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Three-dimensionally growing polyorganosiloxanes. Possibilities of molecular construction in highly functional systems.

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ABSTRACT. An analysis is carried out of general aspects of the construction of three-dimensionally growing structures with an organic or an inorganic skeleton. Problems in the synthesis of novel polymeric forms based on organosilicon monomers are examined. Ways are discussed for overcoming steric effects in the surface layer, caused by the characteristics of the formation of three-dimensionally growing structure.

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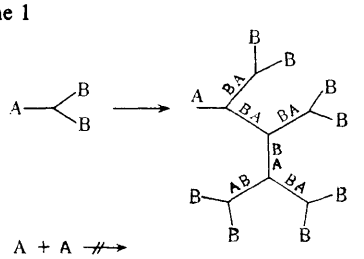
I. Introduction

The present review is based primarily on the material of a report which was presented at the first international school-seminar on non-traditional methods of polymer synthesis.[1] However, a considerable amount of work in this area has appeared recently, as a result of which it can be said that polymer chemistry has developed in a new direction which may be described as the "synthesis of dendrimers" or, more poetically, of polymers of the "starbust" type. The principal achievements and problems and also the characteristics of formation of these structures, including theoretical prerequisites for the emergence of the new polymeric forms, have been reviewed by Tomalia et al.[2] Publication of this detailed review simplified our task to a considerable extent. Here we shall consider only the results and problems arising in the course of the synthesis of three-dimensionally growing organosiloxanes or organosilicon dendrimers. Data for the organic analogues will be used only to the extent that is necessary for an understanding of the similarities in the problems investigated and of the differences in the synthetic approach to their solution.

II. Basic prerequisites, concepts, and general schemes

The basic prerequisites for the creation of macromolecular dendritic systems can be traced back to the work of Flory,[3] who suggested that highly functional systems could lead to the formation of highly branched polymers rather than cross-linked or polycyclic types. To achieve such a result, one main condition, specified by Flory, must be satisfied. Thus, if a monomer contains two or more functional groups, one of which is A, and the others are of type B, and if A does not react with A, or B with B, but the interaction of A with B results in the formation of a chemical bond A–B, then it is possible that a non-crosslinked and non-polycyclic polymer will be formed, as shown in Scheme 1.

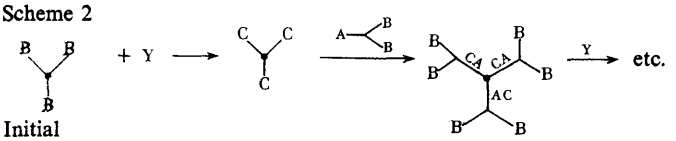
Scheme 1



A + A ⇸
B + B ⇸
A + B ⟶ AB

If, however, in the initially formed oligomer itself, not only does A not interact with A, or B with B, but A also does not interact with B; and if it is possible at a certain stage to convert B into C, a group which can form a chemical bond by interaction with A, then such a scheme can be used to obtain completely controlled growth of the molecule (Scheme 2):

Scheme 2



Initial branching centre



main reagent

A + B ⇸
A + A ⇸
B + B ⇸
B + Y ⟶ C
C + A ⟶ AC

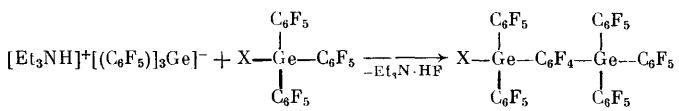
Practically all systems synthesised at the present time can be described in general form by means of Schemes 1 and 2 and we shall therefore make use of these frequently for appraisal of the characteristics of one or another real system.

III. Examples of real structures, and corresponding general schemes

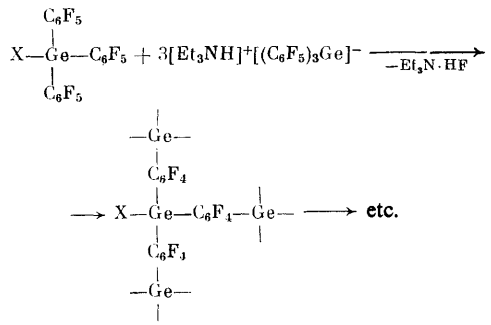
Scheme 1 is well illustrated by work[4,5] using organoelement compounds. During a study of the chemical characteristics of the hydrides of germanium and silicon, with perfluorophenyl substituents at the heteroatom, an interesting fact was discovered. The presence of three perfluorophenyl substituents at the atom of the element leads to such a significant redistribution of the electron density in the molecule, such that on the addition of a base, triethylamine, charge separation occurs with the separation of hydrogen as a proton rather than hydride.

$$(C_6F_5)_3GeH+Et_3N\rightarrow[Et_3NH]^+[(C_6F_5)_3Ge]^-.$$

This fact, in combination with the reactivity of the *p*−F atoms of the perfluorophenyl substituents at the atom of the element, in particular germanium, leads under these conditions to a process at every reaction centre, which can be depicted by the following general scheme:



