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"On the Influence of Side Chains in Molecules of Liquid Polymethylsiloxanes on their Properties," A.A.Zhdanov, K.A. Andrianov, T.S.Vaksheeva, N.A.Polikanin and M.M.Levitskiy, Plastic Materials, (No. 5) 19 (1964)

The properties of polymethylphenylsiloxanes are usually dependent on the number of phenyl radicals in the polymer chains (1)(2). The influence of position in these polymeric chains, of the attached phenyl radicals and their side chains on the properties of the polyorganosiloxanes has so far not been examined, even in the latest reports. There remains obscure the question of what determines the properties of these polymers. The position in the polymeric chains of the attached phenyl radicals or the overall ratio of  $\text{CH}_3/\text{C}_6\text{H}_5$  is shown (reflected) in the properties of the polymethylphenylsiloxanes, with certain definite ratios of  $\text{CH}_3/\text{C}_6\text{H}_5$  and closely paralleling molecular weights- one chain built up of dimethyl- and methylphenylsiloxy units and another of dimethyl- and diphenylsiloxy units.

The answer to this question can be found in the synthesis of appropriate polymers and a comparison of their properties which was the object of this work.

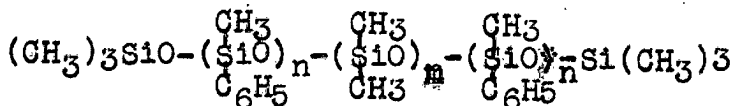
1. Polymers with regular ratios of dimethyl- and methylphenylsiloxy units were prepared by the reaction of disodium derivatives of organosilanol and diorganodichlorosilanes which set up elemental chains by union (of the silanes) with loss of ONa, terminated by trimethylchlorosilane (3)(4).

2. Polymers, not having regulated chain composition, were prepared by the hydrolytic condensation of a mixture of dimethyldichlorosilane, methylphenyldichlorosilane and trimethylchlorosilane in acid at about 50° to 60° C. with subsequent action of 90%  $\text{H}_2\text{SO}_4$ . By this method there was synthesized a group of polymers of different relationships of methylphenyl- and dimethylsiloxy groups giving a mixture of homopolymers of average ratio  $\text{CH}_3/\text{C}_6\text{H}_5$  as appropriate to the task in hand (5)(6). Polymers not so regulated as to chains of dimethyl- and diphenylsiloxy units were prepared by the hydrolytic condensation of dimethyldichlorosilane, diphenyldichlorosilane and trimethylchlorosilane with  $\text{H}_2\text{SO}_4$  at 100° C. with subsequent chain-grouping by the action of 90%  $\text{H}_2\text{SO}_4$ .

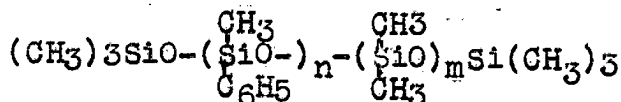
Characteristics of the Polymers

No.	CH <sub>3</sub> /C <sub>6</sub> H <sub>5</sub>	Mol Wt	n <sub>D</sub> <sup>20</sup>	Yield, cc			Temp. of Congealing °C	Formula of Product
				20°	100°	200°		
18	2.32	1712	1.4980	398.2	36.62	12.20	-39°	I n = 2 x 5, m = 1 x 4 1 x 6      2 x 7 1 x 4      4 x 5 4 x 3      1 x 2
17	6.80	1988	1.4600	65.2	13.40	4.45	-73°	
15	9.80	2096	1.4482	63.0	16.50	6.00	-88°	
19	1.83	1905	1.5231	462.5	57.30	14.20	-32°	
1	2.52	1750	1.5051	285.6	27.78	12.17	-40°	II n = 10, m = 5 6      12 4      16 24      3
2	6.69	2119	1.4613	96.4	18.56	9.12	-68°	
7	9.26	2185	1.4500	66.4	15.97	5.44	-91°	
6	1.88	1915	1.5240	551.4	39.06	11.24	-24°	
12	2.80	1659	1.5051	590.0	45.27	10.5	-37°	III n = 4, m = 9 3      15 2      18 6      9
13	6.32	2018	1.4671	157.6	26.78	7.52	-67°	
11	9.68	2162	1.4482	98.1	18.26	6.84	-82°	
10	1.86	1907	1.5215	1337.0	62.34	11.76	-20°	

