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Effect of Conditions of Synthesis on the Structure of Polyphenylsilsesquioxane Macromolecules

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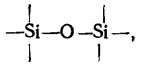
All data published up to 1973 on the hydrodynamic properties and molecular-weight parameters of organosilicon ladder polymers are surveyed. The reasons for the formation of polyphenylsilsesquioxane macromolecules of various structures are assessed. A list of 63 references is included.

Several investigations during recent years have shown that the polymerisation of compounds whose functionality exceeds two produces not three-dimensional cross-linked polymers but polymers having a two-strand linear structure[1-10]. Such systems have been termed *ladder polymers*.

The possibility of a ladder structure for several polymers was predicted by Berlin[11]. Carbon-chain ladder polymers can be obtained by the cyclisation of linear polymers, as well as by the polymerisation of polyfunctional monomers[12-14]. Among known ladder polymers are cyclopentadiene[15,16] and cyclobutadiene[17]. Aromatic ladder polymers can be obtained by the photopolymerisation of acetylenes[18]. The synthesis of ladder polyquinoxalines has been reported[19]. Ladder polymers are known comprising oxygen- and nitrogen-containing heterocycles[20,21], as well as inorganic ladder compounds[22-24]. This is by no means a complete list of work on ladder polymers belonging to various classes of compounds. Broad surveys of this topic have appeared[25,26].

Ladder polymers are of considerable interest in connection with their valuable properties due to their structural peculiarities, notably the two-strand structure of the macromolecules. Such polymers possess solubility, enhanced thermal stability, strength, and inertness towards corrosive media.

Organosilicon polymers, polyphenylsilsesquioxanes, also form ladder polymers[27-30]. Silsesquioxanes are compounds in which every silicon atom is attached to three oxygen atoms and an organic substituent: $[RSiO_{1.5}]_n$. The polycondensation of trifunctional compounds in which the functional groups are equally reactive should produce a disordered, random network[31]. However, because the functional groups differ in reactivity or the latter may vary during the reaction, and also owing to steric factors, ordered structures may be formed. The tendency of the monomer to form rings may also produce a certain ordering. Siloxanes possess the unique ability of varying the bond angle



so that the chain is very flexible, and rings varying in structure and size may be formed. The disordered, irregular structures appearing in the early stages of the reaction are able to rearrange into regular structures only when condensation occurs in the presence of a catalyst which will rupture



bonds. In the hydrolysis and subsequent condensation of phenyltrichlorosilane and other organotrichlorosilanes in the presence of alkali, for example, cagelike silsesquioxanes were isolated, as well as polymers to which a two-strand ladder structure was ascribed[28-30,32]. The main factor governing the formation of silsesquioxanes having a particular structure is the nature of the substituent attached to the silicon atom, as well as the conditions of synthesis.

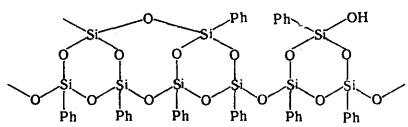


Figure 1. Structure of polyphenylsiloxane macromolecules suggested by Andrianov[2].

The first publication in which condensation of the hydrolysis products of phenyltrichlorosilane was assumed to involve the formation of internal rings, was due to Andrianov[2]. In his suggested structure (Fig. 1) every silicon atom is attached to three oxygen atoms and an organic substituent. Every unit corresponds to the formula $RSiO_{1.5}$.

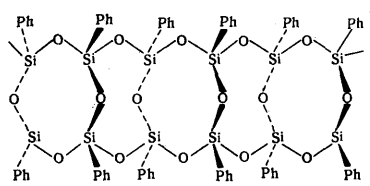


Figure 2. Structure of polyphenylsiloxane macromolecules suggested by Brown[6].

A polymer of general formula $(RSiO_{1.5})_x$ was first obtained by Brown[6] by the equilibrium condensation of hydrolysis products of phenyltrichlorosilane, and was assigned the structure shown in Fig. 2. Brown established that the main conditions governing the formation of a cyclolinear polymer during anionic polymerisation are temperature and solute concentration. Condensation of

the hydrolysis products in dilute solution (up to 5%) yields mainly oligomers of low molecular weight having a cagelike structure[28,29]. Those illustrated in Fig. 3 were isolated as pure crystals[30]. However, the cagelike compounds may also have an incompletely cyclised, defect structure (Fig. 3*b*). In the concentration range 5–7% polymers of low molecular weight (prepolymers) are formed at equilibrium. When equilibrium is established in concentrated (85–95%) solutions at 250°C, a soluble cyclolinear (ladder) polymer of molecular weight exceeding 4×10^6 is formed, to which Brown assigns a *cis*-syndiotactic structure[30]. At 100% concentration a gel is formed. With variation in solution concentration ladder polymers pass into cagelike polymers and conversely (Fig. 4).