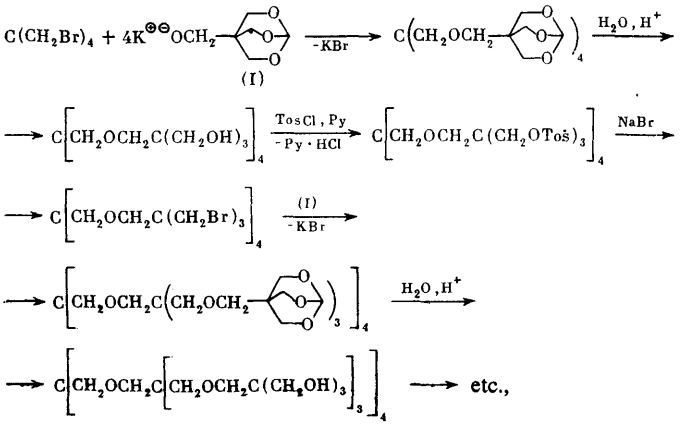
or, bearing in mind the molecule as a whole:



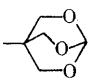
In this system the germanyl hydride grouping (in accordance with the condition of Flory) is the functional group A, and the atom of fluorine in the *para* position of all three perfluorophenyl groupings is the functional group B (Scheme 1).

Let us consider briefly the remarkable properties of this system. First of all, the ease with which reaction occurs at room temperature should be noted: from the moment of introduction of triethylamine to the completion of the reaction and the formation of a polymer, less than a minute elapses. As a result a "live" polymer is formed. The reaction may be resumed again after separation of the precipitate of triethylamine hydrofluoride and the introduction of new portions of reagents. Such an operation can be repeated more than once. In addition, it is possible to obtain a polymer with a molecular mass of several millions, as determined by light scattering. From electron microscope data, the polymeric molecules obtained are seen to be spherical.

The most complete illustration of the general Scheme 2 is possible by a consideration of the following system:[6]



in which the basic reagent is the potassium salt of the tricyclo-orthoester, 4-(hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane (I). Conversion of the functional group B:

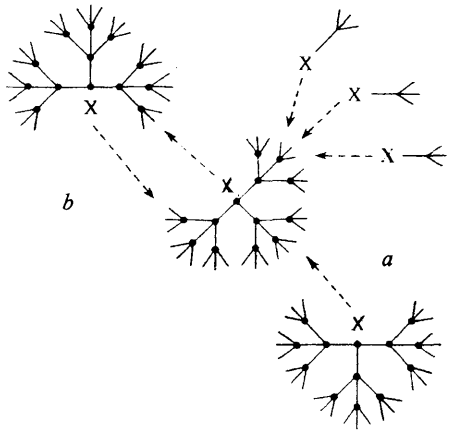


into the form C[−C(−CH_2Br)$_3$] occurs in three stages—hydrolysis, tosylation, and bromination, after which the process is repeated again. As a result, branched dendrimers are obtained (Fig. 1).[6]

Comparing the two basic schemes for the construction of three-dimensionally growing systems, or dendrimers, several principal points should be noted. Scheme 1 occurs in a single step and does not involve regulation of the structure at the molecular level. On the other hand, in accordance with Scheme 2 (and this is confirmed both theoretically and in practice) it is possible to form the structure of the molecule layer by layer with the possibility of termination at any stage. However, such a delicate control of the structure and dimensions of the molecule at the molecular level demands certain sacrifices, both in terms of the purely synthetic target (since a complex and multistage synthesis is involved), and also in general scientific terms (since the molecule grows in an orderly fashion to a definite size, after which there is a rapid reduction in rate on account of steric hindrance). The fact is, that the surface of the molecule grows more slowly than the number of functional groups, leading at a certain stage to steric difficulties.[6] At the same time, the unregulated system (Scheme 1) controls its own growth and therefore in every layer as many functional groups as possible are used without steric complications. In accordance with Scheme 1, polymers can be obtained with a molecular weight of > 1,000,000 a.m.u. The authors[4,5] did not analyse certain additional, purely structural processes, which can take place during the unregulated formation of three-dimensional structures. The basic difference between systems 1 and 2, as schemes for the formation for these structures, is that in the regulated version, if the interaction of the growing molecules between themselves is excluded then growth of the macromolecule is accomplished only by the addition of monomeric units at the growing centre, whereas in the non-regulated variant, the growing molecules are fully able to interact between themselves, especially in the early stages. On the one hand, therefore, it is possible that entire regions of the surface of the growing molecule may become

shielded (Scheme 3, process *a*), but on the other, cyclisation may occur (Scheme 3, process *b*):

Scheme 3



The principles and basic schemes for obtaining macromolecular dendrimeric systems have thus been considered and attention will now be turned to the main subject of this brief review: three-dimensionally growing polyorganosiloxanes.

