Liquid Methylpolysiloxane[1] Systems

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An equilibrium rearrangement of methylpolysiloxanes has been shown to occur upon contact of these materials with concentrated sulfuric acid.[2] The viscosities of the polymeric mixtures, or silicone oils, resulting from the equilibrium rearrangement of octamethylcyclotetrasiloxane with small amounts of hexamethyldisiloxane were found to be dependent in a direct and reproducible manner upon the average functionality of the system.

This paper is concerned with the introduction of trifunctional units derived from the hydrolysis of methyltrichlorosilane into these methylpolysiloxane systems, and its effect upon their properties. The molecular size distribution in these polymers and its relation to their physical properties are considered from both the theoretical and experimental viewpoints.

The statistical distribution of molecular sizes is derived for the equilibrated methylpolysiloxanes following the theories of Flory and Stockmayer, which are based upon the assumptions that all reacting groups are equivalent and that no cyclic molecules are formed. This distribution agrees with that found in experimental siloxane polymers only within a limited range of viscosity and composition. The molecular size distribution in the more viscous polysiloxanes and in those containing a large proportion of trifunctional units is complicated by the presence of cyclic and polycyclic molecules which cannot be treated adequately by a simple theory of statistical size distribution.

Functionality

If some of the bifunctional units, $(CH_3)_2SiO$, in an equilibrated methylsiloxane polymer are

(1) For a discussion of organosilicon nomenclature, see R. O. Sauer, *J. Chem. Ed.*, **21**, 303 (1944).

(2) Winton Patnode and Donald F. Wilcock, THIS JOURNAL, **68**, 358 (1946).

replaced by equimolar amounts of trifunctional units, $CH_3SiO_{3/2}$, and monofunctional units, $(CH_3)_3SiO_{1/2}$, the average functionality remains unchanged. However, the physical properties of the resultant polymeric mixture are altered. The viscosity and the melting range are lowered, the viscosity–temperature coefficient[3] is increased, and the proportion of low molecular weight material is greater when this replacement has been made. The density remains substantially unchanged. These changes in physical properties are the results of a high degree of branching as well as of considerable cyclization in the polymeric mixtures containing trifunctional units.

In order to facilitate discussion, the abbreviations **M**, **D**, and **T** will be used to indicate the polymer units:

Unit	Function-ality	Composition	Unit weight
M	1	$(CH_3)_3SiO_{1/2}$	81.16
D	2	$(CH_3)_2SiO$	74.13
T	3	$CH_3SiO_{3/2}$	67.09

Thus, hexamethyldisiloxane is M_2, octamethylcyclotetrasiloxane is D_4, and the linear polymers arising from their equilibration are M_2D_{x-2}, where x is the number of units. The mole fractions of **M**, **D** and **T** units in a polymer will be denoted by m, d and t.

In a system comprising **M**, **D** and **T** units the average functionality, F, is related to the mole fractions by the equation

$$F = 3t + 2d + m = 2 - (m - t) = 2 - \alpha \quad (1)$$

The constant $\alpha = (m - t)$ expresses the mole fraction of **M** units available for growth termination (assuming complete absence of cyclic material). In the polymer system comprising **M**, **D** and **T** units, the nature of the polymeric mixture

(3) D. F. Wilcock, *Mech. Eng.*, p. 739 (1944); p. 202 (1945).

is dependent not only upon the average function-ality but also upon the relative proportions of **D** and **T** units. These proportions may be held con-stant within a series of compositions where F is varied, and such a series will be characterized by a constant τ, defined as

$$\tau = t/(d + t)$$

Preparation of Fluid Polymers

Several series of polymers were prepared, each series being characterized by a constant value of τ. The oils in each series were prepared by equi-librating various amounts of M_2 with a stock oil containing **D** and **T** units in the desired propor-tions. The stock oil for each series was obtained by the hydrolysis of a weighed mixture of methyl-chlorosilanes. Over the range $0 < \tau < 0.11$ these stock oils contained only **D** and **T** units. Over the range $0.11 < \tau \leq 1$ they contained equimolar amounts of **M** and **T** units in order to avoid gela-tion upon hydrolysis.

The stock oil for the $\tau = 0.103$ series was prepared from 3481 g. (27.0 moles) of dimethyldichlorosilane containing 0.3 mole per cent. of methyltrichlorosilane, mixed with 448 g. (3.00 moles) of methyltrichlorosilane. This mix-ture was hydrolyzed in batches by running 605 cc. slowly beneath the surface of 2650 cc. of water over a period of half an hour. The water was stirred rapidly and main-tained between 10 and 15° by an ice-bath. After washing once with 600 cc. of water, the hydrolyzate was centrifuged until clear, and filtered. It was then neutral, as tested by shaking with neutral ether, distilled water and methyl orange.
The stock oil for the $\tau = 0$ series was the compound D_4, prepared in the following manner. Dimethyldichloro-silane was hydrolyzed as described above, and the hydrol-yzate was then distilled through a 15 inch column, one half inch in inside diameter, packed with one sixteenth inch stainless steel helices. The fraction boiling between 173 and 177° was retained and carefully redistilled through the same column at high reflux ratio. The D_4 fraction boiling at 175.7–175.9° (uncor.) at 758 mm. was separated.

The compositions for equilibration were pre-pared by weighing the desired proportions of stock oil and M_2 on an analytical balance. Equili-bration was carried out by adding 4% by volume of concentrated sulfuric acid and shaking on a reciprocating shaker for twenty-four to forty-eight hours. Preliminary experiments indicated that constant viscosity was attained in sixteen hours. Equilibration was stopped by the addi-tion of 20% by volume of water followed by shak-

TABLE I
PROPERTIES OF EQUILIBRATED POLYSILOXANES

$\alpha =$ $(m - t)$	Kinematic viscosity η_{100} η_{210} (Centistokes)		VTC	Density at 20°	Per cent. volatile (7 days at 150°)
		$\tau = 0$			
0.055	25.9	10.8	0.58	0.960	..
.0393	36.0	14.7	.59	...	13.4
.032	49.7	20.6	.59	.965	..
.0135	184	73.2	.60	...	11.4
.0079	459	185	.60	...	11.0
.0049	1620	646	.60	...	10.6
.000	(Gelled upon hydrolysis)				