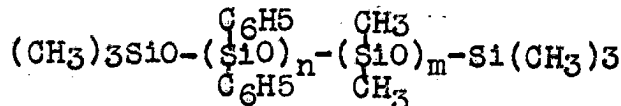
Formula I



Formula II



Formula III



TRANSLATOR'S NOTE: The chief value of these data, with the verbal explanations following (of somewhat confusing value) lies in their relationship to brittle points or congealing points. Thus, in terms of American F temperature readings, these become:

Sample No. 18	-38.2° F	1	-40.0°	12	-34.6°
17	-99.4°	2	-90.4°	13	-88.6°
15	-126.4°	7	-131.8°	11	-115.6°
19	-25.6°	6	-11.2°	10	-4.0°

Any of the above values below -100° F are of considerable interest.

Characteristic polymers were isolated from the mixtures by distillation at 1 mm-2 mm and at temperatures upto 240°, as shown in the tables. The formulae of these polymers were assigned on the basis of analyses.

### Results of the Study of the Properties of Liquid Polymethylphenylsiloxanes

A study and comparison follow of the detailed properties of the polymers.

1. Evaporation experiments (1 g.) of a thin layer (0.5 mm) at 250° and 300° C. in air.

As shown in Figure 1, it will be seen that evaporation of the polymers is practically constant and does not depend on a regular chain structure but only on the sum total of a number of methyl and phenyl radicals. A certain rise in evaporation of the irregular polymer with high diphenyl content (as sample No. 12) and No. 10,  $\text{CH}_3/\text{C}_6\text{H}_5 = 2.8$  and 1.6) at 250° C. is explained by the volatility of certain components of the polymeric mixture and not by a lowering of the thermooxidative resistance.