IV. Three-dimensionally growing polyorganosiloxanes

With the whole expansion of possibilities for controlling the structures of organosilicon polymers, and so also to a certain extent the properties of materials based on them, a search was carried out for new, convenient methods for the synthesis of organosilicon polyfunctional oligomers with reactive functional groups.

From the point of view of choice of reagents, suitable for the construction of three-dimensionally growing systems, organosilicon monomers are not themselves convenient, because of the limited choice of functional groups in comparison with normal organic monomers. This applies especially to the construction of polymers with a purely siloxane skeleton. Analysis of data in the literature showed, in particular, that amongst the organosilicon monomers reported, there were none which could have met the necessary requirements sufficiently (i.e. would have allowed the aim of conversion by general Scheme 2 to be achieved). The majority of traditional monomers employed for obtaining siloxane polymers by polycondensation methods contain functional groups that are the same, undergo exchange with each other, are insufficiently stable, or enter into reaction with one and the same reagent.

The basic reaction, therefore, is not sufficiently selective for the preparation of simple branched oligomers by the use of such organosilicon monomers, or for the subsequent development of the functional system.[7–15] All of these facts stimulated work on the creation of monomers containing two or more differing functional groups. In this connection, our attention was attracted to the alkoxysilane-alkali metal hydroxide system, which, in spite of conflicting reports in the literature,[16–19] allowed one to hope that monomers with independent functional groups could be obtained, containing simultaneously sodiumoxy- and alkoxy-groupings attached to atoms of silicon. The synthesis of such compounds proved to be very simple and the yield of the main substance in the majority of cases reached 95%.[20]

$$\mathrm{RO{-}Si(R')(R'){-}OR + NaOH \longrightarrow RO{-}Si(R')(R''){-}ONa + ROH,}$$

R=Et; R′=R″=Me; R′=R″=OEt; R′=Me, R″=OEt.

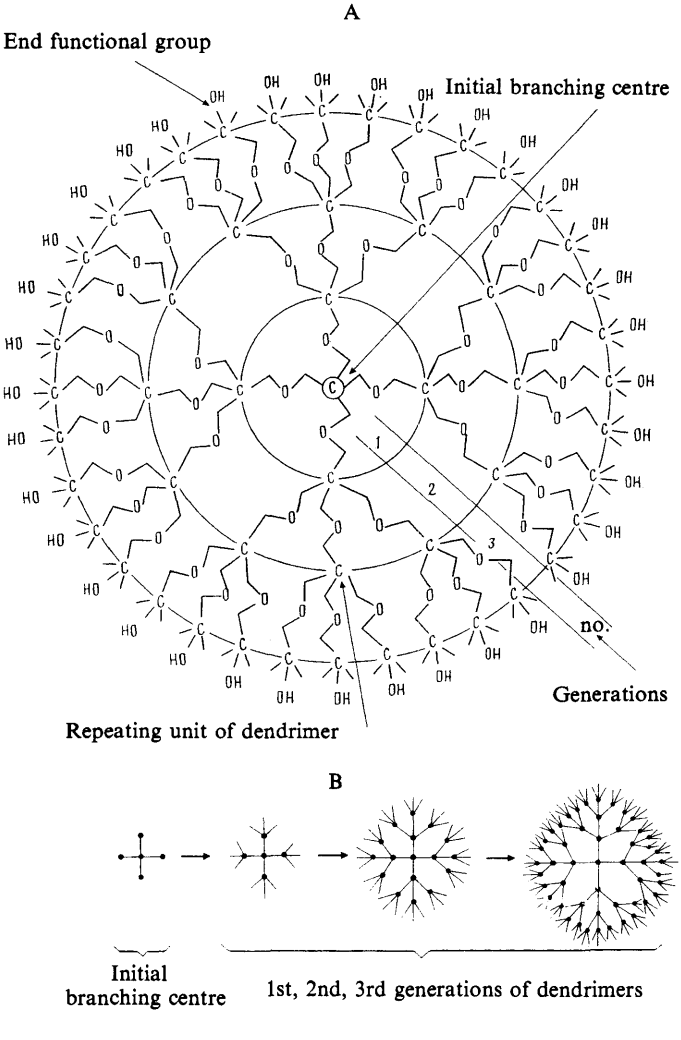
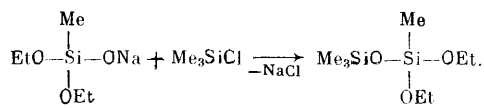


Figure 1. Planar projection of "starbust dendrimer" (A) and scheme for its formation (B).