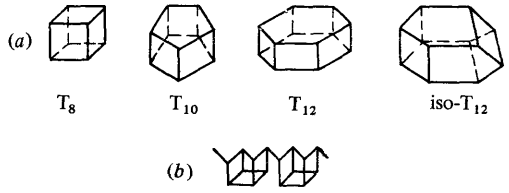


Figure 3. Cagelike compounds[28,29].

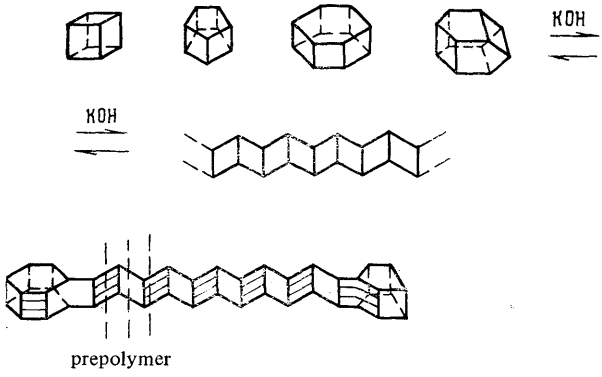


Figure 4. Conversion of cagelike compounds into a ladder polymer (and conversely).

Such ability to pass from cagelike compounds into ladder polymers was responsible for their technical application[31,33,34]. Raising the temperature of the solution converts a lower polyphenylsiloxane coating into a polymer of high molecular weight. The work of Andrianov and his colleagues supports Brown's hypothesis that cagelike compounds may pass into a ladder polymer[35,36] (Fig. 5).

The preparation of a polyphenylsiloxane of high molecular weight by condensing the hydrolysis products of phenyltrichlorosilane in the presence of caustic potash at 250°C was described[27], and the influence of the medium on the mechanical properties, molecular weight, and structure of the polymer macromolecules was studied. The higher the boiling point of the solvent, the larger the molecular weight attained by the polymer. The nature of the solvent had no significant effect on the structure of the polymer macromolecules. A mechanism of formation of a cyclolinear polymer by internal cyclisation at hydroxy-groups was suggested[37].

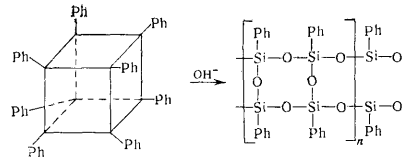


Figure 5. Transition of cagelike compounds into a ladder polymer[35,36].

Brown's conclusion that polyphenylsiloxanes obtained from hydrolysis products of phenyltrichlorosilane had a *cis*-syndiotactic structure was based on a study of the properties of solutions, X-ray examination, infrared and ultraviolet spectra, and calculation of bond angles[30]. The infrared spectra of a cyclolinear polyphenylsiloxane give a well resolved doublet in the region of 1045 and 1155 cm^{-1}. Ultraviolet spectra agree well with the suggested cyclolinear structure[29], and X-ray structural analysis shows that a chain segment comprises four units[7,30]. However, only strictly determined conditions of synthesis can yield a regular polyphenylsiloxane with a two-strand ladder structure.

The use of Stuart–Briegleb models to examine the possible formation of cyclolinear polyphenylsiloxanes suggested[32] that a regular structure could result only from the reaction of rings whose silicon atoms lay in the same plane, with either *cis*- or *trans*-hydroxyls. Analysis showed that only a *cis*-structure in the boat form, when the 1,2-hydroxyls of one monomer condense with the 3,4-hydroxyls of another monomer, can lead to the formation of a *cis*-isotactic polyphenylsiloxane having a double-chain structure. The silicon atoms then lie in one plane, with bridging oxygen atoms on one side, and chain oxygen atoms on the other side of the plane (Fig. 6).

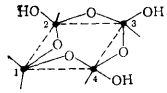
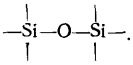


Figure 6. *cis*-Structure of T_4 in the chair form[32].

With bulky substituents (e.g. phenyl), however, the



angles are distorted. It has therefore been assumed[32] that an isotactic structure with phenyl substituents attached to the silicon atom will be formed if it is postulated that the chain can be screwed along its axis.