		$\tau = 0.025$			
.134	8.8	3.8	.57	.942	36.0
.036	35.4	14.4	.59	.965	13.5
.021	61.0	24.7	.595	...	11.8
.018	72.0	28.7	.60	...	12.7
.008	149	55.8	.62	...	11.1
.005	223	85.2	.62	.973	10.5
.004	432	164	.62	...	11.5
.002	387	156	.60	...	12.5
		$\tau = 0.050$			
.100	12.2	5.36	.56		...
.040	27.5	11.0	.60		24.3
.015	61.0	24.4	.60		17.7
.0080	108	42.3	.61		15.2
.0026	365	129	.65		14.3
.0014	253	96.3	.62		14.1
.0000	(Gelled upon hydrolysis)				
		$\tau = 0.103$			
.54	1.21	0.702	.42		97.9
.102	10.6	4.6	.57		...
.040	26.9	11.0	.59		28.5
.020	43.0	17.2	.60		23.7
.015	51.3	20.3	.60		22.9
.010	69.3	27.0	.61		21.6
.0049	88.9	35.5	.60		20.7
.0021	115	44.7	.61		19.5
.0008	127	49.5	.61		
.0000	(Gelled upon hydrolysis)				
— .010	(Gelled before hydrolysis)				
		$\tau = 0.397$			
.0625	14.6	6.35	.57		40.4
.0178	36.3	13.6	.63		33.3
.0083	37.3	13.4	.64	0.982	33.8
.0037	59.7	21.9	.63	.984	31.0
		$\tau = 0.516$			
.0241	25.0	9.35	.63	.970	
.0083	36.8	13.4	.64	.976	
.0068	41.6	14.7	.65	.982	
.0061	41.1	14.7	.64	.978	
		$\tau = 0.697$			
.0591	9.18	3.61	.61		46.5
.0195	14.8	5.34	.64		38.2
.0087	16.0	5.59	.65	0.985	39.1
.0056	22.7	7.70	.66	.988	34.0
		$\tau = 1.000$			
.360	2.44	1.20	.51		69.9
.150	6.06	2.49	.59		...
.074	9.00	3.31	.63	0.958	63.0
.040	9.02	3.73	.59	.962	65.0
.036	12.1	4.04	.67	.966	...
.030	11.8	4.0	.66	...	54.5
.0127	14.7	4.97	.66	.972	...
.011	17.5	5.34	.70	.989	50.5
.0098	15.4	5.19	.66	.974	...
.0094	14.8	4.93	.67	.974	...
.0062	15.2	4.73	.69	.985	48.1
— .001	(Gelled)				

ing for an additional hour. The acid was centrifuged from the equilibrated polymer, which was then dried and neutralized with anhydrous potassium carbonate and filtered.

A typical oil with the constants $\tau = 0$, $\alpha = 0.0135$, was prepared by weighing by difference on an analytical balance 0.530 g. (0.00327 mole) of M_2 into 35.453 g. (0.1196 mole) of D_4 in a two-ounce bottle. The bottle was capped during the final weighing to prevent evaporation of M_2. The two components were mixed by shaking the bottle and then transferred to a four ounce bottle for equilibration. After 1.5 cc. of concentrated sulfuric acid had been added, the bottle was capped quickly and placed in a shaker for equilibration.

The compositions and properties of the equilibrated polymers are given in Table I. Several compositions which did not yield liquid polymers are included. Some gelled during equilibration, while others, with lower average functionalities, did not gel until the siloxane–sulfate esters were hydrolyzed at the end of the equilibration period. The kinematic viscosities were determined in modified Ostwald pipet viscometers at 100 and 210°F. The viscosity–temperature coefficients[3] (VTC) are calculated from the relation

$$VTC = (\eta_{100} - \eta_{210})/\eta_{100} \qquad (2)$$

The per cent. volatiles were determined in a ventilated oven at 150°, by exposing 2 g. of the liquid polymer in a 10-cc. beaker, enclosed in a 25-cc. beaker to minimize error due to creepage. The major portion of the volatile materials was lost during the first few hours after which the rate of loss became very small. Results are reported for a 7-day period.

Determination of Molecular Size Distributions.[4]—The molecular size distribution in a number of equilibrated siloxane polymers was determined by careful fractional distillation, for it was of great interest as a check on the theoretical distribution. The very low viscosity polymers were analyzed directly by fractional distillation of a 300 g. charge through a packed column similar to that described for the purification of D_4. In order to analyze the more viscous polymers, the volatile material was removed from a large quantity of polymer by stripping. This volatile material was then fractionally distilled to determine the amounts of the individual compounds.

At the normal distillation pressures the boiling points of the cyclic and linear compounds alternate[5] so that the compounds are recovered in the order M_2, M_2D, D_4, M_2D_2, D_5, M_2D_3, etc. The intermediate fractions between flats contain only two compounds, which have widely different average functionalities, so that determination of the average functionality by the specific refraction method[6] permits accurate assignment of the intermediate fractions to the proper compounds. Where no cyclic compounds are present, the differences in average functionality between the

(4) Data in this section added April, 1946, in revision of original paper.

(5) D. F. Wilcock, THIS JOURNAL, **68**, 691 (1946).

(6) R. O. Sauer, ibid., **68**, 954 (1946).

shorter linear compounds, M_2D_{x-2}, are sufficient to warrant use of this type of analysis.

The results obtained on three low viscosity polymers, with τ equal to zero, 0.10 and 1.0, are given in Table II. The calculated values will be discussed later. In analysis IIC it was not possible to resolve the compounds boiling higher than M_3T.

TABLE II

ANALYSIS OF LOW VISCOSITY POLYMERS

Compd.	Weight per cent.	
	Found	Calcd.[a]
A. $\alpha = 0.670$, $\tau = 0$		
M_2	31.4	34.8
M_2D	24.9	25.1
M_2D_2	16.1	16.4
M_2D_3	12.2	10.1
M_2D_4	5.6	6.0
M_3D_5	2.6	3.4
B. $\alpha = 0.54$, $\tau = 0.10$		
M_2	24.4	23.0
M_2D	18.1	17.3
M_2D_2 and M_3T	13.1	12.7
C. $\alpha = 0.504$, $\tau = 1.00$		
M_2	49.5	37.8
M_3T	5.8	12.0

[a] See discussion of molecular size distribution, equation (26).