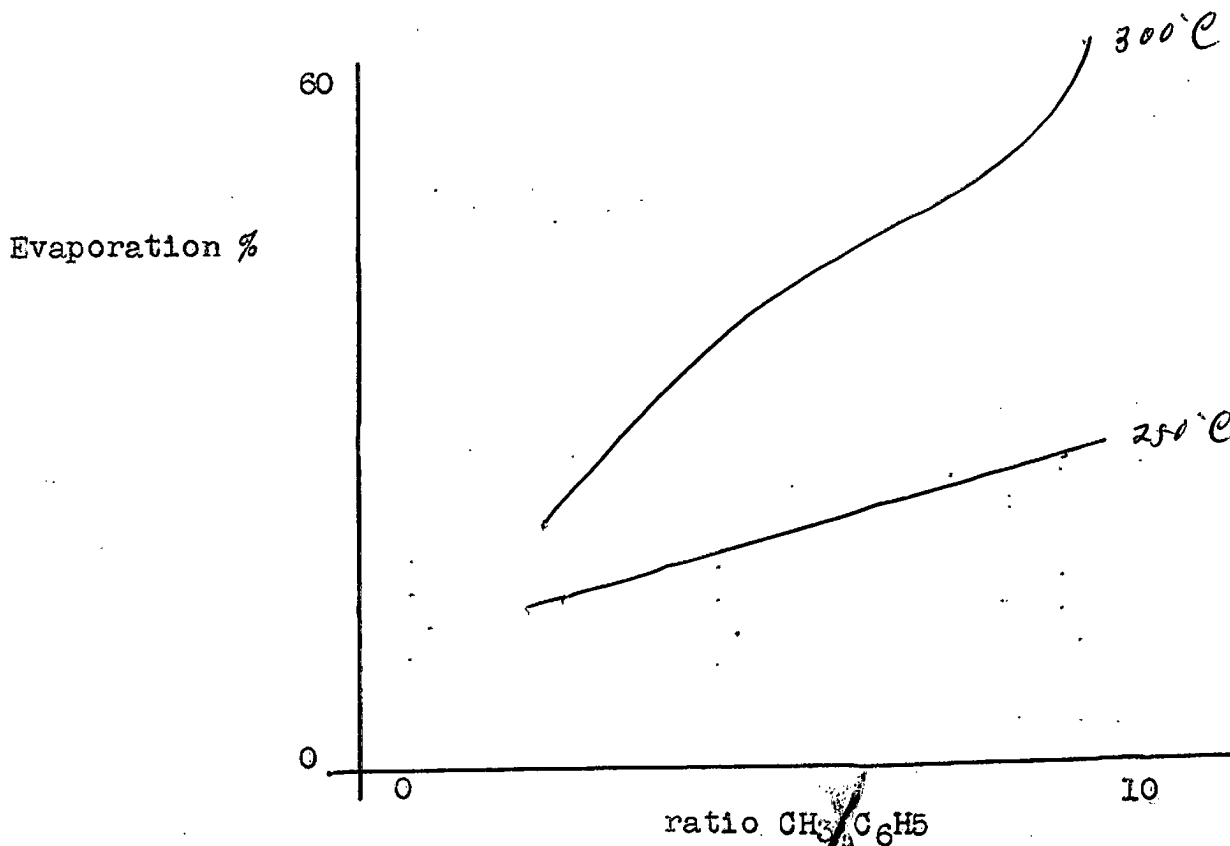


Figure 1, comment: points from all compounds are near or equally near these curves.

2. Thermooxidative Resistance at 250° C. by passage across a volume of polymer of 100 cc. of air at constant speed under controlled cooling, is shown in Figure 2, is also shown to be practically constant for the polymers with given chains of dimethyl- and methylphenylsiloxy units, but related to molecular weight and the  $\text{CH}_3/\text{C}_6\text{H}_5$  ratio.