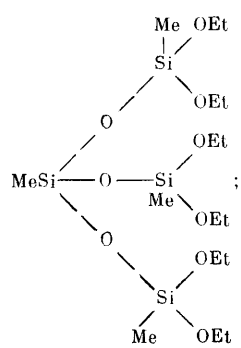
Although it was initially apparent that the presence of two or more identical functional groups in a molecule of alkoxysilane does not permit high selectivity to be achieved in this reaction, a more detailed study of the NaOH–$(RO)_2SiR'R''$ system showed subsequently, that selectivity is an entirely natural result of the marked redistribution of electron density in the molecule of

alkoxysilane that follows the introduction of sodiumoxy-groupings into its structure.[21] A study of the properties of the sodiumoxy-organoalkoxysilanes that were obtained led us to the conclusion that under certain conditions, alkoxy groupings can be considered as latent functional groups or as protected groups that may be activated to become reaction centres ($\geq$Si—Cl). These assumptions were most simply confirmed and utilised by a one-step transformation of the alkoxysilyl grouping into chlorosilyl (Scheme 4). The transformation of $\geq$Si—OR into $\geq$Si—Cl allowed the primary cycle of conversion to be completed and the molecular construction of siloxane systems to commence immediately.

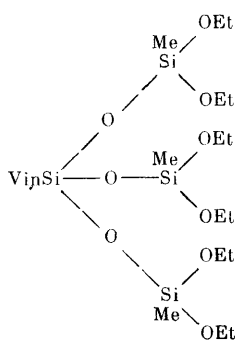
In contrast to the majority of sodiumoxy-derivatives or organosilicon monomers, sodiumoxyorganoalkoxysilanes dissolve readily in practically all organic solvents including those such as hexane, toluene, diethyl ether, etc. The first reactions carried out with the use of the novel reagents have already demonstrated the "independence" of their functional groups; in particular, we have shown that it is possible to carry out the reaction between organochlorosilanes and sodiumoxy groupings with formation of a siloxane bond, whilst preserving the inviolability of the alkoxy groupings. Thus, during treatment of the monomers with trimethylsilyl chloride (a process used by us for the identification of synthesised compounds and estimation of their yield) the formation of by-products was not observed.



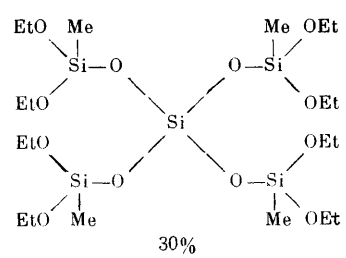
The use of tri- or tetra-functional silanes such as $RSiCl_3$ (R = Me, vinyl) and $SiCl_4$ in these reactions, instead of trimethylchlorosilane, allows the first generation of oligomers to be obtained.



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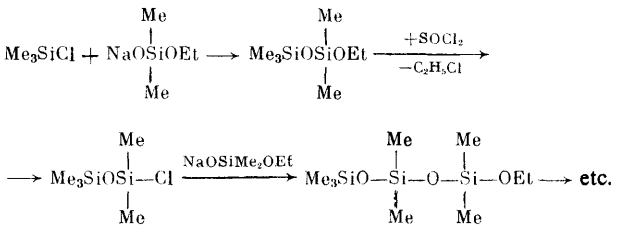
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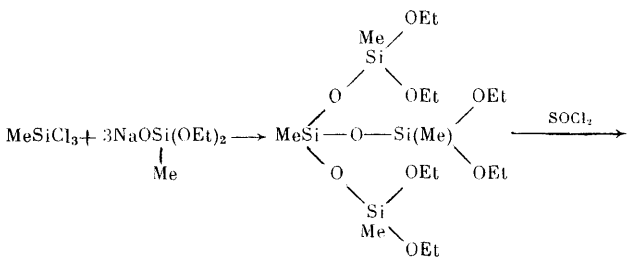
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Differences in the yields are explained by the different stabilities of the central, branching centres towards nucleophilic reagents. Further development of the process—conversion of the functional groups from the form B into C (in accordance with the general Scheme 2)—was carried out through replacement of the alkoxy groupings by chlorosilyl as in the scheme:

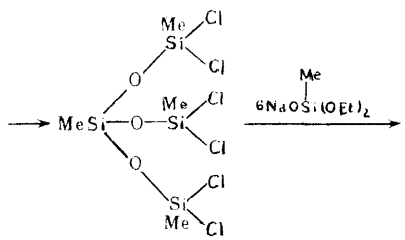
Scheme 4



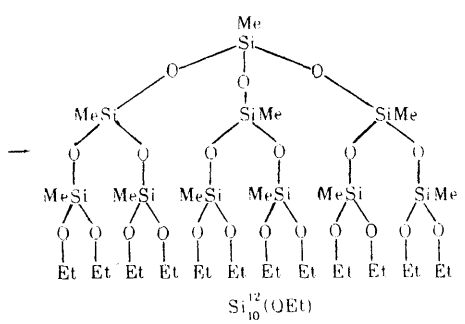
or by use of a trifunctional branching centre.



$Si_4^6(OEt)$



$Si_4^6(Cl)$



$Si_{10}^{12}(OEt)$

In the accepted designation of three-dimensionally growing oligomers the upper index shows the functionality of the oligomer, the lower index shows the number of silicon atoms in the structure of the oligomer, and the type of functional group is shown in brackets.