The analysis of a polymer of 33 centistokes viscosity will be described in some detail: 16,505 g. was stripped to a temperature of 225° at a pressure of 0.1 mm. yielding 2712 g. of distillate. This was separated roughly into the following fractions

Boiling range, °C.	Pressure, mm.	Weight, g.
175	760	326
175–176	760	215
176–200	760	193
90–150	20	759
150–200	20	477
Residue	. . .	742

These fractions were redistilled in turn, yielding the fractions summarized in Table III. Each intermediate cut was analyzed and allocated as shown to the after cut of the lower boiling compound and the fore cut of the higher boiling compound. Since the linear and branched molecules containing the same number of units have identical molecular weights and almost identical boiling points, no separation was attempted, and the proportions given in Tables IIB and III for linear compounds include any branched molecules present, e. g., the entry for M_2D_2 includes the small amount of M_3T also present.

An analysis of the D_4 content of a number of polymers is summarized in Table IV.

Viscosity and Constitution

The definite relationship that exists between the viscosities of the equilibrated siloxane polymers

TABLE III

ANALYSIS OF 33 CENTISTOKE POLYMER

($\alpha = 0.0305$, $\tau = 0.066$)

Compd.	From fore-cut	Weight, grams Center cut	From after-cut	Total	Weight per cent. Found	Calcd.[a]
M_2	5.8	25.3	2.0	33.1	0.20	0.45
D_3	..	1.1	..	1.1	.01	0
M_2D	8.2	81.0	7.5	96.7	.59	0.57
D_4	2.5	418	27.1	447.6	2.71	0
M_2D_2	18.9	99.2	15.0	133.1	0.81	0.65
D_5	15.9	244.7	36.9	297.5	1.80	0
M_2D_3	18.8	112.0	18.2	149.0	0.90	0.70
D_6	10.8	90.0	15.4	116.2	.70	0
M_2D_4	10.3	129.3	5.0	144.6	.87	0.72
D_7	48.7	...	19.5	68.2	.41	0
M_2D_5	10.4	121.8	15.6	147.8	.89	0.74
D_1	16.2	...	38.9	55.1	.33	0
M_2D_6	12.5	108.4	24.6	145.5	.88	0.74

[a] See discussion of molecular size distribution, equation (26).

TABLE IV

D_4 CONTENT OF EQUILIBRATED POLYMERS

Viscosity at 100°F., centistokes	Composition τ	α	m/d	Weight % (D_4)
1.0	0	0.670	2.03	<0.5
1.2	.10	.54	1.54	<0.5
33	.066	.0305	0.106	2.7
78	.062	.0075	.075	3.3
104	0	.0195	.020	4.6

and their molar composition is illustrated by the data in Table I. This relationship is more clearly defined by the curves in Fig. 1 showing log viscosity as a function of log α. Each curve is characterized by a constant value of τ. The curve for $\tau = 0$ has been drawn through the points representing the pure compounds M_2 to $M_2D_9^{5.7}$ (open circles), and is a straight line represented by the equation

$$\log \eta_{100} = -0.272 - 1.301 \log \alpha \qquad (3)$$

The viscosities of the equilibrated polymers for which $\tau = 0$ (solid circles) deviate somewhat from this relation at higher viscosities. The curves for polymers for which $\tau > 0$ deviate more markedly from equation (3), the magnitude of the deviation increasing as the value of τ is increased. Likewise for any given value of τ the magnitude of the deviation becomes greater as α becomes smaller. It has been found that this family of curves may be adequately represented by the following relation

$$\log \eta_{100} = -0.272 - 1.301 \log (\alpha + k) \qquad (4)$$

in which k is an empirical function of τ with the values shown in Table V. The curves in Fig. 1 were drawn using equation (4) with the values of k indicated in Table V.

The constant α is directly related to the average functionality by equation (1), so that a comparison of polymers at constant α is equivalent to a

(7) C. B. Hurd, THIS JOURNAL, 68, 364 (1946).

comparison at constant F. Such a comparison, made from Fig. 1, shows that the introduction of T units into the polymer at constant F greatly reduces the viscosity. This behavior is reflected in the increase in the value of k as τ is increased.

TABLE V

VALUES OF k IN EQUATION (4)

τ	k
0	−0.003
0.025	+0.004
.050	.007
.103	.014
.397	.023
.516	.029
.697	.057
1.00	.065

Molecular Size Distribution

One of the most interesting results of recent polymer research has been Flory's observation[8] that the viscosity of a molten polymer is a function of its weight average molecular weight. His most convincing evidence for the truth of this relationship was the ability to predict the viscosity of a mixture of polymers from the weight average molecular weight of the mixture and the M_w vs. viscosity curve. In order to investigate the applicability of this relationship to siloxane polymers, the statistical relations derived by Flory[8,9,10] for condensation polymers, and extended by Stockmayer[11,12] to the general case for polymers containing groups of any functionality, have been applied to the equilibrated siloxane polymers. These polymers offer unusually felicitous conditions for statistical investigation because not only can their behavior with respect to the M_w vs. viscosity relation be determined, but the proportions of a large number of the lower molecular weight components can be determined directly by fractional distillation.

The desired relations can be obtained from Stockmayer's generalized theory[12] for the case of general cross-linking in branched polymers by making the appropriate substitutions. Since this method is somewhat obscure, and since the weight average molecular weight rather than the weight average molecular size is desired, a very brief derivation is given for the case of polymers built up from mono-, di- and trifunctional units. Stockmayer[11] has treated the case of difunctional and polyfunctional units.

It must be borne in mind that two assumptions are involved in these derivations, namely:

(a) All unreacted functional groups are considered to have an equal probability of reacting, regardless of the size of the molecular fragment to which they are attached.

(8) P. J. Flory, ibid., 62, 1057 (1940).

(9) P. J. Flory, ibid., 58, 1877 (1936).

(10) P. J. Flory, ibid., 64, 2205 (1942).

(11) W. H. Stockmayer, J. Chem. Phys., 11, 45 (1943).