The hypothetical condensation of *trans*-T_4† in the chair form by condensation of the 1,2-hydroxyls of one ring with the 4,3-hydroxyls of another ring should produce a *cis*-syndiotactic ladder structure (Fig. 7). Condensation in other possible ways should produce non-cyclolinear structures, e.g. branched and network. Among such types of ring condensation are those of *cis*-T_4 in the chair form, of *trans*-T_4 in the chair form (1,2-hydroxyls of one ring with the 3,4-hydroxyls of another ring), and *trans*-T_4 in the boat form [32].

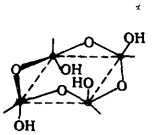


Figure 7. *trans*-Structure of T_4 in the chair form [32].

Thus all the above discussion shows that formation of a cyclolinear structure (Fig. 2) is possible but requires the observance of definite reaction conditions. In cases in which existence of *trans*-T_4 in the boat form is not energetically more favourable than other conformations, the formation of non-cyclolinear structures is possible.

The mechanism of the formation of ladder polymers is complicated and dependent on the conditions of synthesis. Formation of a double-chain structure can probably involve either condensation at free hydroxy-groups of a lower prepolymer [37] or a stage of rearrangement of cagelike compounds [38]. Frey [39] put forward the hypothesis that the resulting polyphenylsiloxane is highly ordered only in individual polycyclic segments distributed at random along the chain.

Table 1. Optical anisotropy and rigidity of various polyphenylsiloxanes (PPS).

Polymer	$10^{-5}M$	$10^{25}(\alpha_1-\alpha_2)$, cm^3	A, Å	S
PPS-1	1.0	—1230	136	54
PPS-2	0.65	—1060	84	34
PPS-3	3.7	—1800	178	71

A double-chain structure should lead to enhanced rigidity of the polymer macromolecules. This is confirmed by several studies both of the properties of polyphenylsiloxane solutions [32,37–47] and of the physicochemical properties of such polymers in the condensed state [7,38,48–52]. High chain rigidity of polyphenylsiloxane obtained by treating hydrolysis products of phenyltrichlorosilane with potassium hydroxide in various solvents was shown by an investigation of its behaviour in solution. The calculated anisotropy of polarisability of a segment $\alpha_1 - \alpha_2$ was compared with experimental values [37,40]. It was shown [53] that $\alpha_1 - \alpha_2 = +4.8 \times 10^{-25}$ cm^3 for linear polydimethylsiloxane (a single-chain polymer). The introduction of 10% of phenyl groups into the flexible polydimethylsiloxane macromolecule diminished the flexibility only slightly, although the sign changed from positive to negative: -2.4×10^{-25} cm^3. Double-chain polyphenylsiloxane was found [40] to have $\alpha_1 - \alpha_2 = -1740 \times 10^{-25}$ cm^3.

Tsvetkov et al. have shown [46] that polyphenylsiloxanes obtained by different workers possess different rigidity parameters (Table 1). According to the results of various workers [7,35,42,44,46,54] the parameter a in the Mark–Kuhn–Houwink (MKH) equation $[\eta] = KM^a$, which is connected with the flexibility of the polymer chain, varied from 0.70 to 1.50 depending on the number of fractions into which the polymer had been separated (Table 2).

Table 2. Parameters a and K in the MKH equation for polyphenylsiloxanes.