The high yields of first and second generation oligomers and the absence in the reaction mixture of products resulting from fission of the siloxane bond, show that the reaction conditions chosen were suitable. Since compounds with chlorosilyl groupings were already used in the first stage of reaction (by interaction with sodium-oxyorganoalkoxysilanes), then the process for obtaining second generation oligomers did not give rise to special difficulties. It was also found that the yield of the oligomer $Si_{10}^{12}(OEt)$, was significantly higher than the yield of $Si_4^6(OEt)$ and that this tendency was repeated for the conversion of $Si_{10}^{12}(OEt)$ to $Si_{22}^{24}(OEt)$, facts that may be

accounted for, apparently, by the characteristics of the structure of the synthesised oligomers and, in particular, the extensive screening of the siloxane skeleton by the surface functional groups. Thus, if the primary branching centre and the surface reaction centres are chemically identical, there is less possibility of fission of the siloxane bonds under the action of sodiumoxy-derivatives. Four generations of oligomer, $Si_4^6(OEt)$, $Si_{10}^{12}(OEt)$, $Si_{22}^{24}(OEt)$ and $Si_{46}^{48}(OEt)$ are reported,[22] providing indisputable evidence of correspondence with the cited Scheme 4 and the conditions for formation of three-dimensionally growing systems mentioned above. From Scheme 4 it is possible to see all stages of formation of the molecular structure by the use of methyltrichloro-silane as the branching centre and sodiumoxymethyldiethoxysilane as the basic reagent. The reaction of chain growth (accumulation of layers) proceeds by the interaction of sodiumoxy groupings with chlorosilane groupings at the branching centre, whilst the ethoxy groups act as protecting groups for the future reaction centres at which, after their conversion into the active form, a new "layer" in the structure of the growing molecule will be formed.

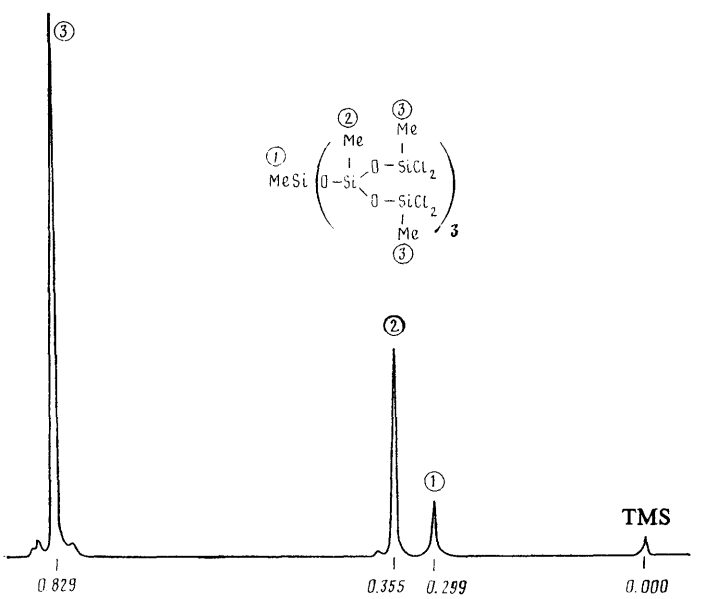
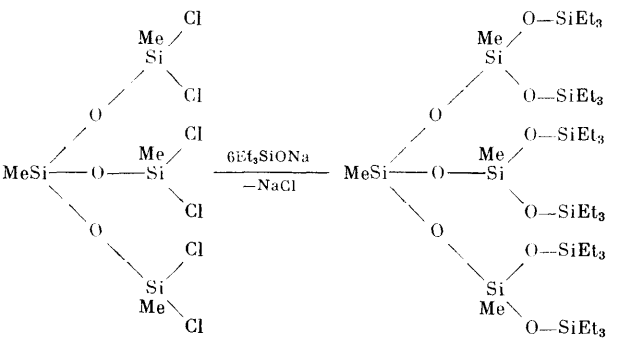


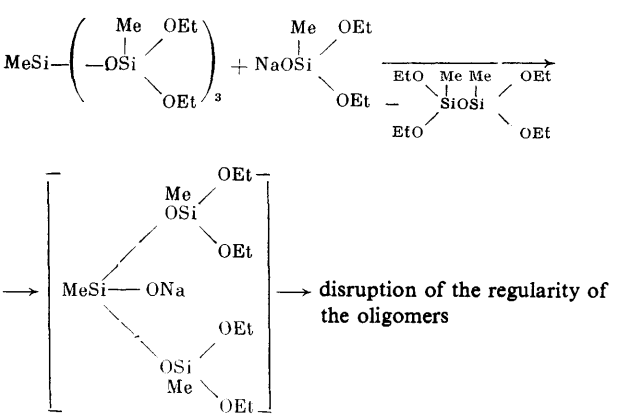
Figure 2. ^1H nmr spectrum of the oligomer $Si_{10}^{12}(Cl)$ in CCl_4 (spectrum recorded on Bruker WP-200 instrument).