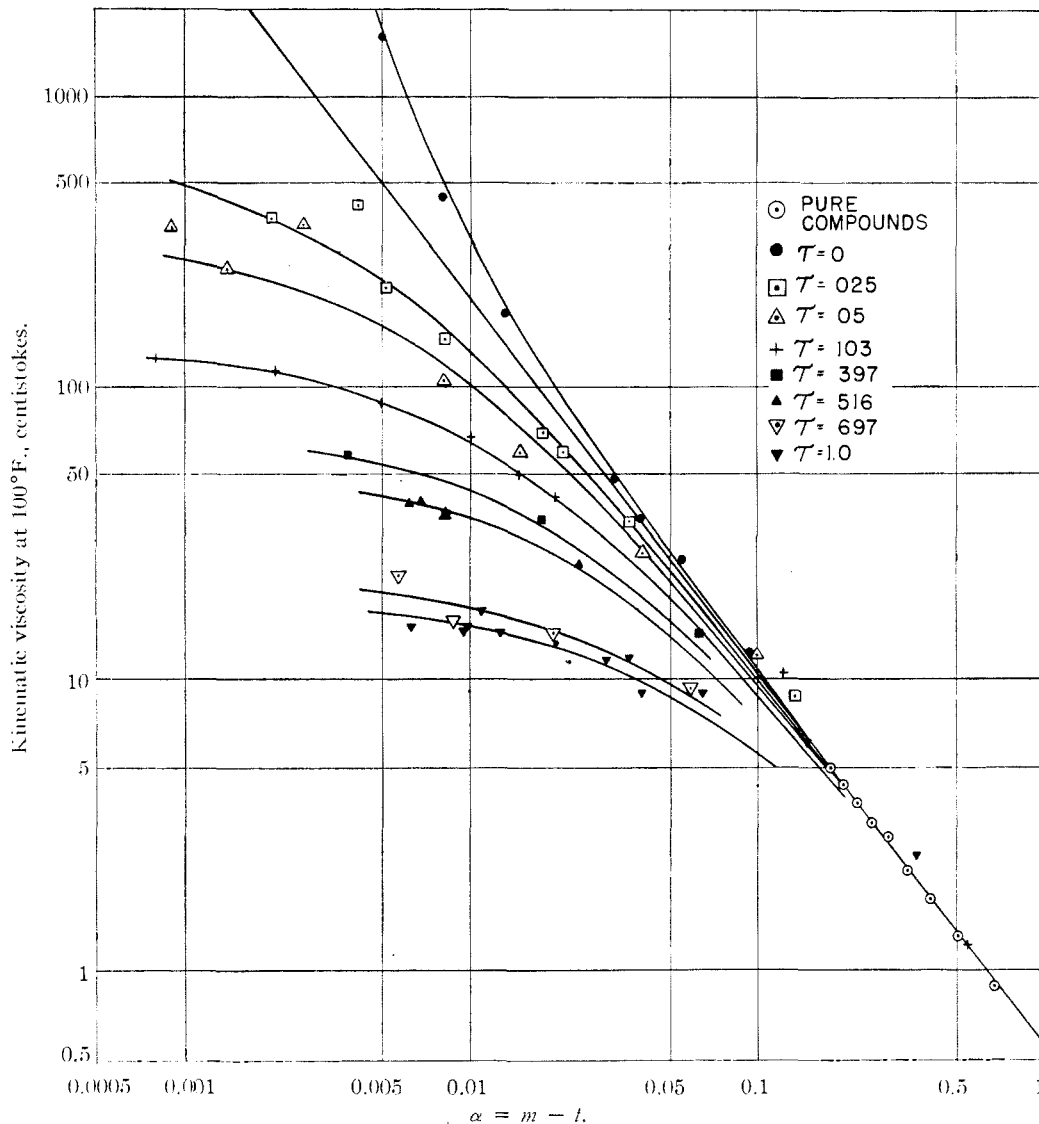(12) W. H. Stockmayer, ibid., 12, 125 (1944).

Fig. 1.

(b) No cyclic or ringed structures are formed during the equilibrium rearrangement. This assumption appears to be strictly true only for siloxane polymers of low viscosity and when the proportion of trifunctional units is small.

The generalized formula for non-cyclic siloxane molecules is

$$\mathbf{M}_{i+2}\mathbf{D}_{x-2i-2}\mathbf{T}_i$$

where x is the total number of units per molecule. Let

M be the number of $\mathbf{M}$ units
D be the number of $\mathbf{D}$ units
T be the number of $\mathbf{T}$ units
N be the number of molecules
N_{xi} be the number of molecules containing x units, i of which are $\mathbf{T}$ units
n_{xi} be the mole fraction, N_{xi}/N
W_{xi} be the weight fraction of molecules containing x units, i of which are $\mathbf{T}$ units
M_{w} be the weight average molecular weight

The boundary conditions are that the number of molecules is

$$N = \sum_{x=2}^{\infty} \sum_{i=0} N_{xi} = \frac{M - T}{2} \qquad (5)$$

and the number of $\mathbf{D}$ and $\mathbf{T}$ units are

$$\sum_{x=2}^{\infty} \sum_{i=0} (x - 2i - 2)N_{xi} = D \qquad (6)$$

$$\sum_{x=2}^{\infty} \sum_{i=0} iN_{xi} = T \qquad (7)$$

The number of ways of obtaining a given distribution is given by

$$\Omega = M!\, D!\, T! \prod_{x,i} \left[\frac{w_{xi}}{(i+2)!\,(x-2i-2)!\,i!} \right]^{N_{xi}} \frac{1}{N_{xi}!} \qquad (8)$$

where w_{xi} is the number of ways of forming an x,

i-mer from x units, i of which are **T** units and $(i + 2)$ are **M** units.

The distribution of greatest probability, obtained by maximizing (8) is

$$N_{xi} = \frac{A w_{xi} \xi^{i+2} \eta^{x-2i-2} \gamma^i}{(i + 2)! (x - 2i - 2)! i!} \quad (9)$$

where A, ξ, η and γ are Lagrangian multipliers. Remembering that the extent of reaction is unity, w_{xi} can be shown to be equal to

$$w_{xi} = 2^{x-2i-2} 3^i (x - 2)! \quad (10)$$

Combining (9) and (10)

$$N_{xi} = \frac{B(x - 2)! (2\eta)^{x-2i-2} (3\beta)^i}{(i + 2)! (x - 2i - 2)! i!} \quad (11)$$

where $B = \xi^2 A$, and $\beta = \xi\gamma$.

