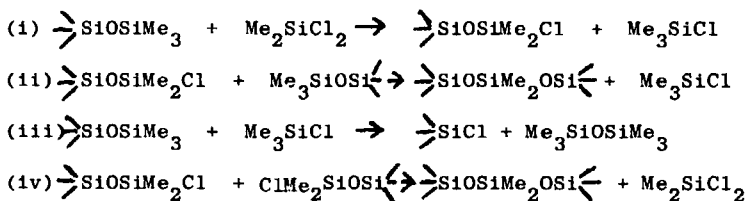and 1730 respectively.   This product, when used
to treat ventile cotton gave a BS water repellancy spray test
rate of 5 compared to the spray test rating of 4 for a similar
sample treated with a typical commercially available silicon
water repellant composition. Saunders and Cox in a further patent
[61] also assigned to the National Research and Development
Corporation covered a process in which greatly improved yields can
be obtained from polysilicate minerals such as wollastonite. They
claimed that in this invention it is important to use the acid
in an amount sufficient to react with at least half the metal
cations of the polysilicate mineral, a water miscible organic
solvent and water in an amount such that the concentration of the
acid in the aqueous phase is not greater than 2 gm equiv.per.lit.
so that silylation of the polysilicate takes place with at least
partial retention of the silicate backbone. A typical example
quotes a reaction medium prepared by dissolving trichloroacetic
acid in a mixture of concentrated hydrochloric acid, water and
acetone. Hexamethyldisiloxane is added and the mixture stirred for
1 hour before addition of powdered wollastonite. The final product
from this reaction mixture is quoted as having a number average
molecular weight of 3000 and a weight average molecular weight
of 9000 with 17% of the polymer having a chain length in excess
of 250$\overset{o}{\text{A}}$.

     Kuroda and Kato [74] produced a glassy product by trimethyl-
silylating para-wollastonite using the Lentz technique - the
product dissolved in a range of organic solvents and its thermal
properties gave a strong sharp exothermic peak at 430 ^{o}C due to
oxidation of organic groups.
Pseudowollastonite has also been converted by treatment with
trimethylchlorosilane in t-butanol and acetone to give
Q_3M_8 (70%) [75] . One of the major drawbacks to the industrial
exploitation of the polymers derived from simple silicates has been
their low number average molecular weights. Q_3M_8 can be successfully
polymerised [64] by stirring with toluene and dmf in the presence
of BuLi in n-hexane for two days to give a polymer M.W.6000.
The recent work on complex silicates to produce high molecular
weight derivatives has centered on two research groups Currell
and co-workers in the United Kingdom and Kuroda and Kato in
Japan. Currell [76] prepared the first soluble polyorgano-
siloxane from an inorganic mineral silicate by trimethylsilylating
chlorite var. daphnite$\left\{(Fe, Al, Mg)_{12}\right\}\left\{(SiAl)_8O_{20}\right\}$ $(OH)_{16}$ to
give a highly viscous material $\overline{M}n$ 1618. In a subsequent paper
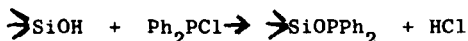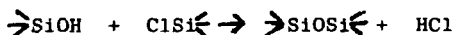the trimethylsilylation technique was applied to a range of single

chain, double chain and sheet silicate anions [59] . Kuroda
and Kato [77] have also attempted to prepare higher molecular
weight materials by the trimethylsilylation of complex silicates
such as biotite. These authors have recently reviewed a series
of their more recent papers [74, 78, 79, 80, 81] in a further
composite paper [82]. The trimethylysilyl derivative of
halloysite was organophilic and resulted from an initial attack
on the interlayer region by hydrochloric acid; the octahedral
layers are decomposed and labile tetrahedral layers, having
silanol groups on one side are generated; the silanol groups in
the tetrahedral layers are then partially trimethylsilylated [79]
Ethylene glycol was used as a linking agent in an attempt to
produce higher molecular weight trimethylsilyl derivatives from
hemimorphite [78] . Kuroda and Kato had previously investigated
the straightforward derivatisation of this mineral in a previous
study [80] and the use of an alcohol in the trimethylsilylation
reaction esterified any residual hydroxyl groups [81] . The glassy
product obtained from parawollastonite dissolved in a wide range
of organic solvents but was insoluble in water [82] .

Currell et al [83] have investigated the further chemistry
of polyorganosiloxanes prepared by the trimethylsilylation
technique, partly with the aim of providing a basis for the
development of methods for the preparation of materials with
increased molecular weight. Material with increased molecular
weight (up to $\sim$6000) with elimination of hexamethyldisiloxane
is obtained on heating up to 300 $^{\circ}$C [84] On heating with dimethyl-
dichlorosilane up to 70 $^{\circ}$C for $\frac{1}{2}$ h in the presence of anhydrous
ferric chloride or the hexahydrate , pseudowollastonite polymer
gives a mixture of products including trimethylchlorosilane,
hexamethyldisiloxane, 2-chloropropane, and depending on the
reactant ratio used, polymer of increased molecular weight [85,86].
The formation of these products was rationalised in terms
of the following reactions:-