The three-dimensionally growing oligomers are obtained as transparent mobile liquids. For identification of the synthesised oligomers a number of methods were used, including functional and elemental analysis, ^1H and ^{29}Si nmr spectroscopy, and high performance liquid chromatography (HPLC). In Fig. 2, the ^1H nmr spectrum of the oligomer $Si_{10}^{12}(Cl)$ is given as an example, showing well resolved signals for three species of methyl group attached to silicon in the central, first and second (external) layers. The integration ratio for the intensities of these signals (1 : 3 : 6) is in complete accordance with calculation. Still more informative is the ^{29}Si nmr spectrum. In particular, for the oligomer $Si_{10}^{12}(OEt)$, three signals are observed in the regions $\delta_1 = -67.91$, $\delta_2 = 67.44$, and $\delta_2 = 51.47$ ppm, corresponding to the central silicon atom and the atoms of silicon of the first and second layers.

At the same time, in the analysis of the oligomers that were obtained, account was taken of the specific character of the highly-functional and very reactive systems under investigation. Because of the high reactivity of chlorosilyl derivatives, the use of HPLC for confirmation of purity was preceded by an additional step involving blocking of the functional groups by triethylsilyl groups to give non-functional derivatives:

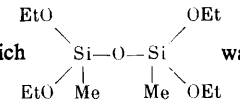


These non-functional derivatives of the three-dimensionally growing oligomers were studied by the method of HPLC and it was shown that the resolving ability of the apparatus, with a column efficiency of 24 000 theoretical plates, was sufficient for the separation of oligomers of the 1st, 2nd, 3rd and 4th generations. HPLC was used to confirm the purity of the standard obtained by Scheme 4 and also proved to be helpful in the selection of optimum reaction conditions for the basic synthetic scheme. The latter circumstance is especially important, as it is known that the siloxane bonds which form the skeleton are sensitive to both the nucleophilic reagent (sodiumoxy-organoalkoxysilane) and the electrophilic reagent (thionyl chloride) which are used at different stages of the synthesis. It was shown that to carry out the synthesis under non-optimum conditions can lead to disruption of the ordered structure of the oligomers as in the following scheme:



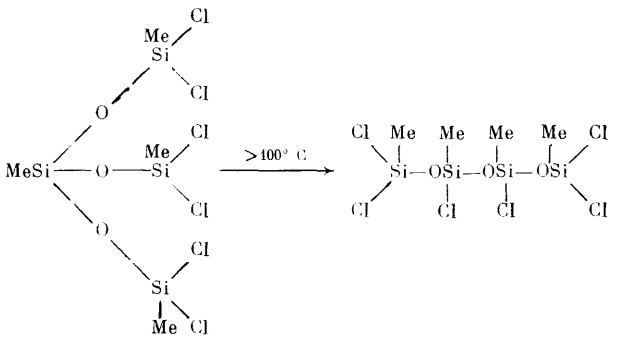
i.e. the fear that the siloxane skeleton of the oligomers may not be stable is not without foundation. Indeed, under certain conditions the fission of the grouping $\diagdown Si-OC \diagup$ by sodiumoxyorgano-alkoxysilanes can proceed quantitatively. Concerning fission of the

$\diagdown\!\!\diagup Si-O-Si\diagdown\!\!\diagup$, grouping, interaction of the sodiumoxy-derivative $NaOSiMe(OEt)_2$ with the oligomer $PhSi[OSiMe(OEt)_2]_3$, gave

products among which  was identified, showing

clearly that this type of interaction should also be borne in mind in the systems under investigation.

There are further experimental factors confirming the instability of the siloxane skeleton. Thus, for example, we have shown[24] that to heat oligomers which contain chlorosilyl functional groups above 100 °C is extremely undesirable, as it can lead to rearrangement.



However, in the presence of chlorosilyl groupings, the oligomer shows desirable stability both of the siloxane skeleton and of the molecule as a whole. It is sufficient to say that the oligomer $Si^{24}_{22}(OEt)$, which has a molecular mass of 2356, was distilled under vacuum without showing any tendency to rearrangement. A knowledge of these processes, of the temperature ranges at which they occur, and of their characteristics, ensures the possibility of accurate control of the formation of products. As a result, the majority of oligomers were made and characterised as individual chemical compounds. It can therefore be affirmed, that by carrying out the reactions under optimum conditions, the synthetic schemes shown can be realised without any perceptible side reactions.