B, η and β are obtained by substituting (11) in (5), (6) and (7) and carrying out the summations. The results are

$$D = \frac{\eta B}{(1 - 2\eta)^2 (1 - \delta)^2} \quad (12)$$

$$T = \frac{B\delta}{3(1 - 2\eta)(1 - \delta)^2} \quad (13)$$

$$\frac{M - T}{2} = \frac{B}{1 - 2\eta}\left[\frac{1}{2} + \frac{\delta(2 - 3\delta)}{\delta(1 - \delta)^2}\right] \quad (14)$$

where δ is given by the lowest positive real root of the equation

$$\delta(1 - \delta) = \frac{3\beta}{(1 - 2\eta)^2} \quad (15)$$

Algebraic solution of equations (12) to (15) gives

$$B = \frac{M^2}{M + 2D + 3T} = p^2(M + 2D + 3T) \quad (16)$$

$$2\eta = \frac{2D}{M + 2D + 3T} = q \quad (17)$$

$$3\beta = \left(\frac{M}{M + 2D + 3T}\right)\left(\frac{3T}{M + 2D + 3T}\right) = pr \quad (18)$$

Substitution in (11) gives, in terms of mole fractions

$$n_{xi} = \frac{2(m + 2d + 3t)(x - 2)! p^{i+2}q^{x-2i-2}r^i}{(m - t)(i + 2)!(x - 2i - 2)! i!} \quad (19)$$

$$= \frac{6(x - 2)! p^{i+2}q^{x-2i-2}r^i}{(3p - r)(i + 2)!(x - 2i - 2)! i!} \quad (20)$$

In terms of α and τ

$$p = \frac{\alpha + \tau}{(1 + \tau)(2 - \alpha)} \quad (21)$$

$$q = \frac{2(1 - \tau)(1 - \alpha)}{(1 + \tau)(2 - \alpha)} \quad (22)$$

$$r = \frac{3\tau(1 - \alpha)}{(1 + \tau)(2 - \alpha)} \quad (23)$$

The weight fraction is given by

$$W_{xi} = \frac{[a(i + 2) + b(x - 2i - 2) + ci]n_{xi}}{\sum_{x=2}^{\infty}\sum_i [a(i + 2) + b(x - 2i - 2) + ci)]n_{xi}} \quad (24)$$

where a, b and c are the molecular weights of the **M**, **D** and **T** units, equal, respectively, to 81.16, 74.13 and 67.09. Performance of the summation and substitution of α gives

$$W_{xi} = \frac{(bx + a - c)(2 - \alpha)(x - 2)! p^{i+2}q^{x-2i-2}r^i}{[b + \alpha(a - c)](i + 2)!(x - 2i - 2)! i!} \quad (25)$$

The weight fraction of molecules containing x units is

$$W_x = \sum_{i=0}^{i=\frac{x-2-\delta_x}{2}} W_{xi} \quad (26)$$

where δ_x is Kronecker's delta.

The weight average molecular weight is

$$M_w = \frac{\sum_{x=2}^{\infty}\sum_i [a(i + 2) + b(x - 2i - 2) + ci]^2 n_{xi}}{\sum_{x=2}^{\infty}\sum_i [a(i + 2) + b(x - 2i - 2) + ci]n_{xi}} \quad (27)$$

The values of the six individual sums involved in (27) are

$$\sum\sum n_{xi} = 1$$

$$\sum\sum i n_{xi} = \frac{2r}{3p - r}$$

$$\sum\sum (x - 2i - 2)n_{xi} = \frac{3q}{3p - r}$$

$$\sum\sum i(x - 2i - 2)n_{xi} = \frac{6rq}{(3p - r)(p - r)} \quad (28)$$

$$\sum\sum i^2 n_{xi} = \frac{2r(p + 2r)}{(3p - r)(p - r)}$$

$$\sum\sum (x - 2i - 2)^2 n_{xi} = \frac{3q(p + 2q - r)}{(3p - r)(p - r)}$$

Substituting equations (28) in (27)

$$M_w = \frac{\frac{(ap + bq + cr)^2}{p - r} + pa^2 + \frac{qb^2}{2} + \frac{rc^2}{3}}{ap + \frac{bq}{2} + \frac{cr}{3}} \quad (29)$$

Values of W_x, calculated by means of equation (26), may be compared with experimentally determined weight fractions in Tables II and III. The polymers analyzed in Table II were of low viscosity and a major portion of each oil is represented in these analyses of the lower boiling constituents, e. g., the compounds **M₂** to **M₂D₅** represent 93% of polymer A. The comparison between the theoretical and experimental weight fractions is good for polymers A and B. However, in the case of polymer C, an **MT** polymer, the theoretical and experimental distributions are somewhat different. The compound **M₄T₂** could not be isolated, and it is suspected that the balance of this polymer, with an average functionality close to two, contained many cyclic and polycyclic compounds.

The presence of cyclic compounds would account for the excess, over the calculated amount, of **M** units present as **M₂** in polymer C. The trend toward this excess is already noticeable in polymer B, at $\tau = 0.10$, where the percentage of **M₂** found exceeds that calculated by 1.4%. The expected tendency of experimental error is toward finding a smaller amount of **M₂** than calculated, as in polymer A, because of the low boiling point and low heat of vaporization of this compound.

Scott[13] has isolated a compound analyzing as MT_9 from an equilibrated MT system, indicating that highly condensed compounds are present. Consequently it seems probable that in the low viscosity polymers the proportion of cyclic compounds increases from zero at $\tau = 0$ to a large value at $\tau = 1.0$, and the basic assumption that only compounds of the type formula $M_{i+2}D_{x-2}T_i$ are formed is strictly satisfactory only for MD systems.

The analysis of a higher viscosity polymer with a low value of τ, Table III, reveals wide deviation from the theoretical distribution in that large proportions of the simple cyclic compounds, D_x, are present. The proportions of the compounds of the series M_2D_{x-2} are larger than calculated, but are in correct proportion, with the exception of the lower boiling compounds M_2 and M_2D.