Equation	Solvent	T, °C	No. of fractions	Ref.
$[\eta] = 1.305 \cdot 10^{-7} \cdot M^{1.29}$				
$[\eta] = 1.93 \cdot 10^{-4} \cdot M^{0.63}$	benzene	20	6—10	37
$[\eta] = 1.47 \cdot 10^{-5} \cdot M^{0.916}$	benzene	25	18	
$[\eta] = 1.33 \cdot 10^{-5} \cdot M^{0.92}$	chloroform	25		
$[\eta] = 1.77 \cdot 10^{-5} \cdot M^{0.895}$	toluene	37		42
$[\eta] = 0.58 \cdot 10^{-5} \cdot M^{0.978}$	*o*-xylene	65		
$[\eta] = 1.568 \cdot 10^{-5} \cdot M^{0.897}$	θ-solvent (ethylene dichloride)	50.5		
	benzene		13	
$[\eta] = 2.38 \cdot 10^{-3} \cdot M^{0.9}$	bromoform			41
	benzene + butyl acetate (6:4)	21		
$[\eta] = 7.7 \cdot 10^{-4} \cdot M^{0.9}$	benzene		13	41
$[\eta] = 7.6 \cdot 10^{-3} \cdot M^{0.7}$	benzene			
$[\eta] = 1.3 \cdot 10^{-4} \cdot M^{1.09}$	benzene			
$[\eta] = 2.1 \cdot 10^{-5} \cdot M^{0.88}$	benzene		10	
$[\eta] = 4.898 \cdot 10^{-4} \cdot M^{0.94}$	benzene		13	44
$[\eta] = 4.624 \cdot 10^{-3} \cdot M^{0.74}$	bromoform			
$[\eta] = 1.09 \cdot 10^{-8} \cdot M^{1.48}$				
$[\eta] = 2.74 \cdot 10^{-7} \cdot M^{1.16}$	benzene	20	26	55, 56
$[\eta] = 1.25 \cdot 10^{-8} \cdot M^{1.47}$	benzene	40		
$[\eta] = 1.54 \cdot 10^{-6} \cdot M^{1.12}$	benzene	20	25	
$[\eta] = 2.66 \cdot 10^{-7} \cdot M^{1.24}$				55, 56
$[\eta] = 6.95 \cdot 10^{-7} \cdot M^{1.17}$	benzene	40		
$[\eta] = 5.41 \cdot 10^{-4} \cdot M^{0.72}$	benzene	20	25	
$[\eta] = 5.03 \cdot 10^{-4} \cdot M^{1.32}$				
$[\eta] = 8.72 \cdot 10^{-4} \cdot M^{0.68}$	benzene	25		55, 56
$[\eta] = 5.60 \cdot 10^{-8} \cdot M^{1.31}$				
$[\eta] = 5.06 \cdot 10^{-8} \cdot M^{1.32}$	benzene	40		

It must be borne in mind that, if the macromolecules possess enhanced rigidity, the intrinsic viscosity is almost independent of the solvent used for its determination and of the temperature of measurement. Its value remains almost unchanged throughout the range of molecular-weight determination in benzene, bromoform, and the θ-solvent [42,46,55]. Similar constancy of intrinsic viscosity has been observed with variation in the temperature of a polyphenylsiloxane solution. This indicated that volume (long-range) effects had no appreciable influence on the dimensions of macromolecules in solution and that the high value of the exponent a in the MKH equation was due, not to volume effects, but to the enhanced skeletal rigidity of the macromolecules [57,58].

Differences in the parameter a are therefore probably due to the presence in the polyphenylsiloxane of macromolecules not having a ladder structure. As shown above, a possible cause of the simultaneous formation of different polymer structures might be the appearance of various

† [For the "T" nomenclature cf.Ref. 29 (Ed. of Translation)].

types of polycyclic prepolymers in the initial stage of condensation[28,29,32]. Another possible reason might be increased probability of detachment of phenyl groups when reaction has proceeded for a long time, with the formation of more complicated structures, in particular strongly branched macromolecules of higher molecular weight (microgels). Guyot et al.[59] have shown that the degradation of polyphenylsiloxane consists not in depolymerisation with rupture of the two-strand siloxane bond but in the detachment of phenyl groups with the formation of benzene. This explains the improved thermal stability of the polyphenylsiloxane, since removal of a chain fragment from a ladder macromolecule—in contrast to a single-chain macromolecule—requires several simultaneous ruptures. In addition, the parameter a may vary with the proportion of defects in the macromolecules, which may be due to the presence of residual, unchanged hydroxy-groups. However, the number of such groups in polyphenylsiloxane macromolecules is so small that no method of physicochemical analysis has yet been able to accomplish their quantitative determination.

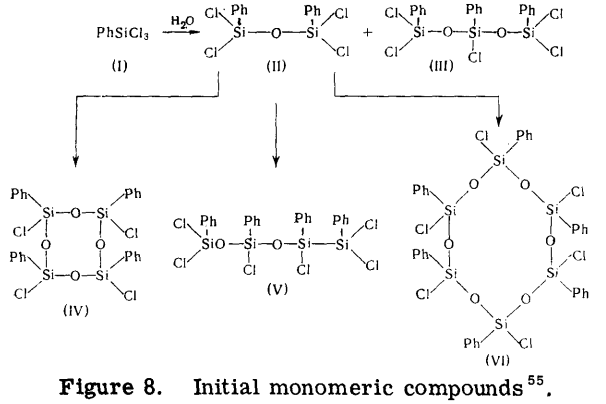


Figure 8. Initial monomeric compounds[55].