V. Separate problems of synthesis of three-dimensionally growing siloxanes

In spite of considerable differences in methods of synthesis for three-dimensionally growing polyorganosiloxanes and their organic analogues, systems of the type under examination develop according to general and objective rules. It was therefore natural to consider the question of saturation of the surface layer by functional groups and the negative consequence of this phenomenon for regular growth of the molecule. We first encountered this in the course of the synthesis of three-dimensionally growing siloxanes, having found that at a definite stage in the progress of the synthesis, the characteristics of the products obtained began to change in a way that was not in accordance with previously observed tendencies. Thus, in Fig. 3, the relationship is given of refractive index, specific viscosity and density for three-dimensionally growing oligomers with ethoxy functional groups, to the ordinal number of the oligomer. It is easy to see that in all cases of change from oligomers of the 6th generation to those of the 7th, these curves show a break, which we believe to be associated with a loss of regularity in the oligomer, on account of arising steric difficulties. The same phenomenon was encountered but at an earlier stage in the blocking of functional oligomers. Thus in the case of the 4th generation oligomer, Si^{48}_{46}, we found that the number of blocked end groups which could be introduced did not correspond to that calculated theoretically. For this reason we do not have available the corresponding chromatograms, confirming the individuality of synthesised oligomers that contain more than 46 atoms of silicon. This earlier breach of the regularity of the system is explained, first of all, by the use of monomeric reagents, and it is not therefore surprising that the increase in the functionality of the oligomer quite quickly outstrips the increase of the surface at which they may be able to attach themselves.

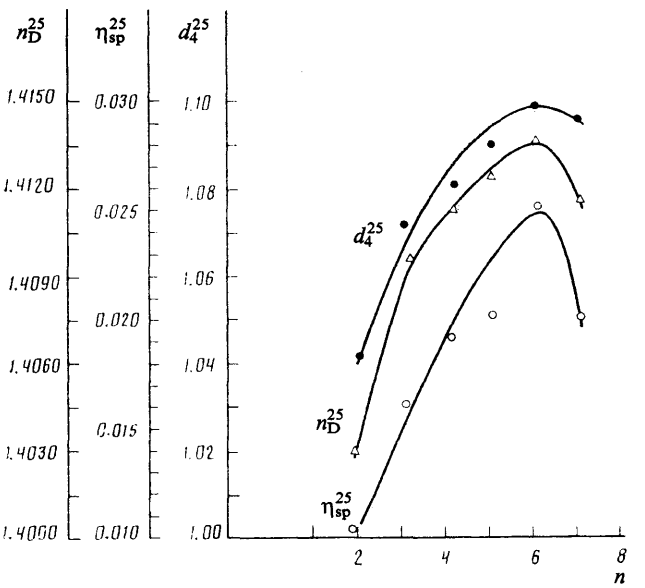


Figure 3. Relationship of density, (d_4^{25}), specific viscosity (η_{sp}^{25} for a 1% solution in toluene) and refractive index (n_D^{25}) for three-dimensionally growing polyethoxymethylsilsesquioxanes to the ordinal number of the oligomer in the homologous series.

The limit to the regular growth of dendrimers should not, however, be considered as an insurmountable problem but should rather stimulate efforts to overcome these difficulties in the field of molecular construction of such polymers. In principle this is possible. A mathematical correlation can be made between the length of the linear section of an oligomer and its functionality, for which steric difficulties on the synthetic pathway for oligomers of a definite size will not arise. There is also another way for solving this problem. In particular, we have shown that during accumulation of

a further layer of monomer, it is possible to use a structure which is different from that of the basic structure.[22]

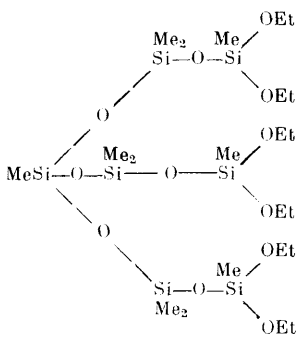
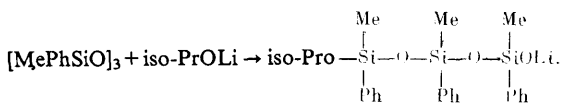


Table 1. Properties of blocked oligomers.

Unit blocked	Blocking group	t_{vit}, °C	η Pa s
$MeSiCl_3$	Et_3SiO-	−138.4	$2.5\cdot10^{-3}$
$Si_4^6(Cl)$	Et_3SiO-	−133.0	$2.5\cdot10^{-2}$
$Si_{10}^{12}(Cl)$	Et_3SiO-	−120.0	0.1
$Si_{10}^{12}(Cl)$	$Me_3SiOSiO-$ (Me, Me)	−110	–
$Si_{22}^{24}(Cl)$	Et_3SiO-	−101.0	6.5
$Si_{46}^{48}(Cl)$	$C_{10}H_{11}-$	−48.0	$2\cdot10^{-2}$
$Si_{46}^{48}(Cl)$	$(CF_3CH_2CH_2)_3SiO-$	−63.8	0.28
$Si_{46}^{48}(Cl)$	Me_3CO-	−85.0	–
$Si_{46}^{48}(Cl)$	$CH_2=CH-SiO-$ (Me, Me)	–	–