How the weight fraction of the cyclic compound D_4 rapidly increases with the viscosity is shown in Table IV. Thus an increase in viscosity as well as an increase in τ has a serious effect upon the form of the molecular size distribution.

Molecular Weight–Viscosity Relations

In view of the observed deviations from the theoretical distribution, it is interesting to see how near the log viscosity vs. $\sqrt{M_w}$ curve is to a straight line relation and how nearly the viscosity of a mixture falls on this same curve, for these considerations lent weight to the deduction that viscosity is a function of M_w in other polymer systems.

The values of M_w for a number of MD polymers have been calculated by equation (29) in Table VI. Log viscosity is plotted vs. $\sqrt{M_w}$ in Fig. 2. The straight line is a good approximation above a weight average molecular weight of 5000. However, as the proportion of M units is increased, and M_w decreases below 5000, the log viscosity vs. $\sqrt{M_w}$ curve must deviate from the straight line to approach the limiting values of viscosity and M_w represented by the point M_2. The dotted curve was plotted from equations (4) and (29), using -0.0028 for the value of k. This curve, derived from the empirical relation (4),

TABLE VI

CALCULATION OF M_w FOR **DM** POLYMERS

η_{100}	m	p	M_w	$\sqrt{M_w}$
17	0.076	0.0397	3660	60.5
25.9	.055	.0283	5170	71.9
30.7	.046	.0235	6250	79
36.0	.039	.0199	7380	86
49.7	.032	.0161	9130	95.6
59.6	.027	.0139	10,640	103
184	.0135	.00680	21,740	147.5
459	.0079	.00397	37,310	193
1620	.0049	.00246	60,290	246
5950	.0034	.00169	87,600	296

(13) D. Scott, private communication.

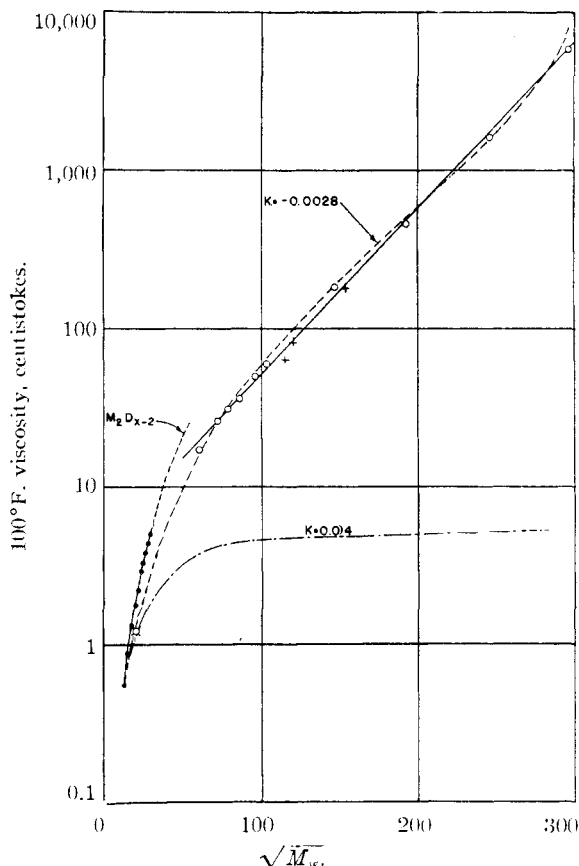Fig. 2.—Log viscosity vs. $\sqrt{M_w}$: ●, compounds M_2D_{x-2}; ○, equilibrated polymers, $\tau = 0$; +, mixtures of $\tau = 0$ polymers; ◌, equilibrated polymers, $\tau = 0.105$.

closely approximates the straight line above $M_w = 5000$ and at the same time deviates from it below $M_w = 5000$ to pass through the point for M_2.

Mixtures of equilibrated polymers, while somewhat lower in viscosity than equilibrated polymers having the same weight average molecular weight, are quite well approximated by the straight line relation between log viscosity and $\sqrt{M_w}$. Points for three such mixtures are plotted in Fig. 2 (crosses). The M_w values were calculated as outlined in Table VII from the relation (30)

$$M_w = w'M_w' + w''M_w'' \tag{30}$$

in which w' and w'' are the weight fractions of the two components.

TABLE VII

VISCOSITIES OF MIXTURES OF EQUILIBRATED **DM** POLYMERS

Major component[a]			Mixture			
Viscosity 100°F.	M_w	Wt. %	M_w	Viscosity Calcd.	Obsd.	% Error
49.7	9130	92.5	14,500	84.3	81.2	4
30.7	6250	91.5	13,200	74.1	62.6	16
59.6	10,640	82.9	23,800	192	174.5	10

[a] Minor component: $M_w = 87,600$, $\eta_{100} = 5950$.

The calculated values of M_w are known to be in error due to the presence of cyclic molecules in the polymers and the resultant distortion of their molecular size distribution from that predicted by the statistical theory (equation (26)). The discordance in the viscosity vs. M_w relationship which is probably caused by the inability to calculate M_w correctly, is illustrated by the curves (see Fig. 2) for the pure linear compounds M_2D_{x-2} and for the $\tau = 0.103$ series of polymers, both of which differ from the curve for the **DM** polymers. For the compounds, the value of M_w is equal to the molecular weight of each compound, and the points have been plotted accordingly. The viscosities of the pure compounds are higher than the viscosities of equilibrated polymers having equal values of M_w.

The calculation of M_w for the $\tau = 0.103$ polymers is summarized in Table VIII. The resultant curve (Fig. 2) shows that for this series of polymers, the viscosities are lower than those of **DM** polymers having the same calculated weight average molecular weights.

TABLE VIII

CALCULATION OF M_w FOR $\tau = 0.103$ POLYMERS

η_{100}	α	p	q	r	M_w	$\sqrt{M_w}$
1.21	0.540	0.3994	0.5126	0.0880	428	20.7
1.68[a]	.400	.2850	.6099	.1051	734	27.1
3.53[a]	.220	.1645	.7128	.1227	3,193	56.5
4.54[a]	.179	.1404	.7333	.1263	9,515	97.5
5.18[a]	.160	.1296	.7425	.1279	79,130	281.3

[a] Viscosities calculated by equation (4), $k = 0.014$.