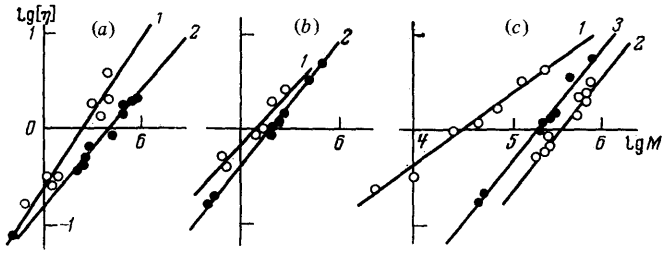


Figure 9. Dependence of $\lg[\eta]$ on $\lg M$ for polyphenylsiloxanes obtained from different monomers[55].

To examine the role of the initial monomeric compounds in forming polyphenylsiloxanes having a ladder structure, the compounds (I)–(IV) (Fig. 8)‡ were each subjected to hydrolysis under the same conditions with subsequent polycondensation and polymerisation in the presence of potassium hydroxide. All the polyphenylsiloxane fractions were found to be identical in elementary composition, which corresponded to the chain unit $(C_6H_5SiO_{1.5})_4$, but they differed considerably in hydrodynamic properties. Fig. 9 shows that the polymers consisted of two types of macromolecules differing in structure or in proportion of structural defects. All the polyphenylsiloxanes synthesised gave two straight lines when $\lg[\eta]$ was plotted against $\lg M$, with different values of the parameter a in the MKH equation: i.e. the precipitant–solvent system chosen[55] enabled for the first time the separation of polyphenylsiloxanes both according to molecular weight and according to structure (Table 2). Intrinsic viscosities obtained for the polymers $PPS(III_{,3})$ and $PPS(IV_{,3})$ (polyphenylsiloxanes produced by polymerising the monomers (III) and (IV) (Fig. 8) for 3 h), as well as the parameters a, were closely similar to the characteristic viscosities and the value $a = 1.29$ found[37] for polyphenylsiloxanes resulting from compound (I).

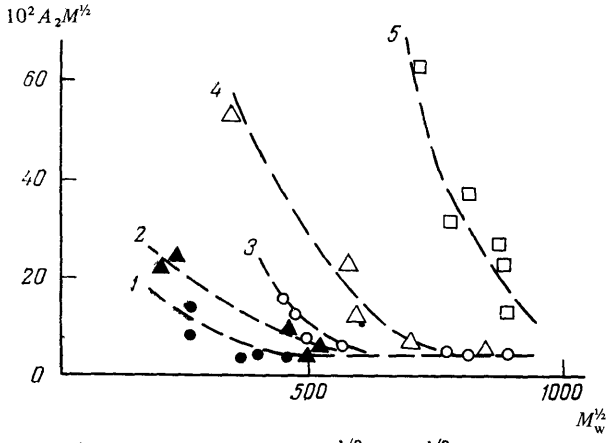


Figure 10. Dependence of $A_2M^{1/2}$ on $M^{1/2}$ for polyphenylsiloxanes with various values of a in the MKH equation: 1) 1.12; 2) 1.24; 3) 1.32; 4) 1.48; 5) 1.49.

Fig. 10 shows that polyphenylsiloxanes obtained from products of the partial hydrolysis of phenyltrichlorosilane and having different values of a in the MKH equation correspond to different variations of $A_2M^{1/2}$ with $M^{1/2}$ (where A_2 is the second virial coefficient)[56,60]. This dependence is non-linear even at quite high molecular weights, which suggests that the macromolecular chains are of finite length in this region and hence are rigid. The graph of $A_2M^{1/2}$ against $M^{1/2}$ moves to the right with increase in a. Calculations of the dimensions of the macromolecules based on several theories showed[61–63] that the rigidity parameter $[\overline{h_0^2}/M]^{1/2}$ increases with a (where $[\overline{h_0^2}]^{1/2}$ is the mean square distance between the ends of a macromolecular chain, and M is the molecular weight).

Thus a polyphenylsiloxane comprising both macromolecules having a two-strand ladder structure and a different, defective structure can be obtained depending on the nature of the initial monomer and the conditions of synthesis.

‡ [Compounds (V) and (VI) are not mentioned in the Russian text (Ed. of Translation)].

The structural defectiveness may be due to the detachment of phenyl groups when reaction continues for a long time. Cleavage of the silicon–oxygen bond under these conditions is less probable. Unchanged hydroxy-groups may also disturb the regularity of the ladder structure.

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