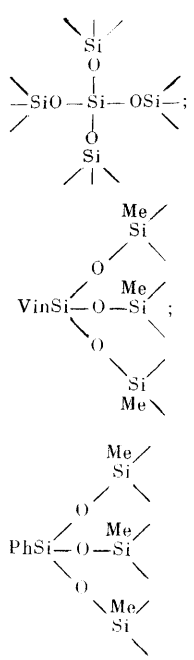
From the chemical formula given, it is seen that the use of a difunctional monomer leads to an increase in the size of the oligomer and consequently also, in the size of its surface, with preservation of the number of functional groups. Such an operation can be described as a distinct "thinning out" of the reaction centres, averting the onset of steric difficulties. Undoubtedly, the effectiveness of such a thinning out is proportional to the length of the linear section between the last branch in the structure and the functional groups. In such a scheme for the siloxane systems considered, there is the prospect of using individual oligomers, synthesised as follows.[25]



It is necessary at once to make the reservation, that the operation of "thinning out" of the functional groups is closely connected with a change in the intramolecular packing of the three-dimensionally growing molecules, and at present it is not clear whether such thinning out has any effect on the properties of the oligomer as a whole. The influence of the surface layer on the properties of the oligomer, especially in blocked oligomers, is considerable, since the blocking groups constitute 50% of the structure of three-dimensionally growing oligomers (out of the total number of monomeric units) and being concentrated in the surface have an independent significance.

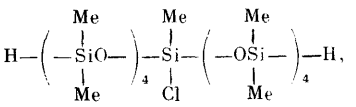
It appeared to be possible within fairly wide limits to change the intermolecular interaction of the oligomers by the use of different organic substituents at the atoms of silicon in the surface layer. For this purpose it was shown to be possible to use blocking compounds such as Me_3CONa, $Me_3SiOSiMe_2OH$, $(CF_3CH_2CH_2)_3SiONa$, and $C_{10}H_{11}MgBr$.[23] For illustration we can use the data in the Table 1, which shows oligomers having identical molecular skeletons but differing in the features of the surface layer as a direct consequence of the use of different blocking agents. From the data that are presented it is seen that both the viscosity of the oligomers and also their temperatures of vitrification vary widely.

The problem of molecular construction in such systems are not exhausted by a guarantee of the possibility of layered growth but require maximum flexibility of approach in order to control the form and density of intramolecular packing and also the quantitative and qualitative composition of the functional groups in the surface layer of the oligomer. Comparing the schemes for dendrimers with organic and inorganic skeletons, it can be noted that in both cases it is possible to use different initial branching centres. Thus Newkome[26] demonstrates tri- tetra- and hexa-functional branching centres for organic systems. For organosiloxane systems in the same way it is possible to use various compounds, for example;[22]

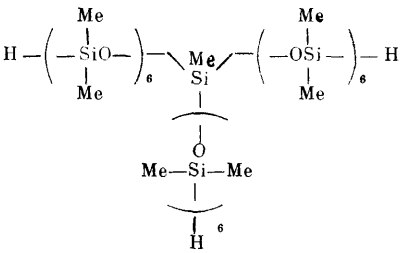


As regards the choice of reagents that meet the requirements for the use of general Scheme 2 for the construction of regular dendritic structures, it can be noted that the number of organosilicon monomers exceeds that of the organic analogues, although at the

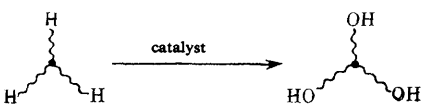
present time they are almost all of the same type. Organic reagents are notable for their diversity, making it possible to obtain amidoamino and polyoxyalkylenic oligomers, in addition to those based purely on carbon. Furthermore, it is clear, that in the use of siloxane systems both the process of building up of the layers, and the conversion of functional groups into the active form involve two reactions, whereas in the majority of organic systems that have been investigated, the conversion of functional groups into the active form requires four different chemical reactions.[6,26] More recently a short communication[27] has appeared on the synthesis of polyorganosiloxanes of the starburst type using a different functional basis and reagents of a larger size than were considered by us above. In this case, the following was taken as a particular reagent:



and as a branching centre:



Conversion of form B into form C was carried out according to the following scheme:



This example also shows that in the field of organosilicon polymers, three-dimensionally growing systems are not excluded and that the reagents which are used can themselves be diverse.

In conclusion let us refer to possible trends in the uses of three-dimensionally growing polyorganosiloxanes. Firstly they find application, as do the organic analogues,[2] as standards for HPLC, electron microscopy, and the calibration of membranes. There are prospective uses in biology and medicine for three-dimensionally growing polyorganosiloxanes as soluble polyfunctional matrices, with variable characteristics in the surface layer at which different biomolecular assemblages can be attached. There are also good prospects for the use of new polymers in the fields of microelectronics, conducting materials, and membrane separation technology, etc. However, in the course of making these new materials, still wider investigations will be necessary into the development of the necessary basic reagents, the properties of three-dimensionally growing polymers of different structure and composition, and new synthetic approaches to the control of structure and properties.

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