The curves for the equilibrated polymers should be coincident and should superpose upon the curve for the compounds. Admitting a relationship between viscosity and M_w for siloxane polymers similar to that proposed by Flory for organic condensation polymers, the curve for the **DM** polymers must be displaced toward larger values of M_w because the presence of cyclic compounds has not been accounted for in the calculations, and the curve for the $\tau = 0.103$ polymers must be even further displaced in the same direction not only because of the presence of cyclic and polycyclic compounds but also because of the differences in viscosity between each branched molecule and its linear isomer. An additional perturbing factor is the fact that cyclic siloxane compounds are known to be higher in viscosity than linear compounds of equal molecular weight.[5]

Analyses such as those in Table II show that for low viscosity polymers ($\alpha > 0.5$) good agreement with the statistical theory at least up to $\tau = 0.1$ is obtained with no measurable trace of cyclic compounds being found. On the basis of a viscosity–M_w relationship, one should expect such polymers, with a value of M_w less than about 1000, to have viscosities very nearly those predicted from the viscosity–M_w curve for the pure compounds, whereas in fact the viscosities are more nearly those predicted from the viscosity vs.

α curve for these same compounds (see Fig. 1). Consequently, it seems doubtful that an exact relationship between viscosity and M_w exists for siloxane polymers.

Gelation

Within the limit of experimental error, gelation occurs during the equilibration process whenever $\alpha < 0$, i. e., when $m < t$. When $\alpha = 0$ ($m = t$), a gel-like material forms during the hydrolysis of the siloxane–sulfate esters at the end of the equilibration process. These gel-like materials, however, are soluble in solvents and are not true gels. When $\alpha < 0$, a gel forms of which at least a portion is insoluble in solvents. When α is only slightly less than zero, this gel forms upon hydrolysis of the sulfate esters, but when α is less than about -0.005, it forms during the equilibration process.

According to the statistical relations developed for these siloxane polymers according to the theories of Flory and Stockmayer, gelation should be noted when the calculated weight average molecular weight is infinite. From equation (29) it is evident that as α is decreased from the value of 1, this condition first occurs when $p - r = 0$, that is, when $m = 3t$. When $p - r < 0$, equation (29) no longer is applicable.

In the composition region $t < m \leq 3t$, gelation is predicted by the theory, but is not found experimentally. The explanation is to be found in the presence of cyclic and polycyclic molecules in the polymers. These cyclic compounds have a high average functionality, two or larger, and hence can leave the balance of the polymer above the theoretical gelation composition, $m > 3t$. Flory[14] found a similar difference between the theoretical and experimental incipient gelation compositions, and ascribed the difference to the presence of intramolecular condensation.

Other Properties

Like the viscosity, other physical properties of the equilibrated siloxane polymers are also related to the composition. These are the density, the per cent. volatile, the viscosity temperature coefficient, and the melting range.

The density is a function of the average functionality, as shown in Fig. 3, but appears to be independent of the molecular size distribution and of the proportion of **T** units. The densities of the pure linear compounds and of the equilibrated polymers fall on the same curve.

The per cent. volatile is a function not only of the average functionality but also of the proportion of **T** units. The variation with both α and τ is shown in Fig. 4. For any constant value of τ, the per cent. volatile varies from nearly 100 at $\alpha = 0.54$ or higher to a constant limiting value as α is decreased. This limiting value is higher the greater the value of τ. Since the volatile fraction represents the lower molecular weight compounds
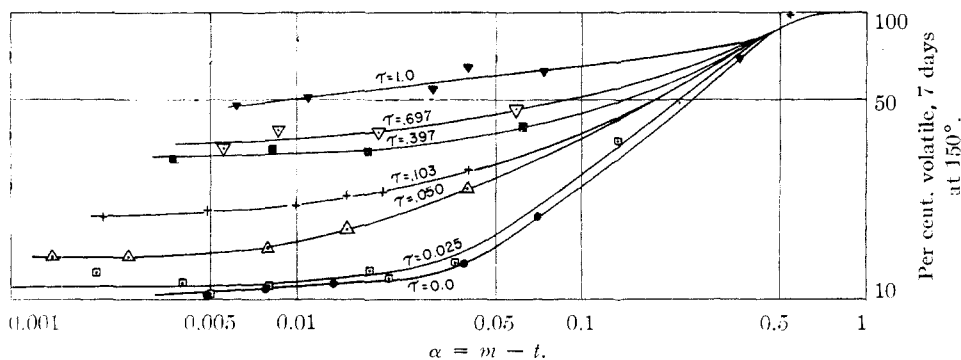
(14) P. J. Flory, THIS JOURNAL, 63, 3083, 3091 (1941).

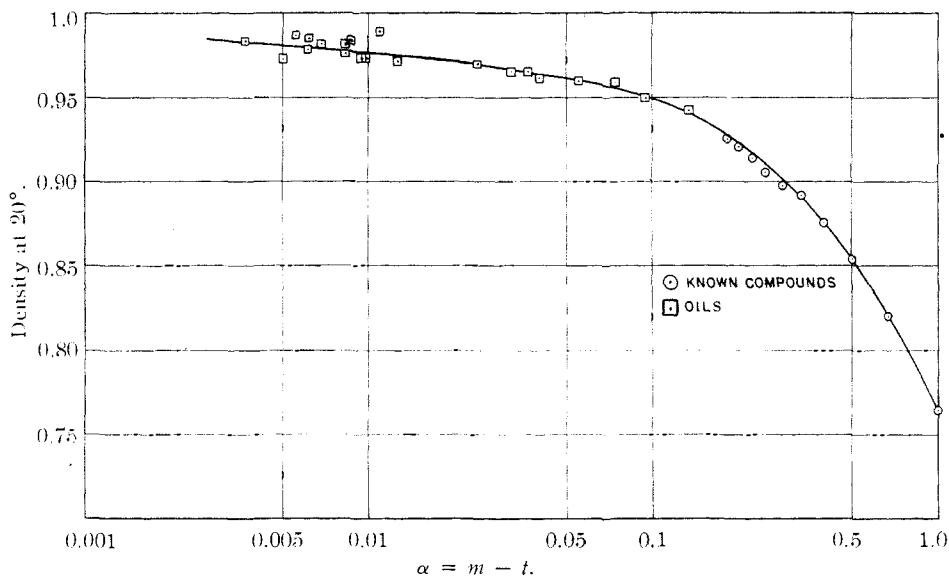$\alpha = m - t.$

Fig. 3.