(i) $\geqslant$SiOSiMe$_3$ + Me$_2$SiCl$_2$ $\rightarrow$ $\geqslant$SiOSiMe$_2$Cl + Me$_3$SiCl

(ii) $\geqslant$SiOSiMe$_2$Cl + Me$_3$SiOSi$\leqslant$ $\rightarrow$ $\geqslant$SiOSiMe$_2$OSi$\leqslant$ + Me$_3$SiCl

(iii) $\geqslant$SiOSiMe$_3$ + Me$_3$SiCl $\rightarrow$ $\geqslant$SiCl + Me$_3$SiOSiMe$_3$

(iv) $\geqslant$SiOSiMe$_2$Cl + ClMe$_2$SiOSi$\leqslant$ $\rightarrow$ $\geqslant$SiOSiMe$_2$OSi$\leqslant$ + Me$_2$SiCl$_2$

These polymers contain -O$_{\frac{1}{2}}$SiMe$_2$O$_{\frac{1}{2}}$ (i.e. D units) as well as the
original Q and M units. A variant of this reaction involves
the interaction of dimethyldichlorosilane with a mixture of
octamethyltetrasiloxane and the trimethylsilylated polymer.
Other methods of incorporating D units include the use of
short chain polydimethylsiloxanes (with trimethylsiloxy end
groups) as the trimethylsilylating agent in place of
hexamethyldisiloxane in the original reaction with the

mineral silicates.   After the preparation of polymer
by trimethylsilylation some residual hydroxyl groups are
present; these -OH groups show very variable reactivity
probably due to steric factors, however reactions have been
reported with compounds containing Si-Cl groups
(i.e. ($CH_3)_3SiCl$, $CH_3(CH_2 = CH)SiCl_2$ and $CH_2 = CHSiCl_3$,
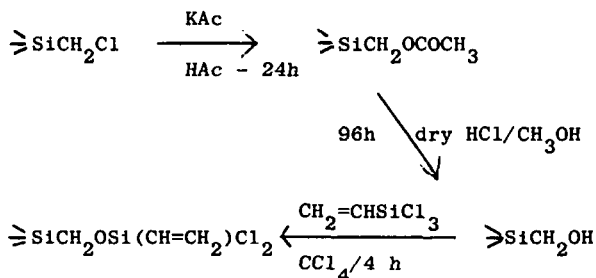and also with Ph_2PCl) [18] .

$$\geqslant SiOH \ + \ ClSi\leqslant \ \rightarrow \ \geqslant SiOSi\leqslant \ + \ HCl$$

$$\Rightarrow SiOH \ + \ Ph_2PCl \rightarrow \ \geqslant SiOPPh_2 \ + \ HCl$$

Using chlorine or bromine gas in the presence of tungsten
light the trimethylsilyl methyl groups may be chlorinated or
brominated.

$$\geqslant Si(CH_3)_3 \ + \ Cl_2 \ \xrightarrow[\text{4 hours}]{\text{W light}} \ \geqslant Si(CH_3)_2CH_2Cl$$
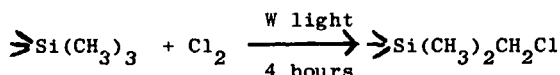
In a subsequent two-step reaction sequence the chlorine atom
was then replaced by an hydroxyl group as shown below:

$$\geqslant SiCH_2Cl \ \xrightarrow[\text{HAc - 24h}]{\text{KAc}} \ \geqslant SiCH_2OCOCH_3$$

$$96h \ \searrow \text{dry } HCl/CH_3OH$$

$$\geqslant SiCH_2OSi(CH=CH_2)Cl_2 \xleftarrow[\text{CCl}_4/\text{4 h}]{CH_2=CHSiCl_3} \ \geqslant SiCH_2OH$$

The reactivity of the $\geqslant SiCH_2OH$ groups with, for example,
silicon-chlorine compounds was shown to be much more reproducible
than that of the previously mentioned Si-OH groups [87] .
The inorganic polymers listed above have a variety of properties
and molecular weights in the range from 10^3 to 10^5. They have
a number of potential industrial uses as   coatings, adhesives
and as anti-corrosive agents. This area is comparatively new
and the search to produce higher molecular weight Q/M polymers
is continuing. The direct production of molecular weight
fragments in the range 3×10^3 - 8×10^3 has been shown by the
trimethylsilylation of xonotlite [88] , a potentially useful
route by silylating water glass has also been reported [89] .

THE FUTURE

The technique of trimethylsilylation has been shown to be a useful tool in the study of silicate structures provided, of course, that the possibility of side-reactions is remembered in the interpretation of these results. Improvements in technique and a better understanding of the reactions involved can be expected to give more accurate information on the structure of the silicates and enable the expansion of the technique to the examination of more complex silicate structures.

Applications have not yet been firmly established for the polyorganosiloxanes prepared by trimethylsilylation and they are not, as yet, prepared commercially. However, it should not be very long before this useful chemistry leads to materials with, for specific applications, properties superior to the 'silicones' and therefore worthy of commercial preparation.

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