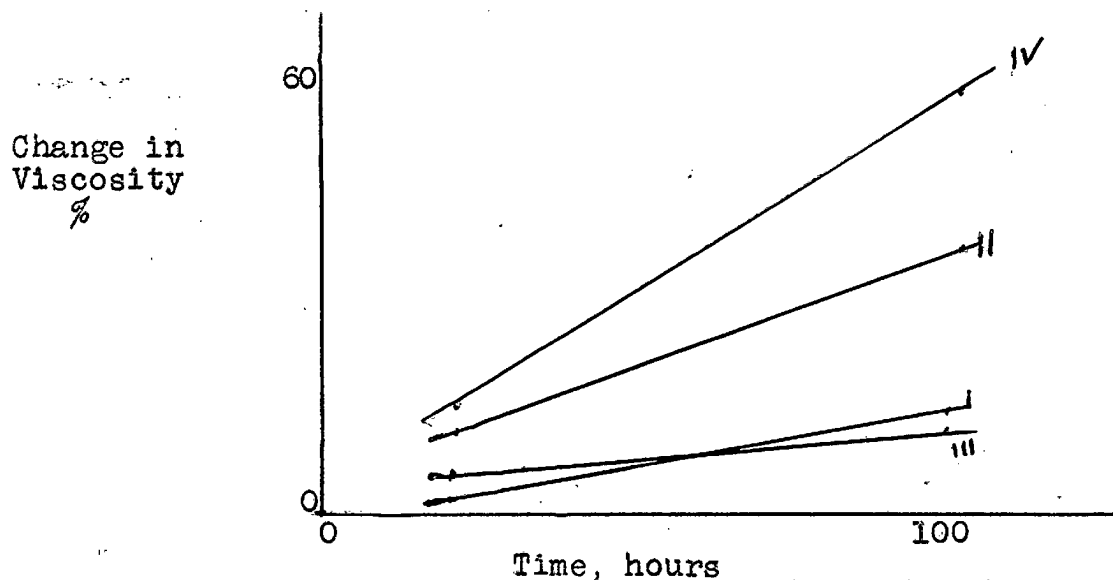


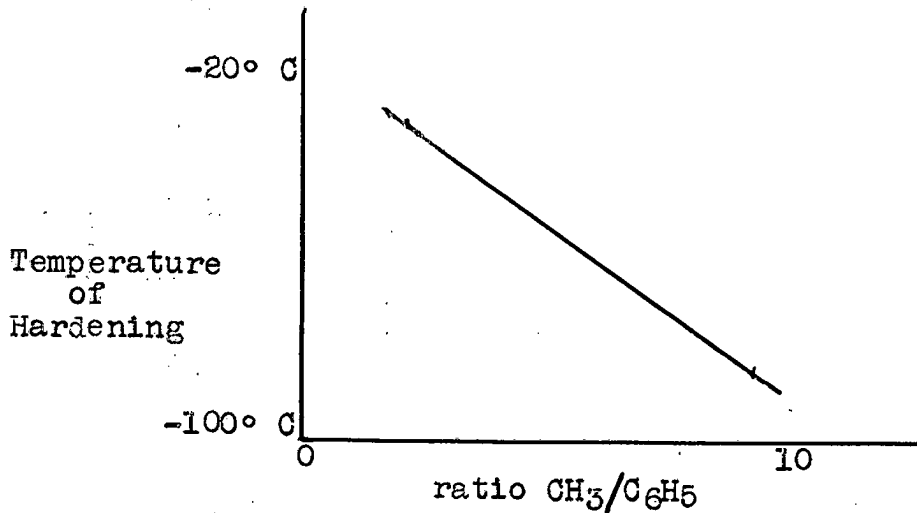
Figure 2; Change in viscosity of polymethylphenylsiloxy chains with calculated chain structure during thermooxidative treatment at 250° C. Ratios  $\text{CH}_3/\text{C}_6\text{H}_5$ : I 1.83-1.88, II 2.32-2.80, III 6.32-6.80, IV 9.26-9.68

From Figure 2, two points may be brought out (among them) that viscosity of polymers with diphenylsiloxy units in the chain and a  $\text{CH}_3/\text{C}_6\text{H}_5$  of 9.68 (curve 4) change in the thermooxidative process to a considerably smaller value than the viscosity of the polymers (without thermooxidation).

In all polymers with a ratio  $\text{CH}_3/\text{C}_6\text{H}_5$  of 6.32-6.80 (curve 3) (Figure 2), the viscosity after thermooxidation change is less than with polymers with a larger phenyl content. The reason for this phenomenon will be examined later.

3. Thermosetting of the polymers (Figure 3) shows straight line relationships in correlation with their methyl and phenyl radical contents. Regular ratios of dimethyl- and methylphenylsiloxy units to diphenylsiloxy units in the chain are practically of no influence in this category, as is shown by substitution of methylphenylsiloxy units by diphenylsiloxy units in two cases of the four. Polymers with maximum and minimum maintained diphenylsiloxy units are more adaptable for thermosetting at 10° C. and above as compared with other polymers.

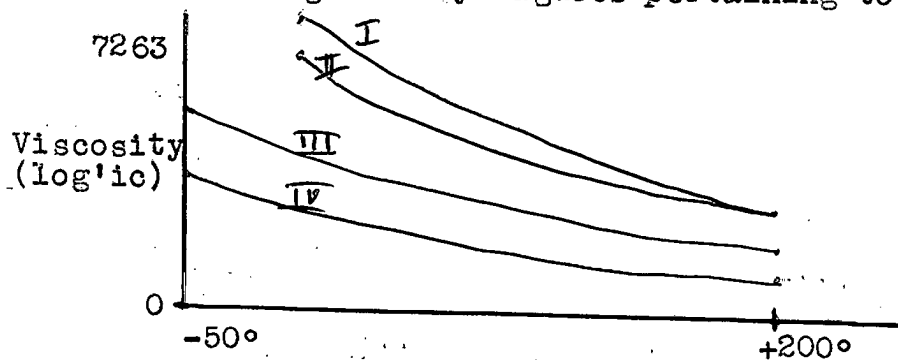
4. The Relation between Viscosity and Temperature (Figure 4) in polymers with definite (regular) and irregular ratios of dimethyl and methylphenylsiloxy units in the chain is identical as far as any definite significance to viscosity is concerned. The greatest slope is with a small amount of phenyl radicals (Curve 4),  $\text{CH}_3/\text{C}_6\text{H}_5$  9.26-9.68.



(points pertaining to different compounds show almost no deviation from the line)

Figure 3 Relation Between Temperature of Hardening of the Polymethylphenylsioxanes with Different Structural Ratios  $\text{CH}_3/\text{C}_6\text{H}_5$

Polymers with diphenylsiloxy units show high absolute viscosities (Figure 4 and Table) and the relation to temperature is reflected somewhat by the large banking curves in the region of low temperatures (the amounts of viscosities of these polymers is marked in Figure 4 by figures pertaining to the numbered curves).



I  $\text{CH}_3/\text{C}_6\text{H}_5$  1.83-1.88, II 2.32-2.80, III 6.32-6.80, IV 9.26-9.68  
Figure 4

At temperatures above  $+150^{\circ}\text{C}$ . the value of the viscosity and the character of the curve of all (of these) polymers are practically the same.