$\alpha = m - t.$

Fig. 4.

in the equilibrated polymers, it should approach zero as α approaches zero if the statistical distribution represented by equation (20) is correct. Thus the limiting values of per cent. volatile are indicative of the deviations from this theoretical distribution caused by the presence of cyclic molecules. The limiting value of the per cent. volatile increases rapidly with increase in τ.

The viscosity temperature coefficient (VTC) likewise reflects the increase in cyclic content as the proportion of T units is increased. The cyclic compounds have been observed to have higher viscosity temperature coefficients,[5,7] as expressed by their energy of activation for viscous flow, than the corresponding linear compounds. In the equilibrated polymers, the VTC is higher the larger the value of τ, varying from a maximum of 0.60 for polymers with $\tau = 0$ to a maximum of 0.67 for polymers with $\tau = 1$. This increase is attributed to an increasing proportion of cyclic molecules in the polymers as τ is increased. For comparison, the VTC of petroleum oils ranges from 0.8 to 0.9.

The melting range of the methylpolysiloxane polymers is greatly reduced by the introduction of small proportions of T units into the polymers. This is contrary to what might be expected from the increase in cyclic content with τ, for while the linear compounds, M_2D_{x-2}, are reported[2] to have melting points of $-70°$ or lower, the corresponding cyclic compounds have relatively high melting points,[2,15] above $-38°$. The introduction of T units reduces the melting range from -25 to $-38°$ for polymers for which $\tau = 0$ to something below the temperature of Dry Ice for polymers with $\tau = 0.05$. In the TDM polymers the tendency to crystallize appears to be suppressed by the greater molecular complexity caused by the branch units. Removal of the volatile fractions neither prevents the solidification of DM polymers nor permits the solidification of TDM polymers at temperatures above Dry Ice temperatures.

(15) J. F. Hyde, et al., This Journal, 68, 667 (1946).

of several of the **DM** oils. The author is also appreciative of the helpfulness and advice of Dr. W. I. Patnode, Dr. R. O. Sauer and Dr. D. W. Scott during the conduct of this investigation.

Summary

The physical properties of a polymeric system arising from the equilibrium rearrangement of methylpolysiloxanes are a function not only of the average functionality of the system but also of the proportion of trifunctional units it contains. As the average functionality is increased toward the value of two, beyond which gelation occurs, the viscosity, density and viscosity temperature coefficients increase, and the proportion of volatile material decreases. As the proportion of branch units is increased, at constant average functionality, the viscosity and melting range decrease, the viscosity temperature coefficient and per cent. volatile increase, and the density and incipient gelation composition remain substantially unchanged.

The statistical theory of molecular size distribution based on the assumptions that only linear or branched molecules are present and that all reacting groups are equally reactive, has been adapted to the **TDM** polymers from the theories of Stockmayer. Distillation analysis of these polymers reveals good agreement with the theory at low viscosities, whereas at higher viscosities considerable proportions of cyclic compounds are found. The viscosity vs. weight average molecular weight curve, calculated with the aid of statistical theory, serves to estimate the viscosity of mixtures of **DM** polymers, but does not accommodate the compounds M_2D_{x-2}. For this reason, the existence of a true relation between viscosity and weight average molecular weight in polysiloxanes is questioned.

Gelation occurs at average functionalities greater than two, rather than when $m \leq 3t$ as predicted by the statistical theory, due to the perturbing effects of the presence of cyclic and polycyclic molecules. The increased proportion of cyclic and polycyclic structures that accompanies the increase in proportion of **T** units, together with the resultant increase in molecular complexity and the deviation from the theoretical size distribution, accounts for the changes in the physical properties that are observed as **T** units are introduced into **DM** polymers.

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C-18 Alcohol Esters of Orthosilicic Acid

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In connection with studies of new types of synthetic drying oils derived from the component fat acids of linseed and soybean oils, the orthosilicic acid esters of the alcohols corresponding to these fat acids were prepared. Since these esters would have a functionality[3] of four, it was anticipated that they would possess superior drying properties. Stearyl, oleyl and linoleyl orthosilicates were also prepared.

The drying times of thin films of refined linseed and soybean oils with and without driers have been compared with those of the orthosilicates of the corresponding alcohols. The drying times of the oils since they give soft tacky films were determined by the "finger" method which defines "set-to-touch time" as a period of drying after which oil will not adhere to the finger when the film is touched gently; those of the orthosilicates were determined with a Sanderson Drying Meter.[4] The driers were added as naphthenates. The results are given in the table.

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Present address: The Maytag Company, Newton, Iowa.

(3) Bradley, Ind. Eng. Chem., **29**, 440 (1937).

(4) Sanderson, Proc. Am. Soc. Testing Material, **25**, Part II, 407 (1925); ibid., **26**, Part II, 556 (1926).

TABLE I

DRYING TIMES IN HOURS

	Oils			Orthosilicates		
Drier	None	0.5% Pb 0.05% Mn	0.1% Co	None	0.5% Pb 0.05% Mn	0.1% Co
Linseed	72	8	6	13	2.75	2
Soybean	144	16-24	12-14	96-120	4.5	3

The hard dry orthosilicate films developed aftertack rapidly at a rate roughly proportional to the original rate of drying, finally becoming soft and greasy or pasty. This effect may be caused by hydrolysis with atmospheric moisture possibly through catalysis by lower fatty acids resulting from oxidation. If the films were both dried and kept in a desiccator over phosphorus pentoxide, they retained their hardness indefinitely. Prolonged desiccation (six months) was found to inhibit materially the tendency to develop aftertack.

When baked three and one-half to five hours at 120°, films of the orthosilicate of soybean alcohols (containing 0.5% lead and 0.05% manganese) showed no change after thirty days. Films were almost water-white and had a hardness of 10 as measured with a Sward hardness rocker. They