The indices of refraction,  $n_D^{20}$  (table) of comparable polymers are close (for four polymers of practically the same molecular weight they are identical).

#### Discussion of Results

The fundamental properties of liquid  $\alpha, \omega$ -hexamethylpolymethylphenylsiloxanes with regular and irregular ratios of dimethyl- and methylphenylsiloxyl units in the chain are practically the same in (the realm of) viscosity with respect to the number of methyl radicals and the number of phenyls and of comparable molecular weights. These properties depend in the main on the size of the ratio  $\text{CH}_3/\text{C}_6\text{H}_5$  and are not dependent on the structure of the main molecular chain.

Notable above is a divergence from this conformity for some polymers with diphenylsiloxyl units (change in viscosity with thermooxidation, thermosetting, dependence of viscosity on temperature and absolute viscosity in the region of low temperatures) entailing moderately large intermolecular force interaction between phenyl radicals of different chains of molecules relatively, one with the other. This is particularly noticeable in the viscosity of the polymers at  $20^{\circ}$ ,  $100^{\circ}$  and  $200^{\circ}$  (table). At  $200^{\circ}\text{C}$ ., the difference in viscosity of all comparable polymers is not noticeable from a practicable point of view but at  $20^{\circ}$  their viscosities differ by 1.5 to 2.0 fold. There is a probability, at lower temperatures (below  $50^{\circ}\text{C}$ .) that structural viscosity controls viscosity and is conditioned on the dimensions of the molecule while at a rise in temperature, structural viscosity has little influence.

These phenomena apparently tie in with the fact that polymers with a ratio  $\text{CH}_3/\text{C}_6\text{H}_5$  of 6 show significantly less change on thermooxidation (Figure 2) than those polymers with a high phenyl content.

In certain cases, there would be a lesser effect on structural viscosity from a change in the thermooxidative process as far as concerns phenyl radicals, arranged over a considerable distance from each other in the polymeric chain with (consequent) little interaction. However, there is a certain probability attached to the shielding of methyl radicals during thermooxidation.

It remains to examine the cause of the small influence of the structure of the molecular chain of liquid polymethylphenylsiloxanes on their properties.

When we speak of distinctive properties of regular and irregular polymers, we have in mind that side groups are present in definite organic content with regard to the main polymeric chain. This stipulates a close packing of the chain, a good opportunity for the formation of crystals or of some sort of crystallization and as a consequence a rise in temperature of softening and mechanical hardening of the regular polymers. Thus the condition is possible only with polymers with long chains which may not freely move (rotate) relatively.

We are considering polymers with comparable short chains (molecular weights around 2000), liquids at a wide range of temperatures. With these cases there is an opportunity for great freedom of lateral rotation of groups and sections of the chain and even transference or shift of chains, relatively, with resulting heat fluctuations. In liquid short chain polymers it could be neither physical positions of lateral groups in space near the main chain nor stability of the crystalline formations involving neighboring chains (two chains) nor the stability of the chains as set up. The molecular chain of the polymer could easily be rolled up as a spiral or straightened out again to take some (other) desired configuration.

It is natural that with these liquid polymeric systems in which the dimensions of the molecule include numerically equal or nearly equal groups and atoms of comparable molecules of the same type, but with groups arranged in the different chains and having freedom of rotation and slight displacement of the organic groups, that these properties reach some stage of equilibrium. In the overall, the mixture in which this is observed properly makes use of a fairly homogeneous volume if the forces are uniformly steady, elastic and uniformly diffused in intermolecular space, for example using acids, freely run in at uniform speed to a given density onto a packed uniform chain.

The form then, of short chain liquid polymers with uniform chain composition and molecular weights, with regular chain structures, is apparently without greatly varying influence on its properties- this is confirmed by the present work.

The difference in properties in these systems could be related, as seen, apparently, to temperature variations or to the limits set by brittle points.



Some exceptions from these rules are observed in the cases of polymers with diphenylsiloxy units; with bonds so arranged with two phenyl radicals on one atom of silicon, the probability is that the intermolecular interaction between several groups in the chain is increased. In these cases it could be that there would appear, in addition, a strong, "intermingling" of aromatic groups with the result that the symmetry of two sequences of groups would lead to an increase in the energy of intermolecular interaction.

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